

An Investigation into the Potential of
Pliocene Speleothems from the
Nullarbor Plain, Southwest Australia, to
Preserve Interpretable Palaeoclimate Signals

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I. Abstract

The Pliocene has been identified as a key time interval from which estimates of future climate scenarios can be made. At present there is a significant paucity of Pliocene climate data from the Southern Hemisphere, and moreover, from terrestrial sources therein. This thesis aims to address both of these scarcities through applications of both traditional and novel techniques of palaeoclimate analysis to speleothems from the Nullarbor Plain, southwest Australia. This thesis focuses on two primary stalagmites, as well as several additional speleothems, that grew during the Pliocene as revealed by U-Pb dating. It provides one of the first detailed studies of speleothems of a greater antiquity than the ~500 kyr dating limit previously imposed by the U-Th method.

This study has provided invaluable insights into the climate of the Nullarbor Plain during the Pliocene, through the application of conventional stable isotope analyses, trace element analyses, fluid-inclusion analyses, clumped-isotope analyses, and modern precipitation isotope analyses. For speleothems of such antiquity, a multi-proxy approach grounded in a site-specific modern isotope study, has provided the means for delineating the key drivers of the geochemical variations present. The use of both traditional and novel speleothem proxies provides key information regarding both temperature and precipitation dynamics in the Nullarbor region during the Pliocene.

Conventional stable isotope and trace element records from the speleothems reflect changes in precipitation above the cave and the overlying vegetation dynamics. Modern precipitation analyses enable a comprehensive understanding of the influences on isotopic variation in current precipitation, with applications to the interpretation of the speleothem data. This study indicates that during the Pliocene, precipitation was significantly higher in the Nullarbor region, suggestive of an increase in moisture sourced from NCBs and the Southern Ocean. The increased precipitation resulted in significantly higher vegetation cover compared to present, as supported by both the carbon isotope and trace element signals. These conclusions are in agreement with both modelled estimates of vegetation and precipitation for the Nullarbor Plain, and also with studies of speleothem-derived pollen data from the region.

Palaeotemperature estimates were derived from combined fluid-inclusion and clumped-isotope analyses; indicating a temperature range of $18.8^{\circ}\text{C} \pm 1.8^{\circ}\text{C}$ to $21.4^{\circ}\text{C} \pm 1.3^{\circ}\text{C}$. While the individual methods provided several additional estimates, the uncertainties associated with each limit the reliability of the absolute temperatures. However, they signify significant temperature variations within the Pliocene, indicating that despite being a period of overall global warmth in

comparison to the present day, the Nullarbor region experienced significant fluctuations in average temperatures.

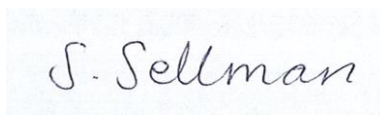
This study has identified several areas for focus in future research in order to further develop the novel application of speleothem research to the more distant past, while providing unique and important information regarding the climate dynamics of the Nullarbor Plain during the Pliocene.

II. Declaration

This is to certify that:

1. The thesis comprises only my original work towards the PhD
2. Due acknowledgement has been made in the text to all other material used
3. The thesis is less than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.

Signed,

A handwritten signature in cursive script that reads "S. Sellman". The signature is written in dark ink on a light blue, textured background that resembles a piece of paper or a card.

Safana Louise Sellman
December, 2019

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1. Introduction

1.1. Significance and Aims of Project

This thesis presents a palaeoclimatic study of the Pliocene, using speleothems as archives. In recent years there has been an upsurge of interest in the Pliocene, largely stemming from the widely held notion that it provides a useful analogue for future climate scenarios (Jansen et al., 2007; Salzmann et al., 2011; De Schepper et al., 2014; Pachauri and Meyer, 2014). This assumption is based on the similarity of boundary conditions compared to today, such as continental configuration and ocean circulation patterns (Dowsett and Robinson, 2009), and the similarity of Pliocene temperature estimates to those projected by climate models, which indicate an increase in mean global temperature of between 2 °C and 5 °C within the next 90 years (Jansen et al., 2007; Salzmann et al., 2011; Pachauri and Meyer, 2014). Within the Pliocene itself, a shorter period of time referred to as the Mid-Piacenzian (previously Mid-Pliocene) Warm Period has been highlighted as being of particular significance, as the geologically most recent period with climatic conditions similar to the best projections for conditions in a future warming world (Jansen et al., 2007). As such, it is a period of time for which a greater understanding of climatic conditions and variability is much needed.

Speleothems (secondary cave carbonates such as stalagmites and flowstones) have become an increasingly important source of palaeoclimate information in recent years (McDermott, 2004; Fairchild and Baker, 2012), as a result of the plethora of environmental and climatic information they can potentially record, and their ability to be accurately and precisely dated. Their potential as 'deep time' palaeoclimate indicators has greatly increased in the past decade following the development of the U-Pb dating method for speleothems (Richards et al., 1998; Woodhead et al., 2006). This method extends the utility of speleothems beyond the previous ~500 kyr limit of the widely employed U-Th dating method. This research utilises a range of conventional (oxygen and carbon stable isotopes) and novel (U-Pb dating, fluid-inclusion isotope analyses, and carbonate clumped-isotope palaeothermometry) analytical approaches applied to speleothem archives. New data from the Pliocene, in particular palaeotemperature estimates, are required to better inform climate models, therefore allowing the development of more precise predictions of future climate states and assisting future adaptation and mitigation strategies (Masson-Delmotte et al., 2013).

Obtaining palaeoclimate data from a range of proxies is also of particular importance, as it is widely acknowledged that multi-proxy comparisons reduce the uncertainties and limitations associated with individual proxy approaches (Masson-Delmotte et al., 2013).

The project uses speleothems collected from the Nullarbor region in southwest Australia. It thus addresses a well-known deficit of Pliocene climate data from terrestrial environments, as well as the general dearth of records from the Southern Hemisphere. It therefore complements the greater volume of data sourced from Northern Hemisphere archives (Cubsach et al., 2013), thus enhancing the regional representation of Pliocene climate change and variability.

1.2. Key Research Aims

The broad objective of this project is to assess the potential of Pliocene speleothems from the Nullarbor Plain to identify key climatic characteristics and variability during the Mid-Piacenzian Warm Period. Crucial to this objective is the suitable preservation of speleothems with an absence of diagenesis or recrystallisation. Within the general theme of this thesis there are four complementary aims:

Aim 1 → To explore the potential for the U-Pb dating of long (>1 m) speleothems to allow applications of proxy data to precise timescales.

Aim 2 → To evaluate isotopic patterns in modern precipitation and investigate their use in informing interpretations of palaeoprecipitation.

Aim 3 → To explore the potential of fluid-inclusion and carbonate clumped-isotope analyses to produce reliable palaeotemperature estimates in Pliocene speleothem.

Aim 4 → To apply a multi-proxy approach, using both traditional and novel speleothem proxies, to the study of Pliocene speleothems.

There is a particular research significance associated with each of these aims. Regarding Aim 1, to date there has been relatively little published work on the application of U-Pb (in comparison to U-Th) dating methods to speleothems (Bajo et al., 2012). Therefore, any additional research in this area is of significance due to its potential for highlighting opportunities and constraints that can inform future practitioners interested in time scales beyond U-Th. Additionally, there has been no previous investigation into the possibility of using U-Pb dating methods to develop internal chronologies (i.e. to distinguish top and bottom ages of samples) for speleothems of Pliocene age. As such, the findings of this research will assist in

defining the scope of the method as it currently stands, and help to identify areas for further research.

Regarding Aim 2, the benefits of using the interpretation of modern precipitation isotope variations for inferring palaeoprecipitation from the analysis of speleothems are widely acknowledged, although applying this approach to a time period as remote as the Pliocene is not without its pitfalls. Despite this, it provides a vital starting point for understanding relationships between regional climatology and isotopic variation, thus providing a fundamental framework for the interpretation of palaeoprecipitation. Influences on precipitation can be highly variable spatially, with site-specific parameters such as topography, longitude and latitude, and continentality having significant influences on the key drivers of isotopic variation. As such, site-specific research is of great importance in understanding key processes influencing isotopic signatures of precipitation. With no previous study of modern rainfall isotopes in the region, it was considered to be a vital aspect of this study.

In terms of Aim 3, both fluid-inclusion and clumped-isotope techniques are relatively novel in speleothem research and have been the subject of comparatively little investigation than the traditional methods used in multi-proxy studies. Obtaining palaeotemperatures from speleothems has been a highly sought-after goal of the palaeoclimate community. The fluid-inclusion and clumped-isotope derived palaeotemperature data produced in this thesis not only contribute to a wider understanding of Pliocene palaeoclimate of southern Australia, but also highlight some of the strengths and limitations of these techniques to the benefit of the wider speleothem community. This will encourage the continued improvement of the techniques used.

As with Aim 2, the importance of multiple speleothem proxies in the study of palaeoclimate, as expressed in Aim 4 is widely acknowledged, and takes on even greater significance when considering the Pliocene because there are many more unknowns in the palaeoclimatology of the Pliocene compared to the Pleistocene and, particularly, the Holocene. The use of multiple proxies, including stable isotopes and trace elements, allows for more robust interpretations of palaeoclimatic conditions. This was considered to be of particular importance in this study as it is the first multi-proxy study to investigate this particular time period using speleothems. The location of the study site also increases the importance of multi-proxy study due the overall deficit of terrestrial palaeoclimate data from the Southern Hemisphere.

1.3. Structure of the Thesis

The structure of this thesis is largely based around the four key aims noted above. A brief background of the underpinning research themes of this study and the speleothem proxies used is provided in Chapter 2. Chapter 3 introduces the study site, particularly its evolution and climatic characteristics, and the methods of sample selection and preparation.

Chapter 4 addresses Aim 1 through discussion of the U-Pb dating undertaken. Chapter 5 addresses the first part of Aim 2 through discussion of modern precipitation isotopes. Aim 3 is addressed in Chapter 6 and Aim 4 in Chapter 7. This is followed by its main conclusions in Chapter 8. The thesis concludes with a full list of the literature referenced, and an appendix presenting additional data pertinent to the thesis but not included in its main body.

2. Background

2.1. Palaeoclimate Research

Palaeoclimatology is the study of Earth's past climates and wider environmental conditions. Palaeoclimate research focuses on interpreting past changes in climate, using archives whose physical and chemical characteristics retain information derived from the environment in which they formed.

Palaeoclimate reconstructions may employ many different archives (**Table 2.1**) and are based upon various measurable and generally well-understood changes in the chemical, physical or biological characteristics preserved within these archives (Naish and Zwartz, 2012; Bell and Walker, 2014). However, a critical requirement for determining the potential utility of a palaeoclimate archive is the ability to date it, either directly or indirectly (Bradley, 2013; Bell and Walker, 2014). Once assigned to a specific growth period, a diverse range of information may be available from these different archives, from which time series of local, regional, and global climate signals can be assembled (Bradley, 2013).

Palaeoclimatology has played an essential role in developing our understanding of modern climatic processes (Masson-Delmotte et al., 2013). The pressure to better understand climate drivers and feedback responses is now even more pressing given concerns regarding the rapidity and unpredictability of current and future (next 100-500 years) climatic changes (Jansen et al., 2007; Pachauri and Meyer, 2014). In this context, palaeoclimatology as a discipline can be viewed in the context of 'reversed uniformitarianism', wherein the conditions of the past are used to inform the present and future as opposed to the present being the key to the past (Haywood et al., 2009). For this reason, the profile of palaeoclimatology has increased in recent decades as it has been recognised that efforts to better predict future climate change can greatly benefit from a more detailed understanding of the past (Howard, 1997; Naish and Zwartz, 2012). This is evident from the use of numerous palaeoclimate archives in models of future climate change (Meissner et al., 2015). In recent decades, such applications have been furthered by technological advances, allowing for more detailed and reliable palaeoclimate reconstructions (Sharp, 2007; Fairchild and Baker, 2012). The higher the level of detail and reliability of the input data for any given model, the higher the likelihood of superior quality output data, thus greatly improving our predictions of future climate change.

Table 2.1 – A summary of the most commonly studied palaeoclimate archives, the main proxy data obtained from them, and some pertinent references for each.

Archive	Environment	Main Proxy Data	References
Marine Sediments	Marine	O isotopes, type and composition	(Eglinton and Eglinton, 2008; Gaines et al., 2009)
Glacial Deposits	Terrestrial	Geomorphology	(Schirmer et al., 2002; Douglass, 2005)
Aeolian Deposits	Terrestrial	Type and composition	(An et al., 1990; Deng et al., 2006; Qiang et al., 2010)
Lake Sediments	Terrestrial	Composition and features of internally preserved material	(Bennett and Willis, 2001; Birks et al., 2003; Cohen, 2003)
Speleothems	Terrestrial	O and C isotopes, trace elements, petrography	(Grimes, 2006; Frisia and Borsato, 2010; Fairchild and Baker, 2012)
Ice Cores	Terrestrial	Stable isotopes, air pocket inclusions	(Alley and Bartlett, 2002; Dansgaard, 2004; Jouzel et al., 2013)
Tree Rings	Terrestrial	Number and morphology of ring growth	(Twining, 1833; Speer, 2010; Vaganov et al., 2010)
Pollen	Terrestrial / Marine	Type and relative abundance	(Moore and Webb, 1978; Moore et al., 1991; Bartlein et al., 2010)
Corals	Marine	O isotopes and growth rate	(Colin et al., 2010; Copard et al., 2012; Medina-Elizalde, 2013)

Commonly, a multi-proxy (and in more recent times, a multi-archive) approach is applied in palaeoclimate research to address the complexity of the climate system. Numerous factors influence how the climate signal is recorded in a given archive, and often, certain types of climatic information are restricted to specific archives (for example marine cores as archives of past sea-surface temperatures – Bell and Walker, 2014). Thus, combining multiple archives and/or

proxies can enable the disentanglement of these influences, ultimately yielding a more reliable interpretation of palaeoclimate.

Despite extensive research, significant gaps in our knowledge of past climate systems and dynamics remain. It is of increasing importance that we explore novel ways to obtain new information regarding past climates. For example, it is essential to look further back into the past to develop a more complete understanding of climate responses to changes in atmospheric CO₂ concentration (Hansen et al., 2008), and to find appropriate analogues for climate predictions for the end of the 21st Century (McDermott, 2004; Haywood et al., 2009). There is also a significant paucity of data from Southern Hemisphere archives, as well as from terrestrial archives (especially when looking at the more distant past – Bradley, 2013). These gaps must be addressed to identify and evaluate regional biases in climate models, and differences in climatic drivers on global and regional scales.

2.2. The Pliocene

The Pliocene has increasingly become a core focus in recent studies of palaeoclimatology (Jansen et al., 2007; Haywood et al., 2009; Pachauri and Meyer, 2014). With similar boundary conditions such as continental configuration and ocean circulation to the present day (Dowsett and Robinson, 2009), it has great potential as an analogue for future climate change. However, there are important differences between the Pliocene and modern cryosphere and orbital configuration (Fedorov et al., 2006; Salzmann et al., 2011). Despite these complications, it remains a vital period of Earth history to study in order to better inform climate change mitigation and adaptation strategies in the future (Dowsett et al., 2013).

The Pliocene (5.33-2.58 Ma (Cohen et al., 2013)) is the uppermost subdivision of the Neogene (Gibbard et al., 2010), and is further divided into two stages: the Zanclean (5.33-3.60 Ma), and the Piacenzian (3.60-2.58 Ma: De Schepper et al., 2014 – **Fig. 2.1**). The chronology of the Pliocene has been finely tuned using a stacked record of published marine benthic oxygen isotope time series as shown in **Fig. 2.2** (Raymo et al., 2006; De Schepper et al., 2014), allowing for the development of a common timescale, which provides a framework against which new palaeorecords can be compared (Lisiecki and Raymo, 2005). It spans the transition of the Earth's climate from relative global warmth into the significantly cooler climate of the Pleistocene and identifies numerous significant climatic variations throughout the Pliocene (Haywood et al., 2009; De Schepper et al., 2014).

Eon	Era	Period	Epoch	Stage	Age (Ma)
Phanerozoic	Cenozoic	Quaternary	Holocene		present
			Pleistocene	Upper	0.0117
				Middle	
				Calabrian	
				Gelasian	
		Neogene	Pliocene	Piacenzian	2.58
				Zanclean	3.6
			Miocene	Messinian	5.33
				Tortonian	
				Serravallian	
				Langhian	23.03
				Burdigalian	
				Aquitania	
				Aquitania	
		Paleogene	Oligocene	Chattian	23.03
				Rupelian	
			Eocene	Priabonian	33.9
				Bartonian	
				Lutetian	
				Ypresian	
			Paleocene	Thanetian	56
				Selandian	
				Danian	
	Mesozoic	Cretaceous	Upper	Maastrichtian	66
				Campanian	
				Santonian	
				Coniacian	
				Turonian	
				Cenomanian	
			Lower	Albian	100.5
				Aptian	
				Barremian	
				Hauterivian	
				Valanginian	
				Berriasian	~145

Fig. 2.1 – A segment of the International Stratigraphic Chart, identifying the Pliocene within the Cenozoic Era, Neogene Period, between 5.33 Ma and 2.58 Ma. The stages of the Pliocene are also presented: the Zanclean 5.33-3.6 Ma, and the Piacenzian 3.6-2.58 Ma. Adapted from Cohen et al. (2013).

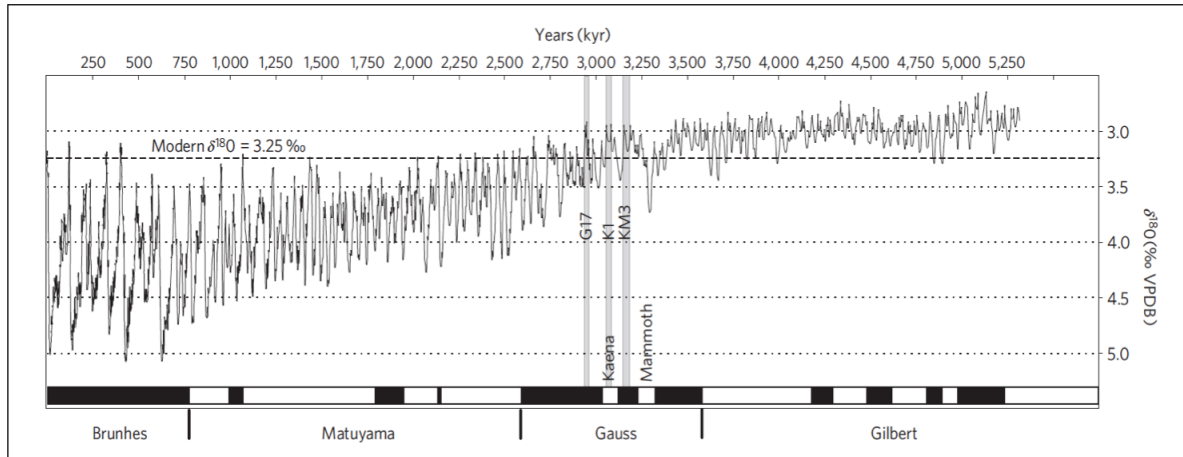


Fig. 2.2 – Stack of distributed benthic $\delta^{18}\text{O}$ record throughout the Pliocene and Quaternary, from 5.33 Ma to present. The three vertical shaded areas represent mid-Pliocene super-interglacials (i.e. periods of extreme warmth). Source: Raymo et al. (2011).

The latter period of the Pliocene is characterised by global climatic deterioration from high-frequency, low-amplitude climate oscillations with relatively low global ice volumes (Dowsett et al., 1994; Dowsett et al., 2013), to a typically high-frequency, high-amplitude Pleistocene regime characterised by glacial-interglacial cycles (Fedorov et al., 2006), with extensive regional-scale glaciation during cold stages (Matthiessen et al., 2009).

Palaeoclimate records indicate that climate during the Pliocene was also driven by Milankovitch oscillations (Becker et al., 2006). Specifically, it was regulated by a ~ 40 kyr periodicity linked to obliquity (Naish and Wilson, 2009; Dowsett et al., 2011), as opposed to the purported 100 kyr eccentricity driven periodicity evident throughout the mid to late Quaternary (Bell and Walker, 2014). Evidence obtained from marine cores (more specifically, the oxygen isotope composition of benthic foraminifera) reveals altered oceanic gateways and consistently increased sea-surface temperatures (LaRiviere et al., 2012) suggesting that Pliocene climate sensitivity may have been higher than at present (Crowley, 1996; Pagani et al., 2009). However, there are contradictions to this evidence suggesting that long intervals during the Pliocene were characterised by relative climatic stability (Draut et al., 2003). Such interpretations suggest that increased temperatures may not necessarily invoke greater climate variability. Such debates have significant implications for the accuracy of future climate predictions, highlighting that this is an area for further research to allow more absolute interpretations to be made.

2.2.1. Key Climatic Characteristics

The Pliocene is known to have been a high- CO_2 world (Crowley, 1996; Jansen et al., 2007; LaRiviere et al., 2012). While there is some disagreement with

the exact levels dependent on the measurement techniques, the general consensus is that CO₂ levels were around 360-400 ppm (Seki et al., 2010). This is ~30% higher (Wara et al., 2005; Ravelo et al., 2006) than pre-industrial levels of ~280 ppm (Petit et al., 1999; Loulergue et al., 2008; Seki et al., 2010), and somewhat comparable to modern levels (Lunt et al., 2009; Clark et al., 2013). This adds weight to the suggestion that the Pliocene should be a period of high interest for assessing potential climatic changes and feedback patterns associated with higher global CO₂ levels.

Global average temperatures during the Pliocene were believed to be 3-4 °C warmer than present (Crowley, 1996; Haywood et al., 2009), with greatest warming in the mid and high latitudes (Draut et al., 2003) – **Fig. 2.3**. Palaeodata from a variety of archives supports these conclusions, including from foraminifera (Dowsett et al., 1996) and diatom records (Barron, 1992) in marine cores, terrestrial vegetation records (Sniderman et al., 2016), and palaeoshorelines (Dowsett and Cronin, 1990; Naish and Wilson, 2009; Clark et al., 2013). The analysis of multiple fossil proxies obtained from marine cores suggests that

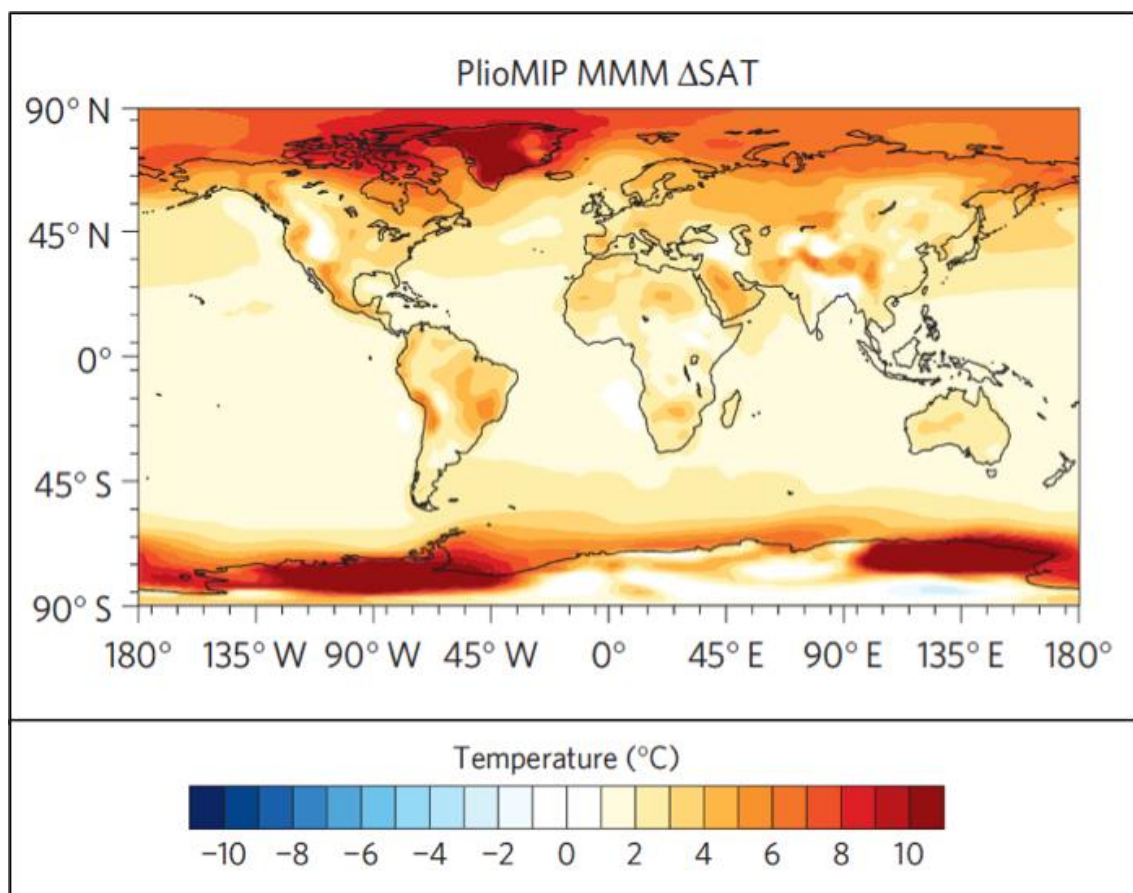


Fig. 2.3 – Modelled average global temperature difference between the Pliocene and pre-industrial temperatures, highlighting the latitudinal variation in increased temperatures compared to present day. Source: Salzmann et al. (2013).

seasonality was far more pronounced, however both summer and winter temperatures were increased in comparison to present day (Haywood et al., 2009). This enhanced seasonality is suggested to have occurred particularly in the high latitudes, as evidenced by the extensive study of shallow marine sediments located along the Antarctic shelf (Clark et al., 2013).

Furthermore, several geochemical proxies obtained from marine cores suggest that sea-surface temperatures (SSTs) were approximately the same as present in tropical regions but increased at high latitudes (Dowsett et al., 1994), resulting in reduced latitudinal temperature gradients. While it is suggested that, overall, warming may have been greater in the Northern Hemisphere (Ballantyne et al., 2010; Salzmann et al., 2011), published reconstructions of the Southern Hemisphere temperatures are currently both sparse and controversial, so warming may have been equally accentuated (Salzmann et al., 2011).

In the later part of the Pliocene, from approximately 2.8 Ma, global temperatures began to decline as a result of the overall climatic deterioration building up to the end of the Pliocene and the conditions that have characterised the climate of the past ~2.6 Ma (Haywood et al., 2009). This cooling occurred during both glacial and interglacial climate states, indicating that it was caused by significant changes in the mean climate state (Lawrence et al., 2010).

The Pliocene has also been highlighted, in both palaeodata and models, as having a generally wetter climate compared to today (**Fig. 2.4**). This increased precipitation resulted in a contraction of both subtropical and semi-deserts (Salzmann et al., 2011), with particularly significant effects on parts of Africa and Australia (Crowley, 1996). It has been suggested that the narrowing of the Indonesian seaway, and the resultant weakening of the Indonesian throughflow (Cane and Molnar, 2001), contributed to increased precipitation over the Australian continent (Krebs et al., 2011; Salzmann et al., 2011; Sniderman et al., 2016). The weakening of the throughflow during the later stages of the Pliocene has been suggested as a potential cause of decreasing precipitation to the region through the Quaternary (Krebs et al., 2011).

As a result of the increased temperatures and precipitation, there were also significant differences in Pliocene vegetation compared to today, both at global and region scales (**Fig. 2.5**). Generally, these changes are consistent among proxy and model data, and support the findings of increased warmth and moisture at high latitudes (Dowsett et al., 1994). There was an overall northward shift of the treeline in the Northern Hemisphere (De Schepper et al., 2014), which, due to the associated decreased albedo, is thought to have contributed to maintaining warmer climates (Lunt et al., 2009).

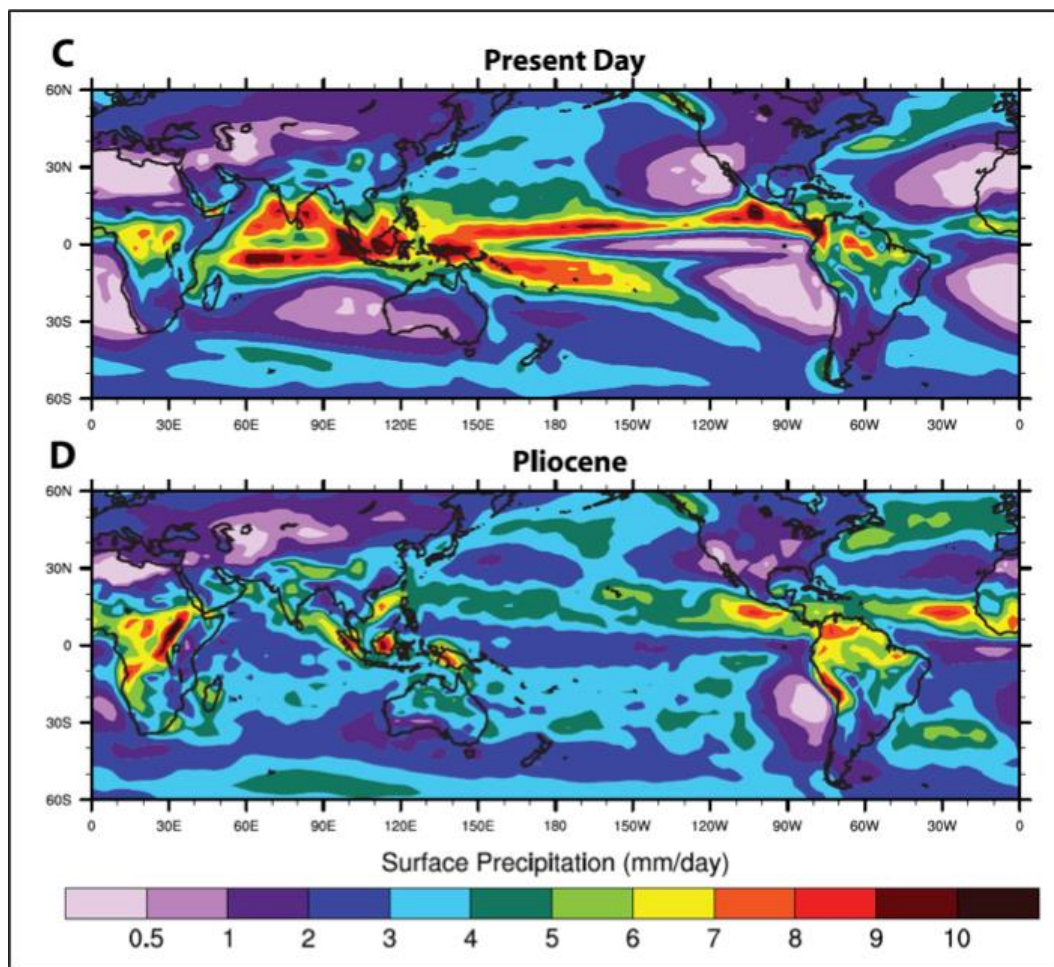


Fig. 2.4 – Modelled average global precipitation for the present day and the Pliocene showing a reduction in precipitation over many oceanic and equatorial regions, but a distinct increase in precipitation over much of Australia, including the Nullarbor Plain. Source: Brierley et al. (2009).

Based on analyses of vegetation data from both marine and terrestrial sources, with the support of model simulations, it has been suggested that many modern arid and semi-arid regions hosted temperate and tropical xerophytic shrublands (Salzmann et al., 2008; Salzmann et al., 2011).

Glaciation appears to have been more common and widespread in the late Miocene and into the Pliocene (Ehlers and Gibbard, 2007). During the Pliocene in general, short-lived episodic glaciations were rare in the Zanclean, becoming progressively more common throughout the Piacenzian (Miller et al., 2012b). While there are only three globally recognisable glacial periods identified within the Pliocene, there were several Pleistocene-like stadial/interstadial events that can be identified in the Northern and/or Southern Hemisphere (De Schepper et al., 2014). Such events have been related to the Earth's orbital geometry and forcing, in particular the ~40 kyr obliquity cycles (Naish et al., 2009), and began to

increase in both amplitude and frequency from the Late Pliocene, where there was a transition from smaller, local-scale to extensive, regional-scale glaciations (Matthiessen et al., 2009; Bailey et al., 2013). Although there are indications of significant fluctuations in global ice-volume throughout the Pliocene (De Schepper et al., 2014), the deep ocean (benthic) $\delta^{18}\text{O}$ record shows consistently depleted isotopic values relative to today, indicating persistently lower global ice volumes than today throughout much of the period (Raymo et al., 2006; Lunt et al., 2008; Lunt et al., 2009).

The transition towards increasing stability of large ice sheets in both hemispheres (Ehlers and Gibbard, 2007) is a result of a shift in the mean climate state (Lawrence et al., 2010). However, as Southern Hemisphere glaciation appears to have significantly preceded that of the Northern Hemisphere, it is likely that there were regional differences in the influence of climatic drivers such as oceanographic changes (Lawrence et al., 2006). The shift from largely ice-free conditions to more extensive continental glaciation outside of the polar regions is one of two major climate transitions to have occurred in the last 5 Ma (Lawrence et al., 2010). While a relatively comprehensive record of Pliocene glaciation has been established (De Schepper et al., 2014), there remain contradictions regarding timings and extents. This discrepancy largely results from the incompleteness of the terrestrial record due to the fragmentary nature of glacial deposits and the dramatically reduced preservation potential of older glacial sequences (Dowsett et al., 1994; De Schepper et al., 2014).

Direct evidence of Pliocene shorelines is somewhat limited (Dowsett and Cronin, 1990), in spite of numerous investigations into Pliocene sea-levels. While there are a wide range of published sea-levels, estimates are frequently cited as being ~25 m higher than present (Dowsett et al., 1994; Raymo et al., 1996; Miller et al., 2012b), based on the palaeontological analyses of marine deposits presented in (Dowsett and Cronin, 1990). These estimates indicate a significantly reduced extent of both the Greenland and Antarctic ice sheets compared to today (Lunt et al., 2009).

It has been suggested that Earth's climate through much of the Pliocene experienced permanent El Niño-like conditions (Wara et al., 2005; Fedorov et al., 2006). The observed characteristics leading to such comparisons include a low west to east SST difference, a deep Eastern Pacific thermocline, and a relatively weak Walker circulation (Wara et al., 2005). It is argued that weaker global atmospheric circulation maintained these conditions through much of the Pliocene (Karas et al., 2011).

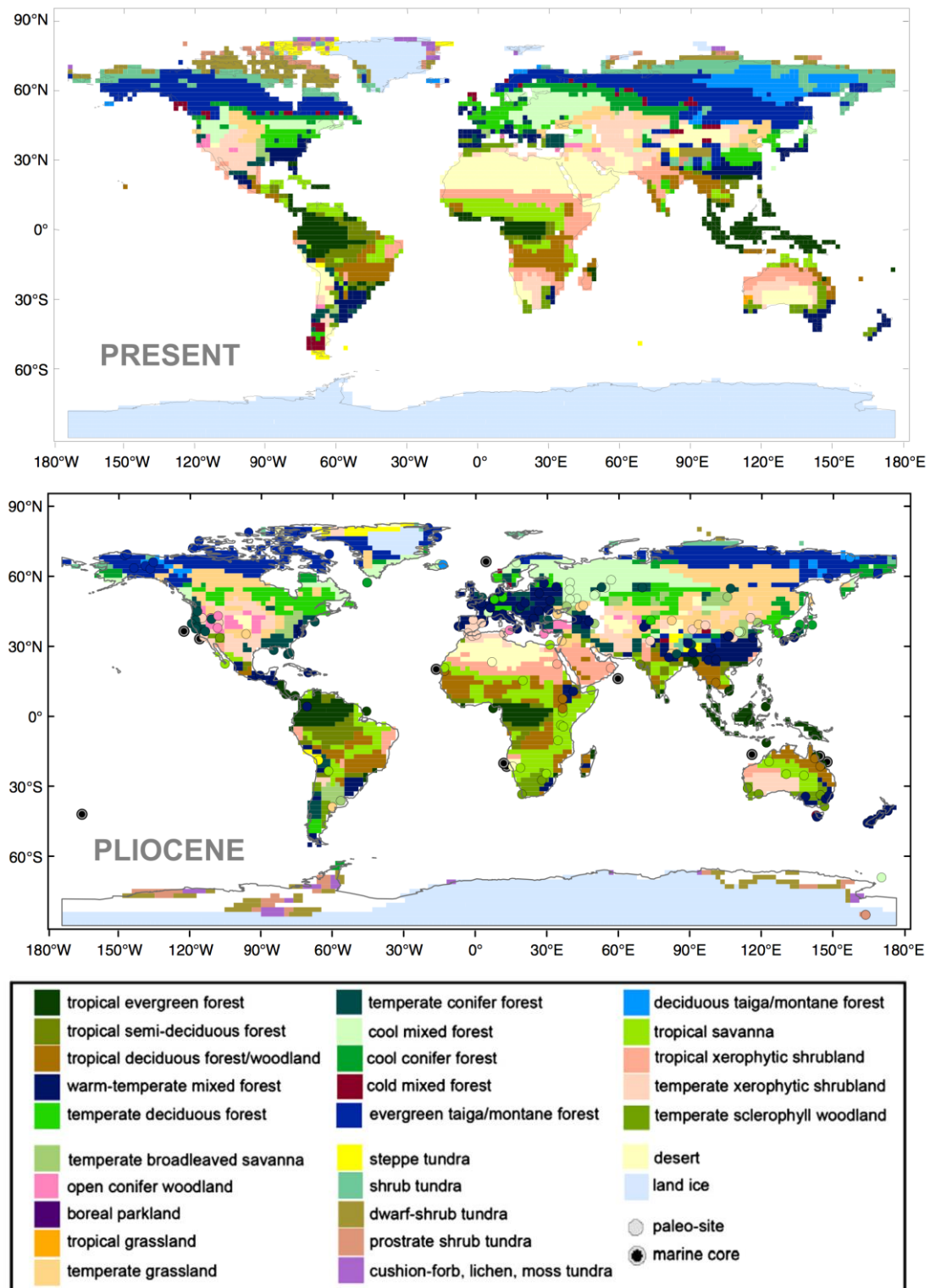


Fig. 2.5 - Observed modern, and modelled Pliocene global vegetation distributions showing a distinct change in vegetation in the Nullarbor region from temperate xerophytic shrubland in the Pliocene, to the modern desert. Source: Salzmann et al. (2011).

The persistence of El Niño-like conditions would have had a significant impact on global climate (Fedorov et al., 2006), and likely contributed to the global warmth evident during the Pliocene (Haywood et al., 2009). Studies of the timing of the termination of these so-called El Niño-like conditions have returned contradictory results, although it has been widely suggested to have occurred at ~3 Ma as a result of the reorganisation of the ocean heat budget (Lawrence et al., 2006). While some models and proxy evidence support the theory of consistent El Niño conditions, others contradict this evidence. For example, model simulations presented in Haywood et al. (2007) and Lunt et al. (2007) indicate significant variability of ENSO states throughout the Pliocene. However, it has also been acknowledged that the present temporal resolution of both model and proxy data for this period is insufficient to reliably prove or disprove the existence of permanent El Niño-like conditions (Haywood et al., 2009), and as such it is an area of research that requires further investigation. It must also be acknowledged that, while it is convenient to associate the past conditions with the modern ENSO phenomenon, such comparisons must be applied with caution due to the uncertainties of specific climatic drivers and controls in the distant past.

2.2.2. Climatic Drivers

There have been numerous suggestions as to the main climatic drivers during the Pliocene. Elevated CO₂ levels are considered to be one of the main reasons for increased temperatures (Salzmann et al., 2011). However, there is evidence of significant global warming occurring with only slightly increased CO₂ (Raymo et al., 1996).

There are also indications that the closure and constriction of two major oceanic seaways – the Central American seaway and the Indonesian seaway (Karas et al., 2011), acted as important driving mechanisms influencing Pliocene climate. Related to the constriction of these seaways was the intensification of the North Atlantic Current carrying warm water northwards during periods of the Pliocene (Naafs et al., 2010). This may have accentuated high-latitude warming in the Northern Hemisphere, leading to decreased sea-ice cover and, through positive feedback effects, decreased global albedo (Raymo et al., 1996).

It is likely that a number of these factors were influencing the climate throughout the Pliocene, as individually none of them can explain the extent of climate differences at this time. It is clear that significantly more research is required in this area in order to make reliable conclusions about drivers of both climatic change and of the maintained higher temperatures within the Pliocene.

2.2.3. Mid-Piacenzian Warm Period

While the Pliocene as a whole is an area of increasing interest, the Mid-Piacenzian Warm Period (3.29-2.97 Ma; De Schepper et al., 2014) has been identified as an interval during which overall conditions were the closest to future predictions (Jansen et al., 2007). In much of the literature this period is referred to as the Mid-Pliocene Warm Period, however, in line with recent revisions to the base of the Pliocene (Gibbard et al., 2010), it is now known as the Mid-Piacenzian Warm Period (MPWP – Haywood et al., 2013; De Schepper et al., 2014), and will be referred to as such herein.

The MPWP was a period of relatively stable global warmth, with only low-amplitude temperature and ice-volume fluctuations occurring in comparison to typical Pleistocene glacial periods (Draut et al., 2003). Its importance is highlighted by its focus in the Pliocene Research Interpretation and Synoptic Mapping (PRISM) studies (Dowsett et al., 1994; Dowsett et al., 1996; Salzmann et al., 2011; Dowsett et al., 2012; Lunt et al., 2012). While there were overall warmer periods earlier in the Pliocene, the MPWP was the last ‘super-interglacial’ prior to the climatic deterioration of the Late Pliocene (Dowsett et al., 1994), and also the most recent time in which temperatures and CO₂ levels were close to estimates of predictions for the end of this century (Jansen et al., 2007). It is also considered an apt analogue for testing the sensitivity of climate models (Salzmann et al., 2009).

Despite extensive study, the precise drivers of the climate of the MPWP remain unclear (Lunt et al., 2009), with numerous explanations having been put forward, each with their own uncertainties (Haywood and Valdes, 2004). For example, enhanced thermohaline circulation has been suggested to have had strong influences on latitudinal heat advection across the globe (Raymo et al., 1996), however, there are difficulties with determining the causal relationship between these altered oceanic circulation patterns and other potential drivers of the MPWP climatic change (Raymo et al., 1996; Haywood and Valdes, 2004; Haywood et al., 2013). Alternatively, while increased atmospheric CO₂ levels have also been suggested as a significant driver of the increased temperatures present in the MPWP and Pliocene more generally, this alone would be expected to present as uniformly increased temperatures across all latitudes, thus not sufficiently explaining the minimal equatorial heating (Dowsett et al., 1996; Haywood and Valdes, 2004). As such, there is a need for further research into both regional-scale variability, as well as variability over shorter timescales, in order to better assess the applicability of the MPWP as an analogue for future climates (Lunt et al., 2012).

2.2.4. Gaps in Research

While it has become increasingly recognised that the Pliocene is a critical time period for study of the Earth's climate system, there are still significant gaps in our knowledge. There is a need for high-resolution studies (Haywood et al., 2009), on timescales that capture short-term variability, in order to better inform predictions of short-term variability in the future (Matthiessen et al., 2009), as well as those that capture orbital-scale variability (Salzmann et al., 2013).

It has also been highlighted that in order to further the use of Pliocene reconstructions in predictions of future climates, more detailed estimates of temperatures and climatic drivers must be published (Haywood et al., 2009; Haywood et al., 2013). This is a particular issue with modelling studies, where two main agendas for future research have been proposed: it has been identified that there is a significant need for more of a focus on quantifying the uncertainties in model predictions (Salzmann et al., 2011), and that there must be further comparisons of past reconstructions and future predictions using individual models (Fedorov et al., 2006). Additionally, further analyses of the synchrony and/or diachrony between proxy records and models would allow a more critical understanding of the key climatic drivers at play, as well as improving the reliability of models of future climates.

Further investigation into potential climatic drivers and precise timings of shifts within them is also vital. A better understanding of the probable responses of significant bodies of ice such as the East and West Antarctic Ice Sheets under differing degrees of climatic change is required in order to better constrain and predict future behaviour (Naish and Wilson, 2009). Similarly, better-developed insights into ice-related feedback effects are also essential for more accurate predictions of future climate change (Raymo et al., 1996; Raymo et al., 2006). Other key climatic drivers requiring further investigation include the influence of prolonged high CO₂ levels (Haywood et al., 2009), the timings of major oceanic pathway changes (Karas et al., 2011), and the influence of albedo related feedback systems (Raymo et al., 1996).

Future work also needs to focus on filling the data gaps in proxy records (Dowsett et al., 2011), particularly between marine and continental records (Dowsett et al., 1996), in that they are yet to be directly compared to identify any synchrony or diachrony between them (De Schepper et al., 2014). It has also been identified that there is a significant imbalance between records from the Southern Hemisphere and the Northern Hemisphere, with large gaps and uncertainties in the record from the Southern Hemisphere (Salzmann et al., 2011). This needs to be resolved with future research placing an additional focus on obtaining estimates

from data sparse and regionally important locations (Dowsett et al., 2011). In particular, the role of high latitudes in the Southern Hemisphere has been highlighted as an area requiring further research (Lawrence et al., 2006).

2.3. Speleothems

Speleothems are secondary minerals commonly referred to as cave deposits. They typically form in limestone or dolostone caves and are primarily composed of calcium carbonate (calcite or aragonite) or calcium sulphate (gypsum). In recent decades speleothems (e.g. stalagmites) have become an increasingly important archive for terrestrial palaeoclimate reconstruction (Krüger et al., 2011). While speleothems occur in several forms (**Fig. 2.6**), stalagmites have been used significantly more than other forms of speleothem (Fairchild and Baker, 2012), and are favoured due to their more regular growth habit. In order to fully understand the potential of speleothems as an archive, it is important to understand the mechanisms by which they are formed (**Fig. 2.6**). Speleothem growth is dependent on a number of environmental factors, evidence of which is then preserved in both their stratigraphy and geochemical properties (Kaufmann, 2003). While there are several variables by which speleothem formation is determined, it is essentially a result of percolating water transitioning from a high $p\text{CO}_2$ region in which carbonate dissolution occurs, into a low $p\text{CO}_2$ region in which CaCO_3 precipitation occurs (Fairchild and Baker, 2012). As rainwater infiltrates through the soils above the cave, the decay of organic matter and plant respiration result in the water being exposed to high partial pressures of CO_2 (Fairchild and Baker, 2012); this makes the water aggressive, causing it to interact more strongly with the soil and dissolve the surrounding bedrock, usually in existing fractures (Frisia and Borsato, 2010). It is during this period of dissolution and transportation that other environmental signals, such as trace elements, are incorporated into the percolating water (Fairchild and Treble, 2009b). It is essential that during this stage the water becomes saturated with calcium carbonate, as this is the factor that determines the ability of the drip water, once in the low $p\text{CO}_2$ cave environment, to precipitate calcite. Where percolation waters have not reached equilibrium with bedrock *en route* to the cave, corrosion, or dissolution, of existing speleothems can occur (Kaufmann, 2003). Once the saturated water reaches the cave, there are a number of different morphologies that can result, largely dependent where within the cave the infiltrating waters emerge (e.g. flanks versus ceiling), and the rate of the dripping (Frisia and Borsato, 2010).

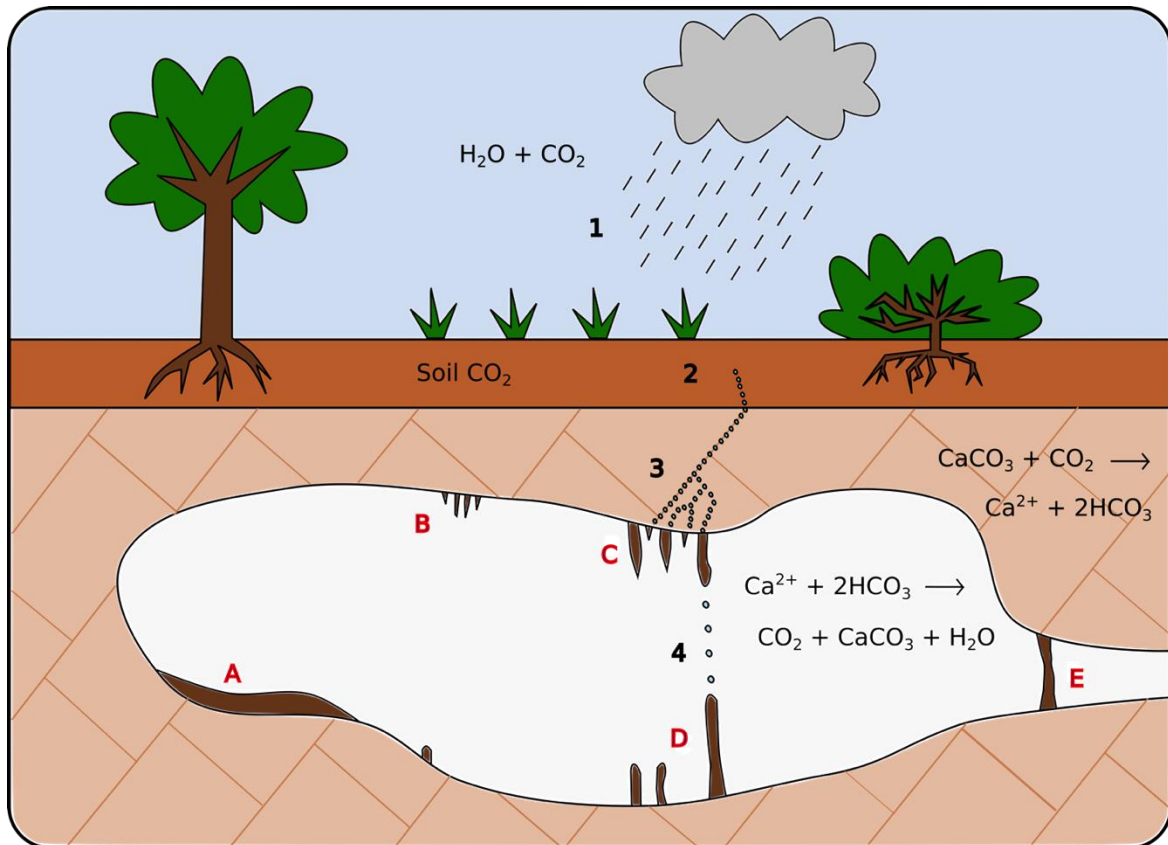


Fig. 2.6 – Processes leading to the formation of speleothems from precipitation (1), to percolation through the soil (2), and bedrock (3), to degassing and precipitation within the cave (4). Main forms of speleothem shown are flowstone (A), soda straws (B), stalactites (C), stalagmites (D), and column (E).

Speleothems grow as a succession of thin calcite layers, or laminae, that can represent a variety of timescales dependant largely on growth rate (Fairchild and Baker, 2012).

In the case of stalagmites, the form of speleothem that will primarily be utilised in this study, the drip water hits the top of the formation resulting in a thin film spreading out radially. Due to the low $p\text{CO}_2$ in the cave atmosphere relative to the dripwater, CO_2 degasses from the solution and calcite is precipitated in a thin layer around the impact area. Crystal growth occurs perpendicularly to the surface resulting in continual upward growth (Kaufmann, 2003). Speleothem growth rates vary greatly – by at least two orders of magnitude (McDermott, 2004) – in warm humid regions, the average growth rate of a stalagmite can be of the order of a millimetre per year, while in cool temperate regions it is generally less than $100 \mu\text{m}$ per year (Fairchild and Baker, 2012). It is acknowledged, however, that the growth rate of a speleothem is likely to have been variable throughout its lifespan, thus resulting in variable resolutions of its recorded geochemical properties (Finch et al., 2001).

It is important to note that there is significant variation in the hydrochemical behaviour of drip water, with different drip rates resulting in the preservation of climate signals at different temporal resolutions (Baldini et al., 2006). Hydrological variability in drip rates can also potentially imprint on several of the proxy records preserved in stalagmites, such as certain trace element concentrations including Mg and Sr, therefore having implications for the validity of palaeoclimate interpretations (Mariethoz et al., 2012). Finch et al. (2001) also acknowledge that while environmental variation and patterns of cyclicity at both local and regional scales can be preserved within speleothems, it can often be difficult to identify these patterns. These difficulties arise from the numerous factors that can obscure these signals, such as growth hiatuses, variations in water residence time in the bedrock, and local phenomena such as tectonic activity, bushfires, and periods of drought or flood. All of these factors have the potential to obscure any cyclicity in the speleothem record and/or provide palaeoclimatic reconstructions unrepresentative of larger regional climate variability. The ability of speleothems to preserve interpretable palaeoclimate signals is also dependent upon a lack of diagenetic alterations post-deposition. Recrystallisation in speleothems has been shown to significantly alter numerous proxy data, thus disturbing the palaeoclimate signal (Fairchild and Baker, 2012; Scholz et al., 2014).

Speleothems can grow continuously for up to 10^5 years and, due to the stable environments in which they form, they can remain remarkably well preserved for millions of years (Fairchild et al., 2006). As such, they provide the potential for long, continuous records to be developed. This potential is furthered by the ability to 'stack' records from multiple precisely-dated speleothems from within a single cave system or region (e.g. Wang et al., 2008; Boch et al., 2011) thus allowing continuous records to be developed that far exceed the average growth span of a single speleothem.

2.3.1. Reasons for Study

Speleothems capture the response of the cave to the external environment (Fairchild et al., 2006). Due to the mechanisms by which they form, they are highly sensitive to climatic variability; while there are a number of factors that affect the growth of stalagmites the predominant controls are mean annual temperature and the amount of CO₂ in the soil (Kaufmann, 2003), the latter often closely related to the former. The mechanisms by which speleothems form have been highlighted as one of the reasons that they are such an important archive of palaeoclimate (Griffiths et al., 2010).

Another significant benefit of speleothems over some other archives is the potential for providing robust chronologies using U-Th (Hellstrom, 2003; Kluge et

al., 2008; Schölz et al., 2012), and more recently U-Pb, techniques (Richards et al., 1998; Woodhead et al., 2010). They are also advantageous over some other archives as they represent a terrestrial source of information that has the ability to record, in a largely quantitative manner, information regarding mean temperatures, precipitation, and surface vegetation at high resolutions (Woodhead et al., 2010). In addition to the ability for robust chronologies to be developed, they are one of the few archives available at all latitudes (Fairchild and Baker, 2012).

The potential for speleothem records to be compared with, and to complement, other archives of palaeoclimate, such as marine and ice cores (e.g. Boch et al., 2011), further justify their study. Through detailed comparisons of palaeoclimate records from multiple archives it becomes possible to better define the timings of key climatic events such as glacial-interglacial transitions and specific cold events (e.g. Drysdale et al., 2007). Additionally, these comparisons can allow a better understanding of the extent of local and regional influences and helps to identify synchrony and diachrony between the hemispheres and continents. In general, such multi-archive studies are increasingly important to maximise the accuracy, precision and reliability of palaeoreconstructions (Bell and Walker, 2014), thus supplying the much-needed data for the advancement of models of future climates (Jansen et al., 2007).

2.4. Speleothem Proxies

There are numerous proxies available for study in speleothems including, but not limited to, stable isotopes, trace elements, fluorescence, petrography, fluid-inclusions, noble gas-inclusions, and clumped-isotopes. This section provides pertinent background information for the proxies applied in this study.

2.4.1. *Stable Isotope Analyses*

The first investigations of stable isotope ratios date back to the 1940s (Urey, 1947). This early developmental work was quickly followed by the pioneering studies of the Chicago group (McCrea, 1950; McKinney et al., 1950; Epstein et al., 1953), greatly expanding the applicability of stable isotopes as a palaeoclimate proxy. In more recent years the field of isotope geochemistry has been expanding at unprecedented rates; its growth was initially attributed to technological advances, which promoted investigation into new isotope ratio systems, and made isotopic studies more widely available (Woodhead et al., 2010). Technological advances have also facilitated improvements to existing methods, which have in turn allowed for more accurate and precise datasets to be obtained (Sharp, 2007). Additionally, advances in sample preparation and analytical measurement, including the use of increasingly sophisticated automated lines (e.g.

Werner and Brand, 2001; Revesz and Landwehr, 2002; Spötl and Vennemann, 2003), has increased the feasibility of generating high-resolution time series. These advances have encouraged the application of stable isotopes to a growing range of scientific problems, further increasing the scope of the field of isotope geochemistry (Eiler et al., 2014). Despite the application of isotope geochemistry to speleothems beginning in the 1960s (Hendy and Wilson, 1968; Hendy, 1971), the recent applications of new and improved techniques has led to a significant increase in their interest in recent years (Fairchild and Baker, 2012). To date, analyses of the stable isotopes of both carbon and, in particular, oxygen (Lachniet, 2009; Fohlmeister et al., 2020), have been among the most important sources of palaeoclimate information held in speleothems (Sharp, 2007).

Among the most widely used stable isotope ratios for palaeoclimate studies are those of oxygen, whose isotopes are ^{16}O , ^{17}O , ^{18}O , and carbon, whose isotopes are ^{12}C , ^{13}C . Variations in the ratios of these isotopes are controlled by a number of climate-driven environmental factors at the time of calcite deposition (White, 2015). Decades of research into the stable isotope signatures preserved within speleothems has provided a detailed understanding of these processes, however, it has also become clear that there is no universally applicable interpretation due to the numerous parameters that influence their values on multiple spatial scales (i.e. global to local). As such, speleothem stable isotope studies must be considered on a site-specific basis.

In general, oxygen isotopes reflect processes that occur throughout the entire hydrological cycle, while carbon isotopes are more commonly controlled by local aspects of the terrestrial carbon cycle, such as soil and vegetation dynamics (Spötl and Matthey, 2006), and cave ventilation processes (Tooth and Fairchild, 2003b). A variety of processes control oxygen isotope ratios throughout the hydrologic cycle prior to their incorporation into the calcite (or, more rarely, aragonite) of a speleothem (Lachniet, 2009). These processes are discussed in further detail in **Chapter 5**. The stable isotopes of oxygen traditionally used in speleothem studies are ^{18}O and ^{16}O (Fairchild and Baker, 2012). Their variations are measured relative to a reference material and are expressed in delta (δ) notation as $\delta^{18}\text{O}$ (Sharp, 2007):

$$-\delta^{18}\text{O} = \left(\frac{^{18}\text{O}/^{16}\text{O}_{\text{sample}} - ^{18}\text{O}/^{16}\text{O}_{\text{standard}}}{^{18}\text{O}/^{16}\text{O}_{\text{standard}}} \right) \times 1000$$

The international reference materials used for this purpose are VPDB (Vienna Pee Dee Belemnite) for the oxygen and carbon isotope analyses of carbonate, and VSMOW (Vienna Standard Mean Ocean Water) for oxygen and hydrogen isotope analyses of water. Interpretations are then based on the permil variations of isotopic values and whether they are more isotopically enriched (positive values) or depleted (negative values) with respect to the aforementioned international standard. In addition to the traditional investigations into $\delta^{18}\text{O}$ there are an increasing number of studies using ^{17}O , which have been shown to preserve signals of subtle hydroclimatic fluctuations that are not evident in traditional $\delta^{18}\text{O}$ analyses (Sha et al., 2020; Voarintsoa et al., 2020).

Subsequent to any precipitation effects, there are still several factors that can further influence $\delta^{18}\text{O}$ through the soil zone, the epikarst, and within the cave chamber. Prior to infiltration through the soil, evaporation from the surface can result in increasingly enriched $\delta^{18}\text{O}$, a process more common in arid to semi-arid climates (Cuthbert et al., 2014). There can also be significant mixing of multiple precipitation events within the soil and epikarst zones leading to a dampening of the $\delta^{18}\text{O}$ signal preserved within a speleothem (Lachniet, 2009). This generally occurs where there are long transit times through these zones, e.g. in deep caves (Williams, 2008). This can be a common occurrence in karst systems as a result of particular precipitation characteristics (regarding amount and frequency), the saturation level of the karst, and transmission time to the cave. When frequent mixing occurs, climate signals from individual events or seasons may become indistinguishable within the speleothem $\delta^{18}\text{O}$ record, thus only allowing for long-term climate trends and variations to be identified (McDonald et al., 2007; Lachniet et al., 2014). Within the cave chamber, the $\delta^{18}\text{O}$ can be influenced by evaporation and cave temperature (Fairchild and Baker, 2012). Evaporation within the cave is influenced by the humidity and/or air circulation intensity, and, where evaporation is high, the $\delta^{18}\text{O}$ becomes increasingly enriched.

The stable isotopes of carbon are ^{12}C and ^{13}C , and their ratio is expressed as $\delta^{13}\text{C}$. These ratios are also controlled by a number of factors, such as the photosynthetic pathways of vegetation above the cave, i.e. C3 (generally cool, wet climate species) or C4 (generally hot, dry climate species), processes within the karst environment (such as prior calcite precipitation due to degassing in fractures of the bedrock), atmospheric and soil CO_2 variation, and, indirectly, temperature variations (**Fig. 2.7**). The $\delta^{13}\text{C}$ is significantly less reported than $\delta^{18}\text{O}$ (Fohlmeister et al., 2020), largely due to uncertainties in the systems and processes driving their variation, the difficulty of replicating records between coeval speleothems from

the same cave, and the overall complexities of controls on its variation (Brandstätter et al., 2019).

Overlying soils are generally considered to be the most significant influence on $\delta^{13}\text{C}$ variation as they form the largest source of C in speleothems (White, 2015). Soil CO_2 originates from C in the atmosphere. It is passed into the soil through photosynthesis and the consequent respiration and/or decomposition of overlying vegetation. The type of vegetation dominant above a cave system can significantly influence the $\delta^{13}\text{C}$ values: C3 vegetation results in $\delta^{13}\text{C}$ values significantly more depleted than those of C4 vegetation (Smith and Epstein, 1971; Green et al., 2015).

The $\delta^{13}\text{C}$ signal of a speleothem can also respond to strong seasonal variations in plant activity above the cave in some cases, where high-resolution studies are then able to resolve sub-annual signals. For example, in some Northern Hemisphere locations where seasonality is well pronounced, the CO_2 of soils has been shown to vary from approximately 1,000 ppm in winter to 10,000 ppm in summer (Baldini et al., 2008). Signals such as these can then be identified in the inter-annual variations of $\delta^{13}\text{C}$ in speleothems.

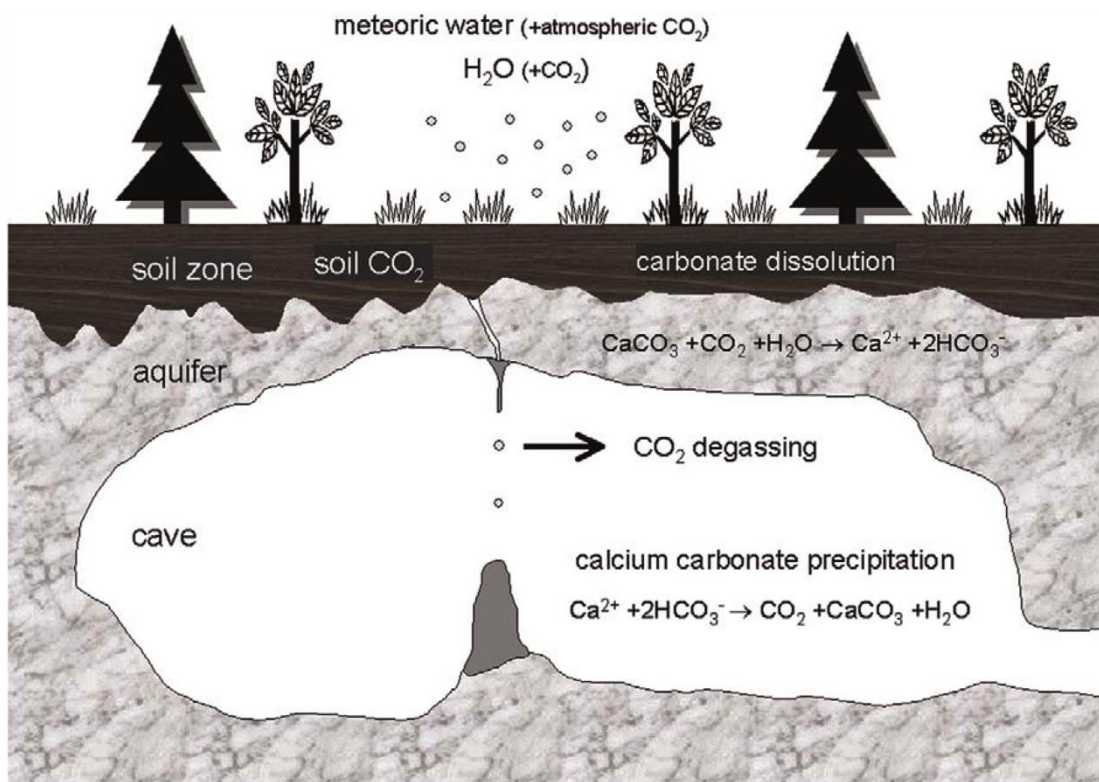


Fig. 2.7 – The key influences on carbon isotopes prior to speleothem precipitation. Source: Frisia and Borsato (2010).

While it has been suggested that carbon isotopes relate primarily to the CO₂ content of the overlying soils through which the recharge water percolates, in certain locations the isotopic composition of the host rock can be influential, particularly where soils are exceptionally thin or absent (McDermott, 2004). Host rock contributions to C are generally considered to account for approximately 10-20% of total C in speleothems (Hoffmann et al., 2010; Noronha et al., 2014), while soil inputs are significantly more variable. This variability results from a number of factors, including soil thickness (McDermott, 2004), vegetation density (Drysdales et al., 2007), and whether or not closed-system conditions are continuous along the percolation path of water into the cave chamber (McDermott et al., 2006). As with O, $\delta^{13}\text{C}$ can also be altered prior to reaching the cave chamber through processes of kinetic fractionation, which can occur through prior calcite precipitation (PCP), a process associated with factors such as periods of low precipitation (Johnson et al., 2006), humidity and/or air circulation variations (Treble et al., 2015). Low humidity and/or high air circulation encourages kinetic fractionation, thus resulting in increasingly enriched $\delta^{13}\text{C}$ (Emrich et al., 1970; Hendy, 1971; Matthey et al., 2010). In general, disentangling the influences on $\delta^{13}\text{C}$ can be greatly assisted by the use of other speleothem proxies, such as trace elements and pollen data (McDermott, 2004; Sniderman et al., 2016; Fohlmeister et al., 2020).

When employing isotopic variations in speleothems as proxies for palaeoclimatic change, it is important to understand the complexity of the systems in which speleothems develop, and the multitude of factors that affect their isotopic signals (McDermott, 2004). For example, kinetic fractionation during calcite precipitation can severely alter the isotopic signal preserved (Hendy, 1971), and must be accounted for during interpretation (Kluge et al., 2008). Kinetic isotopic fractionation is caused by physical processes during speleothem deposition, such as evaporation and rapid CO₂ degassing (Hendy, 1971). It is revealed by measuring the amount of isotopic variation along a series of individual laminae (Fairchild and Baker, 2012), specifically the extent to which $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ co-vary, a process referred to as the Hendy Test (Hendy, 1971). However, in recent years there have been debates regarding the suitability of this method. The main focal points of such debates are the practical difficulties associated with obtaining a sequence of samples along an individual growth laminae, and the potential for equilibrium conditions to vary from the central growth axis to the flanks of a given sample (Dorale and Liu, 2009; Day and Henderson, 2011). There is also the problem of temporal variations in equilibrium conditions as Hendy tests may indicate equilibrium conditions, however there may be unsampled periods of

speleothem deposition during which disequilibria occurs. This is perhaps the most significant controversy in the use of the stable isotopes of speleothems as indicators of palaeoclimatic conditions: there is no certainty of the equilibrium conditions required for an undisturbed palaeoclimate signal to be preserved. The most commonly applied solution to this limitation is the replication of records from multiple speleothems from within the same cave system or region. There have been suggestions that the recently developed application of clumped-isotope analyses may be useful in exploring the effects of precipitation out of equilibrium (Kluge et al., 2013; Daëron et al., 2019). However, this is an area in which further research is required prior to its application to speleothem research.

More generally, the interpretation of stable isotope patterns in speleothems can be complicated due to the plethora of influences on them. The numerous environmental and climatic influences discussed above, and the potential variability both spatially and temporally, results in difficulties disentangling the dominant influences. Replicate records from a cave system, and the study of modern processes, both above and in the cave, via long-term monitoring programmes offer partial solutions (Baldini et al., 2006; Tremaine et al., 2011; Markowska et al., 2015).

2.4.2. Trace Element Analyses

Trace elements can provide insights into the climate at the time of speleothem deposition. Geochemically, the term trace elements refers to those elements whose abundance totals to less than 0.1% of the total bulk composition (Faure, 1998). However, in speleothem science the term is expanded to include elements of interest exceeding this threshold. In the incorporation of trace elements into the speleothem, different elements are preferentially transported into the speleothem lattice in different forms (**Fig. 2.8**), and resultantly, different conditions and processes drive variations in their compositions. It is this inclination to reflect different environmental conditions that provides their potential for palaeoclimate reconstructions.

The main source of trace elements is the bedrock through which the drip water percolates (Fairchild et al., 2000b); the rate of infiltration through the bedrock, often related to the amount of effective precipitation above a cave site, is particularly influential on trace element variation (Fairchild and Treble, 2009b). However, several other sources can be important, which may have a greater impact on their variations, such as dry and wet atmospheric deposition, vegetation and overlying soils (Fairchild and Treble, 2009b). These contributions tend to exist as aeolian particles, transported into the cave chamber via vents and circulation systems and are generally more complicated to interpret due to the complexity of

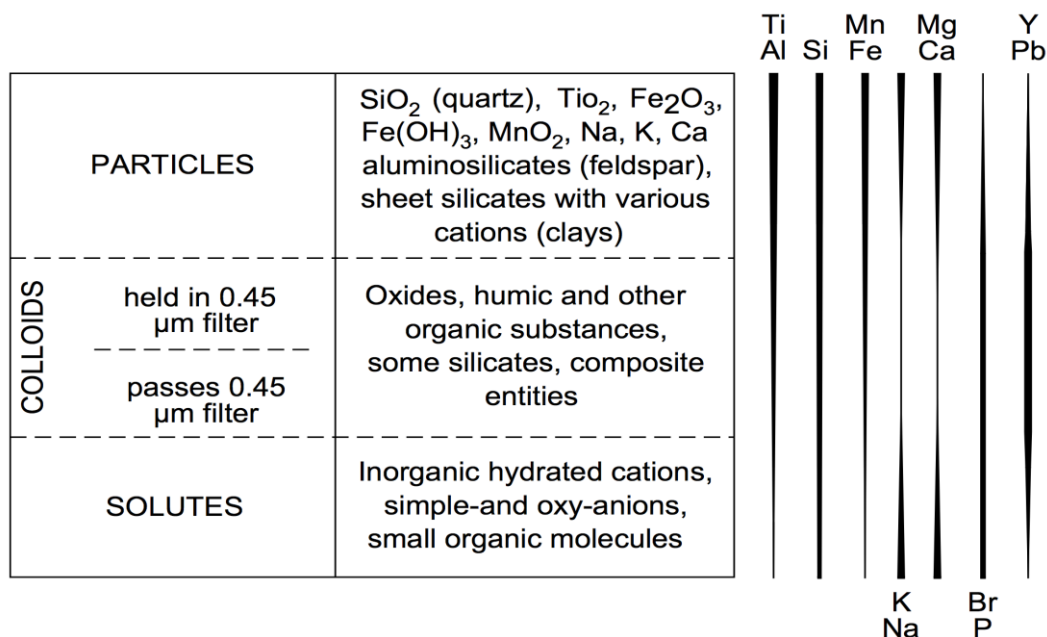


Fig. 2.8 – The possible modes of transport of trace elements, and a schematic of the tendency of several common elements to be transported in the various modes. Source: Fairchild and Treble (2009b).

processes leading to their incorporation into speleothems (Fairchild et al., 2006). Therefore the ratios of particular elements relative to calcium have been suggested to be indicative of environmental conditions at the time of deposition (Hellstrom and McCulloch, 2000; Finch et al., 2001) and the composition of the host rock (Fairchild and Treble, 2009b).

Particular trace elements can be targeted to assist the interpretation of other climate proxies obtained from speleothems, such as stable isotopes. For example, Mg has been shown to be a strong indicator of palaeohydrology, while Sr and Na are primarily influenced by growth rate variations, and P has been related to seasonal variations in temperature and precipitation (Treble et al., 2005c; Borsato et al., 2007). A number of trace elements, including P and Mg, have also been shown to closely correlate with seasonal cycles, thus providing annual chronological markers (Roberts et al., 1998; Treble et al., 2005c; Smith et al., 2009; Vansteenberghe et al., 2020). Consequently, there is potential for trace elements to be used for the development of internal chronologies of speleothems where radiometric dating cannot resolve internal ages. P is a particularly strong seasonal indicator as it is closely related to the overlying vegetation, such that there is often limited soil uptake of P during the summer, thus enhancing the release of dissolved P in the autumn months (Heathwaite et al., 1997; Huang et al., 2001; Treble et al., 2003). Variations in P have also been suggested to relate to variations in precipitation over longer timescales, with some studies identifying close

relationships with P to both inferred cold and dry periods (Baldini et al., 2002), and to instrumental rainfall records (Treble et al., 2003).

Mg has also been used as an indicator of palaeo-aridity in many cases (Tooth and Fairchild, 2003a; McDonald et al., 2004; Ban et al., 2018; Liu et al., 2019), and thus has significant potential in characterising the onset of aridity on locations such as the Nullarbor. There is also the potential to assess the relationship between Mg and $\delta^{18}\text{O}$ in order to differentiate between changes in rainfall and variations in effective water excess (Cruz et al., 2007). However, this is an area in which further research is still required, and it is suggested that a multi-proxy approach be taken to confirm such interpretations (Fairchild and Treble, 2009b). The relationship between various trace elements can also be informative of local conditions. For example, where systematic covariation of Mg and Sr has been identified, it has been possible to associate this with the occurrence of prior calcite precipitation (McMillan et al., 2005; Johnson et al., 2006).

The largest problem associated with trace element analyses at present is uncertainty in their interpretations due to the multiple and complex processes at work. These uncertainties largely result from the numerous mechanisms by which trace elements can be incorporated into a speleothem, and the multitude of potential interruptions to any given signal (Fairchild and Treble, 2009b). With continued research, understanding of these processes is progressing and allowing for more refined and reliable interpretations. However, as with analyses in speleothem science in general, a multi-proxy approach is preferred, and all interpretations should be made on a site-specific basis.

2.4.3. Fluid-inclusion Analyses

As a speleothem forms, small pockets of cave drip water, known as fluid-inclusions, can become trapped during mineral growth (Dublyansky and Spötl, 2009). They are typically arranged parallel to the dominant growth direction, along the calcite growth bands (**Fig. 2.9**) (Krüger et al., 2011). The analysis of these inclusions can be used to determine the isotopic composition of the percolating water from which the speleothem formed (Wainer et al., 2011). The abundance and size of fluid-inclusions is highly variable; inclusions are generally between 20 μm and 1 mm in size (Zhang et al., 2008), and typically account for between 0.1 and 1‰ of the total weight of the speleothem (Kluge et al., 2008). Lower concentrations have little impact on the geochemistry of a given sample, however, if over-abundant, it has been shown that crystal growth can be impeded resulting in alterations to the natural geochemical composition of the sample (Kendall and Broughton, 1978). They are usually considered to be of primary origin, i.e. their age is equal to that of the surrounding calcite (Krüger et al., 2011). As such, fluid-

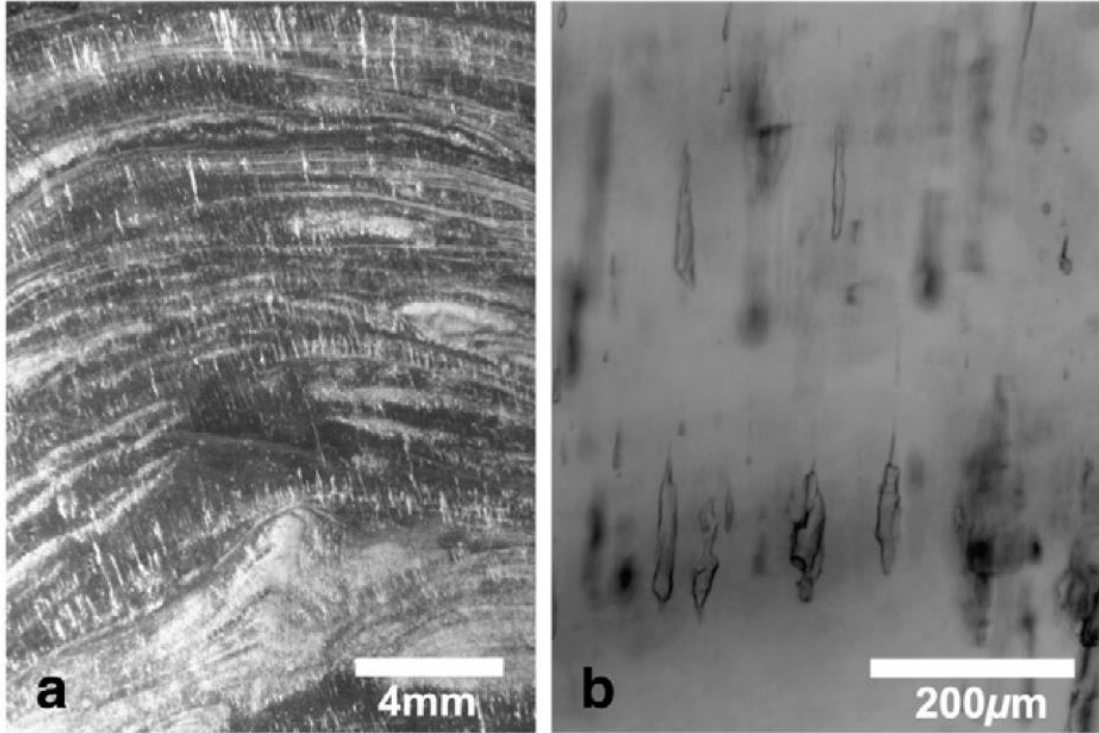


Fig. 2.9 – An example of fluid-inclusions along growth bands, visible under fluorescence. Source: Krüger et al. (2011).

inclusion samples can be dated through the uranium-series dating of the adjacent calcite.

As fluid-inclusions are considered to be of primary origin and a product of the water percolating through the system from which the speleothem forms, they are considered to be a direct proxy of past dripwater composition, and by inference, past precipitation (Dublyansky and Spötl, 2009). Under this assumption, it is therefore possible to use their isotopic composition for regional rainfall reconstructions (Griffiths et al., 2010; Callow et al., 2014). In addition to this, they have the potential to solve the $\delta^{18}\text{O}$ palaeotemperature equation that requires knowledge of the original water composition from which the carbonate was formed (Schwarcz et al., 1976). The palaeotemperature equation was initially developed to obtain high-resolution temperature profiles, which was unachievable using the other archives of the time such as deep-sea sediments (Hendy and Wilson, 1968). The classic palaeotemperature equation (Epstein et al., 1953), as presented in Lachniet (2009), is:

$$T = 15.75 - 4.3 (\delta^{18}\text{O}_{\text{calcite-PDB}} - \delta^{18}\text{O}_{\text{water-SMOW}}) + 0.14(\delta^{18}\text{O}_{\text{calcite-PDB}} - \delta^{18}\text{O}_{\text{water-SMOW}})^2$$

A number of alternative formulae have been also been derived from a variety of experimental and empirical origins (Craig, 1965; O'Neil et al., 1969; Schwarcz et al., 1976; Grossman and Ku, 1986; Kim and O'Neil, 1997; Tremaine et al., 2011). Three of the most commonly applied equations, and those used for all preliminary analyses in this study, are those of Craig (1965):

$$T = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2$$

O'Neil et al. (1969):

$$T = 16.9 - 4.38(\delta_c - \delta_w) + 0.1(\delta_c - \delta_w)^2$$

and Kim and O'Neil (1997 – as presented in Leng and Marshall, 2004):

$$T = 13.8 - 4.58(\delta_c - \delta_w) + 0.08(\delta_c - \delta_w)^2$$

While the form of the equations is identical, the different constants for the fractionation factor between calcite and fluid-inclusions results in slight differences in the derived palaeotemperatures (**Fig. 2.10**). A common problem identified with the Kim and O'Neil (1997) equation is that it produces temperatures that are too low (Coplen, 2007; Labuhn et al., 2015), in some cases producing negative temperatures, at which speleothem deposition is impossible. In such cases, the Craig (1965) equation (e.g. Griffiths et al., 2010), or the O'Neil et al. (1969) equation (e.g. Zhang et al., 2008), have been shown to produce more plausible palaeotemperature estimates. There have also been several more recent attempts to develop a palaeotemperature equation (Coplen, 2007; Kim et al., 2007; Tremaine et al., 2011; Daëron et al., 2019), highlighting the continued problem with deriving reliable temperature estimates from fluid-inclusions alone.

While such equations provide the potential for palaeotemperature estimates to be obtained, there are several theoretical and methodological issues that may influence the accuracy of such estimates (Coplen, 2007; Dietzel et al., 2009). One of the most significant issues is the known complexity and variability of the precipitation of calcite from dripwater, even under consistent climatic conditions (Fairchild and Baker, 2012). However, this problem is largely overcome when using fluid-inclusions to calculate palaeotemperatures, as the $\delta^{18}\text{O}$ of the water is directly measured from the inclusions. Where it is believed that the $\delta^{18}\text{O}$ value of such inclusions may have undergone isotopic exchange with the surrounding calcite, it is possible to use the hydrogen isotope ratio (δD) to

calculate the original inclusion water $\delta^{18}\text{O}$ value using either the local or global meteoric water line (Lachniet, 2009). In this case, calculating the correct meteoric water line for the period of speleothem growth is critical, as the use of an incorrect meteoric water line can significantly alter the calculated palaeotemperatures (Lachniet, 2009). This becomes of particular importance in older samples where this line is difficult to constrain.

While there are significant problems with this method, in the last decade there have been advances in resolving these issues; for example, targeting the adsorption of water within the preparation line (Dennis et al., 2000), and the reduction of sample size through the use of continuous-flow system analysis (see Vonhof et al., 2006, with later adaptations made by Dublyansky and Spötl, 2009). More recently developed methods involve the use of wavelength scanned cavity ring down spectroscopy instruments that allow online fluid-inclusion extraction and isotope analyses (Affolter et al., 2014). There have also been investigations into alternative methods that can be used to obtain palaeotemperature reconstructions from fluid-inclusions. For example, there has been an increasing focus of the use of noble gases within fluid-inclusions in order to obtain direct palaeotemperature information (Kluge et al., 2008; Vogel et al., 2013; Ghadiri et al., 2018).

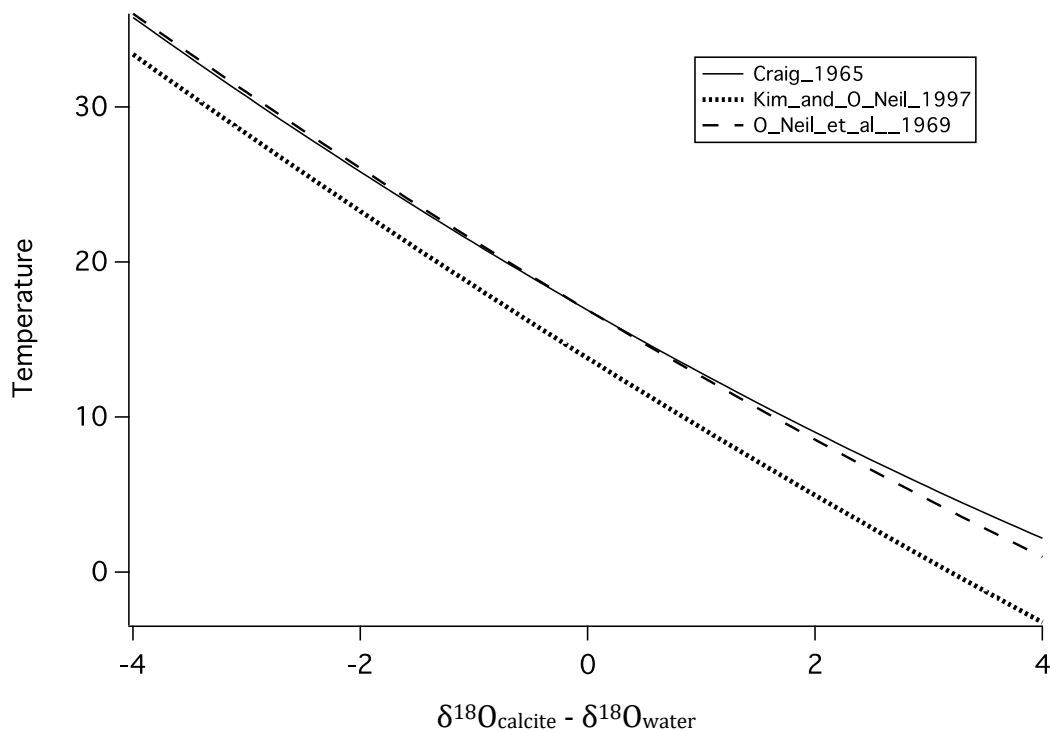


Fig. 2.10 – Comparison of three of the most commonly applied palaeotemperature equations to speleothems.

2.4.4. Clumped-isotope Analyses

Until recently, the main sources of palaeoclimatic information obtained from speleothems (namely stable isotopes, annual laminae, and trace element analyses), have failed to provide accurate palaeotemperature estimates (Kluge et al., 2008). This problem has recently been addressed through the development of the carbonate clumped-isotope palaeothermometry technique. The use of clumped-isotopes in palaeoreconstruction research has rapidly expanded since its inception and initial applications to atmospheric gases (Eiler and Schauble, 2004), and is now being extensively applied to carbonates (Ghosh et al., 2006a; Ghosh et al., 2006b; Guo, 2008; Daëron et al., 2011; Affek, 2013; Kluge et al., 2013; Dux, 2015; Daëron et al., 2019). Although relatively recently established, the method has been applied to a number of archives, both terrestrial and marine (Wacker et al., 2014; Chivas and Dux, 2015), such as corals (Thiagarajan et al., 2011; Saenger et al., 2012), marine organisms (e.g. brachiopods, molluscs) (Finnegan et al., 2011; Dennis et al., 2013), terrestrial fossils (Eagle et al., 2010; Csank et al., 2011; Eagle et al., 2011), soil carbonates (Snell et al., 2012; Peters et al., 2013), palaeosols (Ghosh et al., 2006b; Huntington et al., 2010), atmospheric gases (Eiler and Schauble, 2004), and speleothems (Affek et al., 2008; Daëron et al., 2011; Kluge et al., 2013; Daëron et al., 2019). Additionally, despite its relatively recent development, there are several variations of the analytical method that have been applied in different institutions including Yale University (Affek et al., 2008; Huntington et al., 2009; Zaarur et al., 2013; Kluge et al., 2014), Harvard University (Dennis et al., 2013; Fernandez et al., 2014), The California Institute of Technology (Ghosh et al., 2006a; Ghosh et al., 2006b; Guo et al., 2009), LSCE Paris (Daëron et al., 2016; Daëron et al., 2019), The Geological Institute ETH Zurich (Wacker et al., 2014), and The University of Wollongong (Dux, 2015). This is advantageous for both exploration of the potential applications of the method, and for future developments of its accuracy and precision; however, it does cause some difficulties in maintaining inter-laboratory consistency regarding standards and calibrations.

The carbonate clumped-isotope palaeothermometry technique has been suggested to be one of the most significant advances in speleothem palaeoclimatology to arise in the last decade (Daëron et al., 2011). It has built on the conventional uses of stable isotopes, as pioneered by Urey (1947), and has provided a potential solution for the difficulties with obtaining reliable palaeotemperatures from carbonates (Kluge et al., 2008). Analyses are performed on the CO₂ gas extracted from the speleothem through phosphoric acid digestion. Despite its potential, it is less widely understood than the majority of

palaeoclimate methods, and still holds significant technical challenges (Huntington et al., 2009; Eiler, 2011). However, due to the unique information it can provide, it is rapidly expanding (Fairchild and Baker, 2012).

Clumped-isotope palaeothermometry is based on the thermodynamic preference for the heavier isotopes, ^{13}C and ^{18}O (quantified as Δ_{47}), to bond with each other within carbonate minerals compared to bonding with lighter isotopes, ^{12}C and ^{16}O (Eiler, 2007). The theory of clumped-isotope thermometry overcomes the barriers of conventional isotope thermometers as it examines the homogenous equilibrium process within a single phase as opposed to the phase change occurring in the use of conventional isotope methods (i.e. water to mineral). It also differs in that the equilibrium constants are unaffected by the total isotopic composition of the mineral and its precipitating fluid (Ghosh et al., 2006a). As a result, Δ_{47} theoretically varies only as a direct result of variations in temperature, thus forming the principle of clumped-isotope thermometry (Eiler, 2007, 2011; Eiler et al., 2014). Under equilibrium conditions, the thermodynamic preference is such that, as the temperature decreases, there is an increase in the clumping of the heavy isotopes. At high temperatures, Δ_{47} approaches zero as the isotopes favour a stochastic, or random, distribution (Eiler, 2007; Affek, 2013); it is the quantification of the deviation from this stochastic distribution that is used as a proxy for temperature at the time of carbonate formation.

Another distinct advantage of the clumped-isotope method is that it provides an opportunity for palaeotemperatures to be determined with no knowledge of the source water. Additionally, the information obtained from Δ_{47} analyses can also be used to calculate $\delta^{18}\text{O}$ values of precipitating host water. In the case of speleothems, such information can be very useful in interpretations of palaeoprecipitation as the host water is theoretically a direct representation of the precipitation that fell above the cave. This is particularly important in light of the known limitations of fluid-inclusion analyses, and in samples where water contents are too low for any such analyses. With further development of the method it is possible that uncertainties and errors associated with temperatures produced from the clumped-isotope analyses will be reduced to the extent that it will become the preferable method over fluid-inclusion analyses.

While the measurement of Δ_{47} follows similar procedures to that of traditional stable isotopes in speleothems, there are some significant differences. These differences largely relate to the extra requirements that result from the significantly lower concentrations of the isotopologues of interest for Δ_{47} calculations (Huntington et al., 2009; Eiler, 2011). Firstly, the purification of gas samples prior to measurement is a vital step preceding analyses. This step is

primarily focussed on removing potential contaminants such as water (a precaution also undertaken in conventional stable isotope analyses) and volatiles, which may interfere with the isotopic signature measured (Dux, 2015). Also, higher precision dual-inlet mass spectrometers must be used as opposed to continuous flow instruments, and must be fitted with additional and more sensitive collectors to allow for the measurement of masses 47-49 as well as the masses 44-46 that are used in the measurement of conventional stable C and O isotopes. Similarly, sample sizes and measurement times are also significantly increased.

As with fluid-inclusion analysis, there have been numerous attempts to derive a universally applicable equation for attaining temperatures from Δ_{47} measurements. This includes theoretical, experimental and empirical approaches, each of which has shown to present significant differences in calculated temperatures (**Fig. 2.11**). There have been concerns surrounding the application of the theoretical calibrations and focus thus far has been on developing and improving experimental and empirical calibrations. Discrepancies between curves are hypothesised to result from subtle differences in analytical and data reduction methods; however, only further research in the field will be able to clarify this.

The technique is complicated somewhat by the lesser natural abundance of the heavier isotopes in comparison to the lighter isotopes (Huntington et al., 2009). Due to the significantly lower concentrations of the isotopologues of interest (approximately 0.4‰), a comparatively large sample size (usually in excess of 10 mg, although some laboratories are applying methods with significantly smaller sample sizes e.g. Meckler et al., 2014) and prolonged data measurement time (approximately 3-4 hours per sample) is required relative to those required from conventional techniques (Huntington et al., 2009; Chivas and Dux, 2015). These are issues that are beginning to be addressed through methodological advances (Eiler, 2011). There can also be very small temperature differences between samples; in such cases, it becomes critical to conduct replicate analyses in order to obtain accurate and precise estimates (Zaarur et al., 2013). It is also important to note that Δ_{47} only directly reflects the temperature at the time of mineral growth under equilibrium conditions, and that any disequilibria must be accounted for in calculations and interpretations (Affek, 2013).

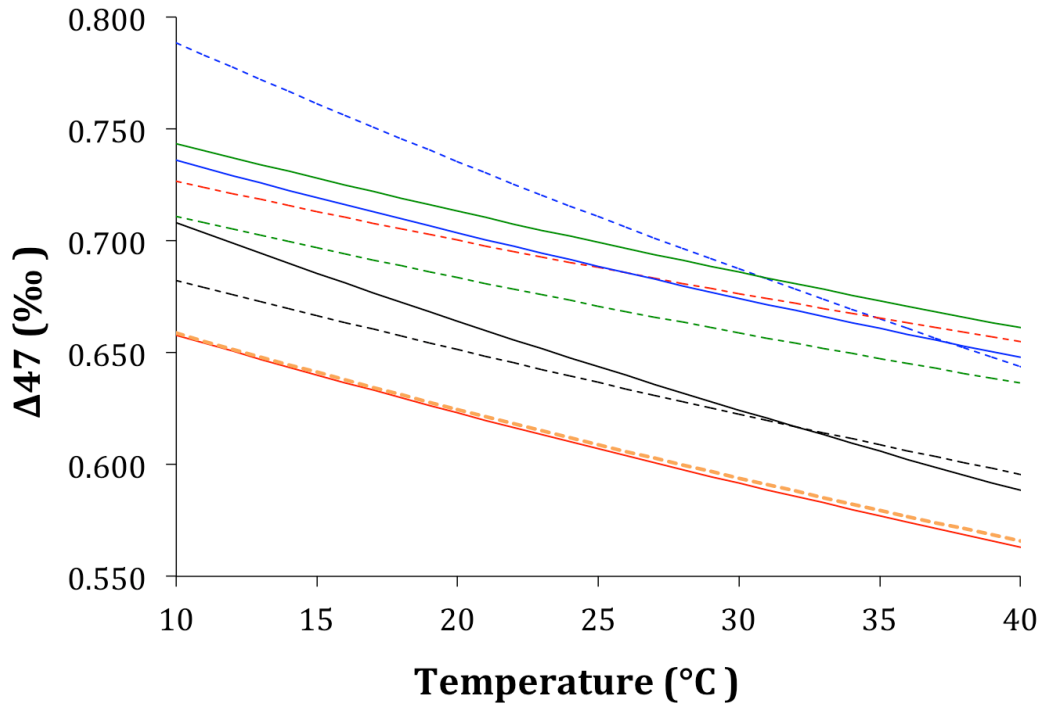


Fig. 2.11 – Comparison of calibration curves for Δ_{47} : solid black line (Zaarur et al., 2013), dashed black line (Guo et al., 2009), solid red line (Kelson et al., 2016; Kelson et al., 2017), dashed red line (Defliese and Lohmann, 2015), solid blue line (Tang et al., 2014), dashed blue line (Ghosh et al., 2006a), solid green line (Dennis and Schrag, 2010), dashed green line (Wacker et al., 2014), dashed orange line (Daëron 2016, pers. comm.).

Kinetic isotopic fractionation and the resultant disruption of homogenous equilibrium conditions is one of the most significant challenges currently observed in carbonate clumped-isotope palaeothermometry (Eiler et al., 2014), particularly of speleothems, which are amongst the most susceptible of carbonates to disequilibrium isotopic fractionation. It has been found in several previous studies that records utilising speleothems exhibit a disequilibrium isotopic effect, thus limiting their application. Stalagmites have commonly been reported to present temperatures of up to 8 °C higher than actual (or expected) cave temperatures (Affek and Zaarur, 2014; Dux, 2015), in comparison to fluid-inclusion analyses, which tend to underestimate temperatures (Daëron et al., 2011). It is argued that this reflects varying kinetic isotope effects, such as rapid degassing and/or crystallisation reactions (Guo, 2008). Furthermore, the isotopic dynamics of speleothem deposition are highly complex and influenced by a number of external processes (Fairchild and Baker, 2012), adding to the difficulty of applying Δ_{47} as a direct palaeotemperature signature. A key problem in the application of the Δ_{47} technique to speleothems is that equilibrium conditions at the time of precipitation cannot be assumed; therefore, the magnitude of the offset identified in Δ_{47} measurements cannot be accurately estimated, particularly in old or inactive

cave systems (Dux, 2015). Some attempts have been made to account for such fractionation processes (e.g. Affek and Zaarur, 2014), however, thus far these processes have been identified to be site specific and therefore not applicable as a general correction procedure. Additionally, there have been indications that their use alongside other geochemical proxies, such as fluid-inclusions, may assist in identifying and accounting for such uncertainties (Wainer et al., 2011).

In addition to problems associated with fractionation processes, it has been found that samples with significantly high organic matter may be difficult to measure accurately, as the volume of organic matter may be in excess of the abilities of the purification process, resulting in contamination of the Δ_{47} measurements. Additionally, there is the possibility that where samples are rich in organic material, there may be interactions between the organics and the H_3PO_4 during the sample gas preparation, which has the potential to significantly enrich the Δ_{47} signal, thus producing significantly lower than true temperatures. Such problems may account for some variations and uncertainties in temperature estimates from Δ_{47} measurements.

While unlikely to be a problem in the context of speleothems, it is also important to note that prolonged exposure (in the timeframe of 10^6 to 10^8 years) to temperatures exceeding approximately 100 °C, or any length of exposure to temperatures exceeding 1000 °C, will result in the significant alteration of the original formation temperature preserved due to the return to stochastic distribution (Henkes et al., 2014; Chivas and Dux, 2015).

2.5. Significance of Thesis

The ability to date speleothems beyond the previous ~500 kyr limit of U-Th dating using the U-Pb method creates a wealth of opportunities in speleothem research. This thesis explores some of this potential, and in doing so, attempts to address several significant gaps in the literature, thus providing significant additional knowledge in the fields of speleothem palaeoclimatology and Pliocene palaeoclimate research. In particular, the gaps in literature that the thesis addresses are:

- disproportionate palaeoclimate literature for the Southern Hemisphere in comparison to the Northern Hemisphere;
- a paucity of terrestrial sources of palaeoclimate information for the Pliocene period;
- the few applications of speleothem research beyond the previous ~500 kyr limit of U-Th dating;

- attempting to determine multiple ages (i.e. internal chronology) within a Pliocene speleothem;
- the use of novel techniques in obtaining palaeoclimate information from speleothems;
- obtaining reliable palaeotemperatures from speleothems; and
- developing an understanding of drivers of isotopic variation in precipitation in the Nullarbor region.

3. Study Site

3.1. Geography

Australia is an important region for palaeoclimatic study, as one of the largest landmasses in the Southern Hemisphere and encompassing a range of climatic zones, where palaeoclimate records are relatively rare. The Nullarbor Plain is located in southwestern Australia, straddling the South Australia - Western Australia border (**Fig. 3.1**), and extends ~900 km east to west, and ~300 km north to south (James and Bone, 1991), representing the onshore section of the Eucla Platform. The Nullarbor Plain occupies approximately 240,000 km², making it one of the largest karst systems in the world (Webb and James, 2006). It has been slightly tilted in accompaniment to the gentle subduction along Australia's northern margin (Sandiford, 2007; Miller et al., 2012a) creating a near-continuous cliffline of 40-90 m a.s.l. (Webb and James, 2006; Miller et al., 2012). The surface of the Plain reaches ~200 m a.s.l. at its highest point (Doerr et al., 2012).

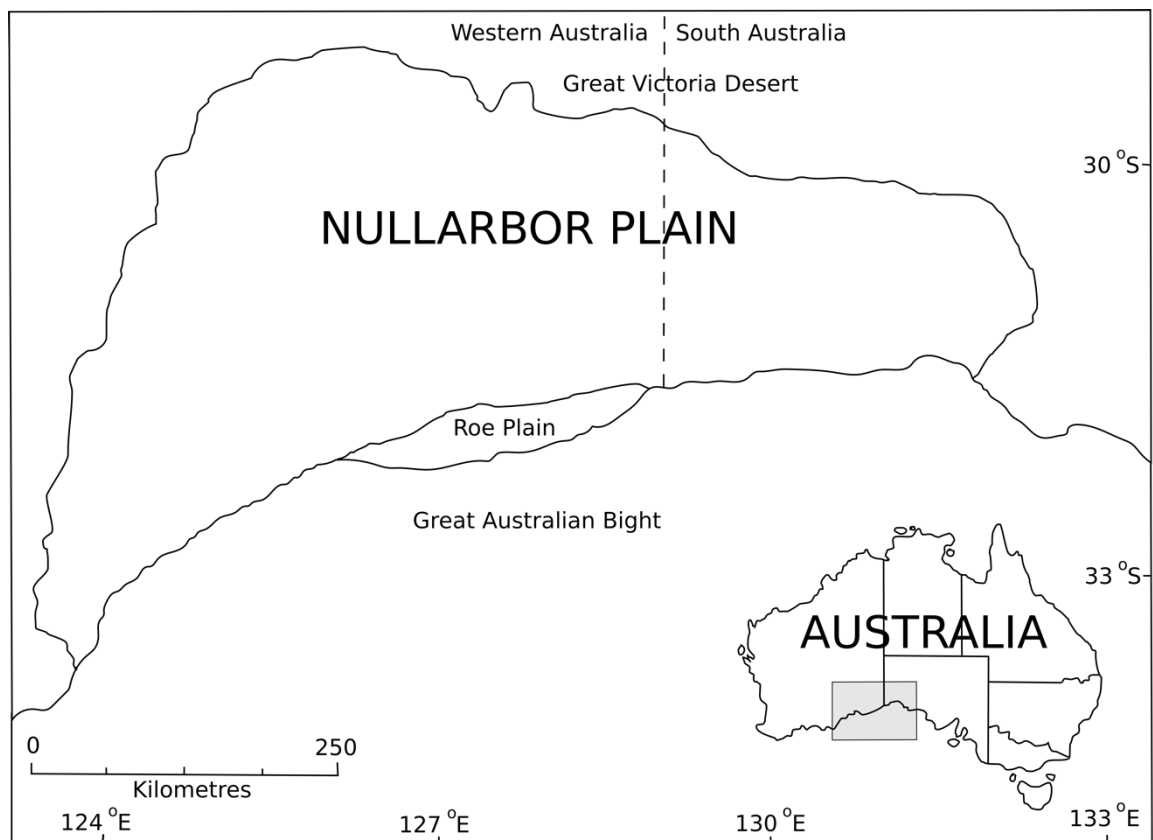


Fig. 3.1 – Location map of the Nullarbor Plain, and position within Australia (inset).

The region has remained a relatively stable continental margin throughout the Cenozoic era (Feary and James, 1995), and thus the Nullarbor Plain has remained relatively undisturbed with the exception of the aforementioned uplift (Doerr et al., 2012). There are a vast number of caves across the Nullarbor Plain, predominantly in the southern region, many of which were formed during the Pliocene (Webb and James, 2006). Miller et al. (2012) note that the speleothems in these caves contain critical information regarding past climate and hydrogeologic systems, reconstructions of which can be used to contribute to the wider understanding of the climate of the Southern Hemisphere during the Pliocene. It has also been suggested that further study of the region could provide a clearer picture of the timing and causes of the transition from a wetter climate during the Pliocene to the arid to semi-arid climate experienced at present (Woodhead et al., 2006). These arguments support the importance of both the selected study site, and the overarching aims of this thesis.

3.2. Geological History

The Nullarbor Plain comprises a succession of limestones that have been deposited in the Eocene-Miocene Eucla Basin atop Precambrian basement rocks (James and Bone, 1994; Doerr et al., 2012). The basin hosts the largest onshore example of Cenozoic marine sedimentation in the world (Clarke et al., 2003) that is up to 300m thick (Hou et al., 2008). There were three major periods of deposition (**Fig. 3.2**) of dominantly cool-water carbonates (Hou et al., 2008), resulting in three distinctive limestone successions (**Fig. 3.3**) that together comprise the Eucla Group (James et al., 1994; Webb and James, 2006). A thin, non-calcareous deposit separates the underlying basement rocks and the lowermost limestone deposits over much of the Nullarbor Region; this ~30m thick estuarine-fluvial to marine unit (Hou et al., 2008), known as the Hampton Sandstone, is believed to have been deposited in the middle to late Eocene (James et al., 2006).

The earliest limestone member of the Eucla Group succession is the Wilson Bluff Limestone, which has an average thickness of ~300 m and extends across most of the Nullarbor Region (James et al., 2006; Webb and James, 2006). It is widely considered to have been formed via non-continuous deposition, in an open marine shelf environment (O'Connell et al., 2012). It is composed of predominantly fine to medium grained bryozoan and planktonic foraminifera (O'Connell et al., 2012) resulting in a high porosity and low permeability (Doerr et al., 2012). Following the deposition of the Wilson Bluff Limestone, during the Early Oligocene, the sea retreated from the region for a period of ~10 Ma, leaving it exposed to weathering and erosional processes (Webb and James, 2006). During

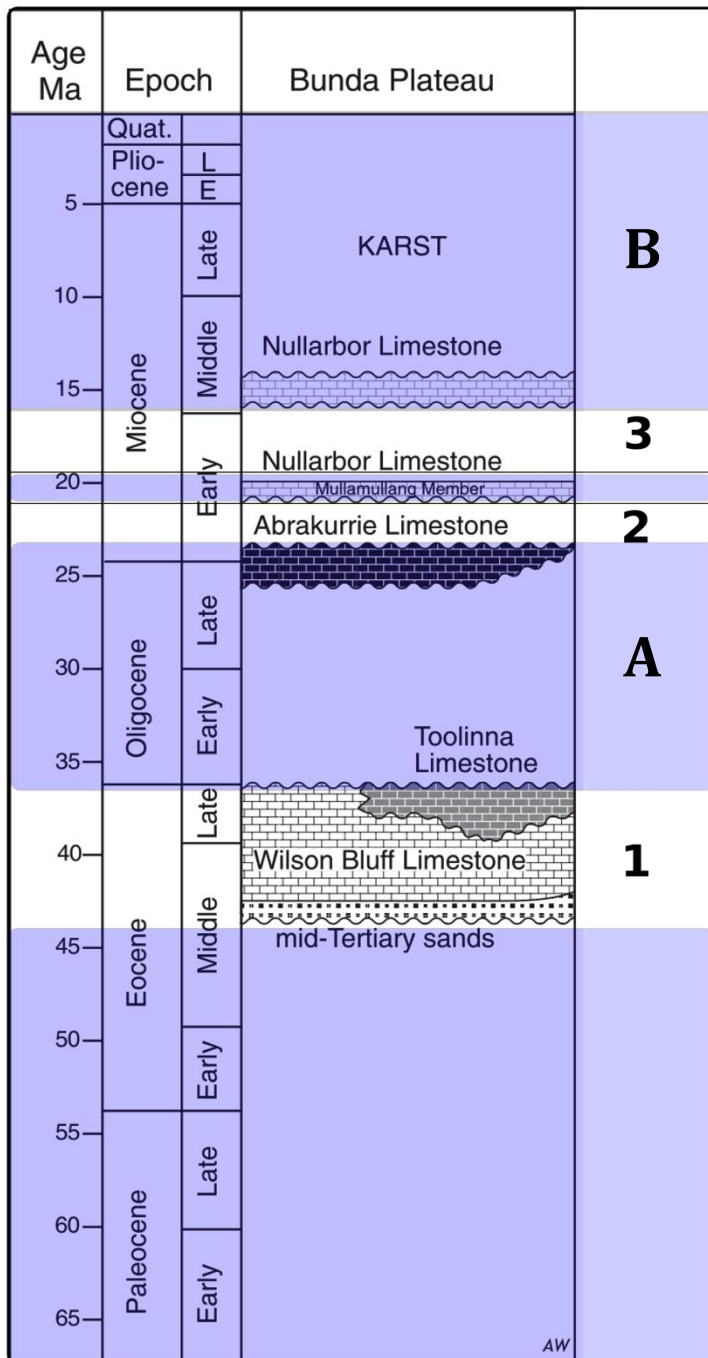


Fig. 3.2 – Stratigraphy of the deposition stages of the Nullarbor Plain. The three major periods of limestone deposition are highlighted chronologically as 1, 2, and 3. The two periods of major cave formations are highlighted chronologically as A and B. Modified from Webb and James (2006).

this period a modest surface topography was developed, with a prominent thin reddish soil layer, likened to that of the modern day (Webb and James, 2006; Doerr et al., 2012). In some locations, predominantly the southwest and central regions of the Plain, the Wilson Bluff Limestone is overlain by the Abrakurrie Limestone (Hou et al., 2008). This succession was deposited between the Late Oligocene and the Early Miocene, and is approximately 100 m thick in its centre, thinning towards its edges (James and Bone, 1991; Webb and James, 2006). This variable thickness results from a period of minor subsidence (Hou et al., 2008), which has been suggested to have occurred concurrently with the deposition of the Abrakurrie Limestone (Webb and James, 2006). The latter is both porous and permeable (Doerr et al., 2012), resulting from its dominant composition of

medium to coarse grained bryozoans (O'Connell et al., 2012). At the end of the Early Miocene the sea retreated for ~1 Ma before advancing again in the Middle Miocene. During this advance the Mullamullang Member of the Nullarbor



Fig. 3.3 – Photograph of the exposed Bunda cliffline from a tourist viewpoint east of Eucla, showing the distinctive successions of Tertiary Nullarbor Limestone deposition.

Limestone was formed, deposited as a nodular algal limestone covering a similar extent to the Abakurrie Limestone (Webb and James, 2006).

Following the deposition of the Mullamullang Member, the sea expanded further across the Nullarbor Region (Webb and James, 2006), resulting in the deposition of the uppermost succession of the Eucla Group, the Nullarbor Limestone (James and Bone, 1991). While it is a relatively thin layer of generally ~20 m or less (Webb and James, 2006), it has a more extensive coverage than the Abakurrie Limestone, covering the entirety of the Nullarbor Plain (Doerr et al., 2012). In comparison to the earlier limestone successions of the Eucla Group, there is a relatively high proportion of aragonitic fossil material within the Nullarbor Limestone (Doerr et al., 2012). It also differs from the lower sections of the Eucla Group as it is composed mostly of large benthic foraminifera and corals that indicate deposition during warmer conditions (O'Connell et al., 2012).

Shortly after the deposition of the Nullarbor Limestone, the surface was once again exposed by a combination of sea level retreat and local tectonic uplift. There is some uncertainty regarding the timing of these events. It is generally agreed, however, that sea level retreat marginally preceded the uplift event (James et al., 2006; Webb and James, 2006). The near-continuous exposure of the

Nullarbor Limestone since this time has resulted in the development of the vast, flat landscape apparent on the Nullarbor Plain today (James and Bone, 1991; 1994).

In some coastal regions, extensive erosion of the Eucla Group limestones occurred during the Early to Late Pliocene forming the Roe Calcarene, a thin marine calcarenite (James et al., 2006). This forms the Roe Plain, which extends ~300 km east to west and is ~35 km at its widest point (James et al., 2006). Sr-isotope dating and integrated biostratigraphic studies suggest that this region is Late Pliocene in age (James et al., 2006). The dominant species of molluscs and foraminifers present indicate that the water temperatures were slightly warmer than present at the time of deposition (Murray-Wallace, 2002).

Since the exposure of the Eucla Group succession ~14 Ma, there has been relatively little erosion of the surface. While this erosion has been slightly greater towards the coast where rainfall is higher, it has been relatively uniform across the region (Webb and James, 2006). The proposed exceptionally low erosion rates of 2-4mm/kyr (Webb and James, 2006) have been hypothesised to relate to the increasing aridity of the region from the late Miocene onwards (Webb and James, 2006; Hou et al., 2008).

3.3. Cave Formation on the Nullarbor

Early explorations of the Nullarbor caves differentiate cave types into two basic categories – shallow and deep caves (Thomson, 1949). Although oversimplified, it is argued that such a classification reflects the dominance of cave development at just two horizons within the karst system (Goede et al., 1990a). The most commonly occurring cave entrance types are either vertical solution pipes, or those occurring at the base of collapse dolines (Goede et al., 1990a). Early investigations of the Nullarbor caves also revealed that the majority of caves have either a single entrance, or multiple entrances occurring at approximately the same topographic level resulting in minimal seasonal dependent air currents (Jennings, 1967). Despite this, in several caves significant blowholes and other breathing phenomena have been identified, with a number of them shifting from influx to efflux on a regular (i.e. daily) basis (Wigley and Wood, 1967; Burnett et al., 2013).

There are two periods in which it has been suggested that cave development in the Nullarbor Region occurred (Webb and James, 2006), noted in **Fig. 3.2** as 'A' and 'B'. The larger and deeper caves in the Nullarbor are thought to have formed during the first period of limestone exposure, from the late to early Oligocene following the deposition of the Wilson Bluff Limestone, during a period

of seasonally wet conditions (Doerr et al., 2012). During this period conduit development and enlargement was favoured by the lower water tables and subsequent increased hydraulic gradients associated with the retreat of the sea from the region (Webb and James, 2006). It has been suggested that the preservation of these caves during the subsequent limestone deposition was assisted by the flooding of the region associated with the returning sea, thus isolating the caves from any diagenetic processes (Webb and James, 2006). The extensive breakdown and collapse of these Oligocene caves is hypothesised to have been triggered by the uplift event that occurred following the deposition of the Nullarbor Limestone, which resulted in the draining of these conduits thus significantly weakening them (Webb and James, 2006).

A second hypothesised period of cave development followed the deposition of the Nullarbor Limestone ~14 Ma (Webb and James, 2006). It has also been suggested, based upon the U-Pb dating of numerous Nullarbor speleothems producing ages of 3-6 Ma (Woodhead et al., 2012; Woodhead et al., 2019), that the majority of cave development may have occurred in the relatively wet climate of the Pliocene (Webb and James, 2006). There is little evidence for cave formation following the deposition of the Roe Calcarene as all known caves on the Roe Plain are in the underlying limestones, exposed through accidental collapse (Grimes, 2006). The majority of caves in the region occur within the wetter coastal regions of the Nullarbor Plain (Dunkley, 1967), with most occurring within ~60 km of the coast (Webb and James, 2006). Relative to the size of the Nullarbor Plain, the number of known caves is comparatively low when compared with other karst regions (Goede et al., 1990a).

The caves of the Nullarbor are largely wild and unmapped, including that from which the primary speleothems used in this study were obtained. As such, there is little information available regarding cave sizes, depths, and networks; however the caves are largely relatively shallow and contained within the uppermost stratigraphic unit of early – middle Miocene Nullarbor Limestone (Lowry, 1970; Woodhead et al., 2019). It was not deemed necessary to undertake further investigation into these aspects of the caves, as it is likely that significant modifications have occurred since the Pliocene when the speleothems used in this study were deposited. Furthermore, fossil evidence (or the lack thereof) in Nullarbor caves suggests that in the Pliocene the caves were predominantly closed at this time, with the majority of fossils being dated to within approximately the last million years (Prideaux et al., 2007; Double, 2017). As cave ventilation and the proximity to cave entrances are the factors most likely to alter the palaeoclimatic signals preserved in speleothems, if the caves were largely closed throughout

speleothem deposition, it is unlikely that these features need further consideration for the context of this thesis.

3.4. Modern and Past Climatic Conditions of the Nullarbor

3.4.1. Modern Conditions

Australia encompasses a number of broad climate zones (**Fig. 3.4**), with the Nullarbor Plain fitting broadly into the desert and grassland Koppen classification groups as determined by the Bureau of Meteorology. The present-day climate of the Nullarbor Plain is semi-arid to arid with average rainfall varying from 150-250 mm per annum across the plain (Webb and James, 2006). Globally, there are three 'cells' of atmospheric circulation, which are referred to as the Polar cell, Ferrel cell and Hadley cell (**Fig. 3.5**). These circulation cells influence dominant precipitation zones and are governed by the insolation gradient between the low and high latitudes and Earth's rotation. They are thus stronger at the equator – the Hadley cell – becoming increasingly weaker towards the poles (Harrington Jr. and Oliver, 2000; Johanson and Fu, 2009).

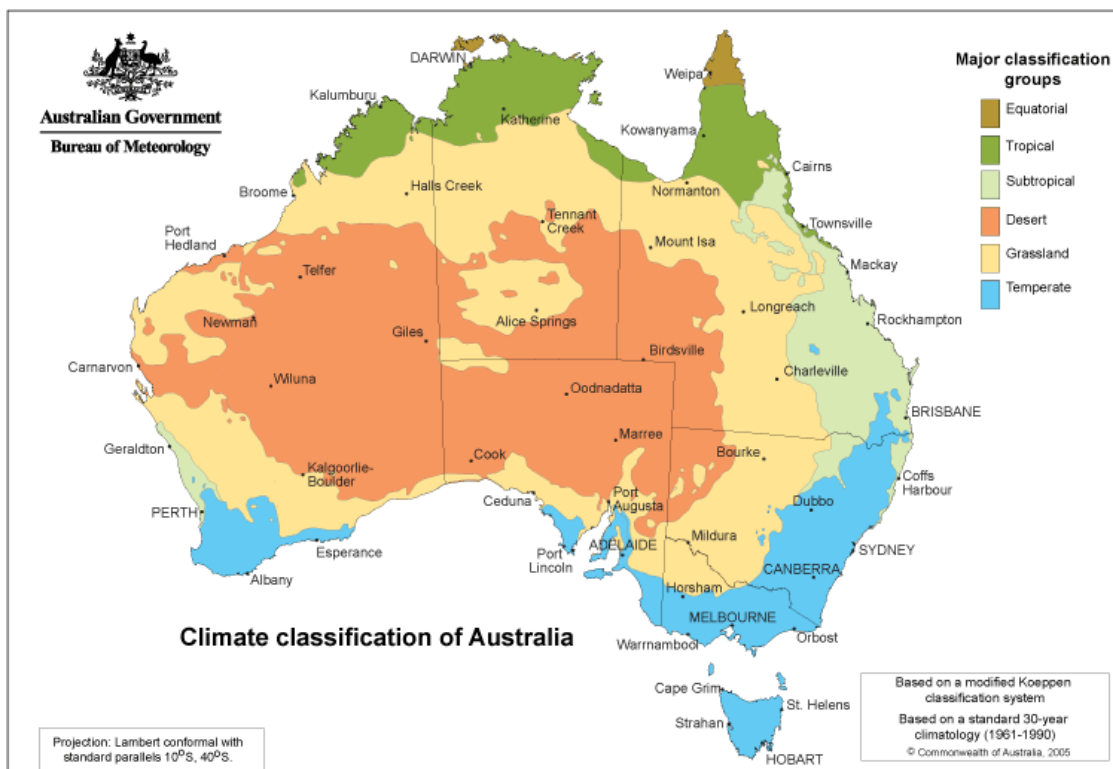


Fig. 3.4 – Koppen climate classifications of Australia. Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

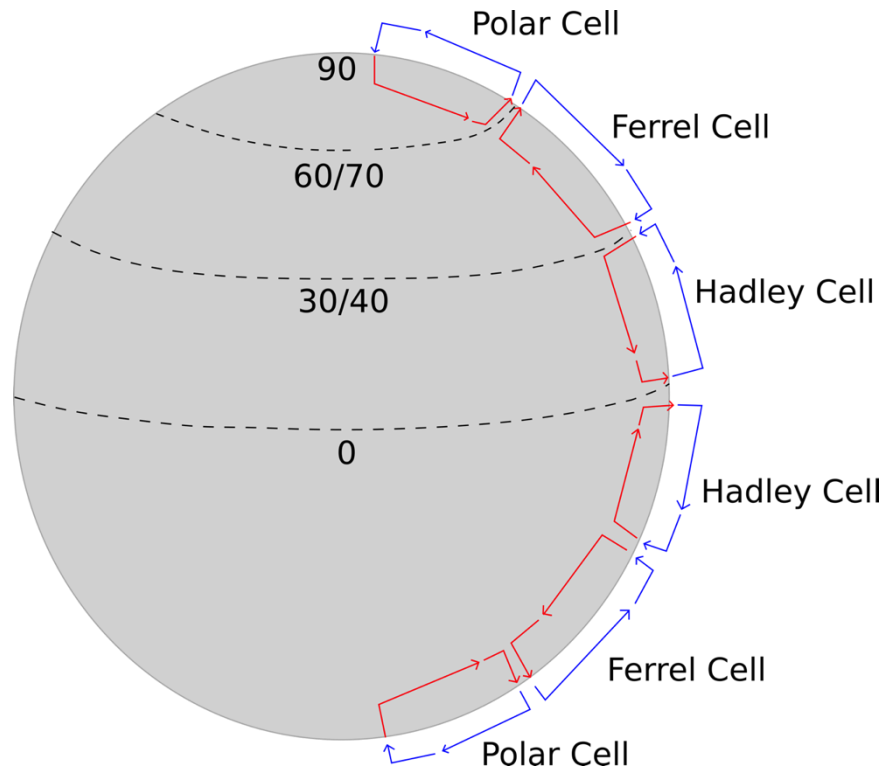


Fig. 3.5 - The three global cells of circulation at their respective latitudes (°).

The Hadley cell circulation has the largest influence on precipitation in Australia and will form the focus of the following discussion. The Hadley cell is driven by the rising of moist warm air near the equator, and the subsidence of warm, dry air in the subtropics (Johanson and Fu, 2009), with similar conditions driving the cell circulations at other latitudes. These circulation patterns are altered (typically in terms of expansion, an equatorwards migration, or contraction, a polewards migration) by variations in climate, in particular temperature. Some models have suggested that, following current global warming trends, it is likely that the Hadley cell will noticeably expand by the end of this century as a direct result of increased mean global temperatures (Fu et al., 2006; Seidel et al., 2008). An expansion of the Hadley cell will have significant influences on global climates, including that of Australia. Under present conditions dominant rainfall zones are concentrated in equatorial regions where ascending branches of Hadley cells uplift moisture thereby promoting rainfall (Seidel et al., 2008). The opposite is the case in the lower latitude regions of the tropical belt at the locations of the descending branches of Hadley cells, which bring down drier air masses resulting in notably drier conditions (Seidel et al., 2008). As a result, expansions and contractions in these Hadley cells can result in significant differences in the locations of dominant rainfall and dry zones. This is important to consider not only

when predicting future climatic changes but also when looking back to past conditions.

While there has been research into the modern drivers of precipitation in several locations of Australia (Smith et al., 2000a; McDonald et al., 2004; Treble et al., 2005b; Hendon et al., 2007; Meneghini et al., 2007; Barras and Simmonds, 2008; Barras and Simmonds, 2009; Liu et al., 2010; Callow et al., 2014), there has been no investigation of the Nullarbor region specifically. However, it is possible to identify the dominant climate modes and systems influencing the climate of the Nullarbor based on the current understanding of their influence and geographical spread. The modern day climate of Australia is highly variable geographically, and is influenced by a number of large-scale climate modes and systems including the El Niño Southern Oscillation (ENSO – McDonald et al., 2004), the Southern Annual Mode (SAM – Hendon et al., 2007) and the Indian Ocean Dipole (IOD – Smith et al., 2000a). These climate modes act both independently and in conjunction to influence weather patterns across Australia.

ENSO is a variation in the winds and water temperatures seen in the tropical eastern Pacific, expressed in an oscillation between El Niño and La Niña phases which have significant influence on the climate of much of Australia (Cai et al., 2011). El Niño phases are characterised by warming across the eastern and central Pacific, often associated with a weaker Walker circulation, whereas La Niña phases are characterised by cooler than average SSTs in the eastern and central Pacific (**Fig. 3.6**). La Niña conditions generally result in significantly increased rainfall over much of southern and eastern Australia (Risbey et al., 2009a), including the Nullarbor region, primarily during the winter and spring months (**Fig. 3.7**), whereas the opposite is the case for El Niño conditions (**Fig. 3.8**). These oscillations are particularly significant in the context of reconstructions of Pliocene climates, due to the commonly posed (although not universally accepted) argument for near-constant El Niño conditions during this time period (Wara et al., 2005; Fedorov et al., 2006), and the impact this is likely to have had on the climate of the Nullarbor region.

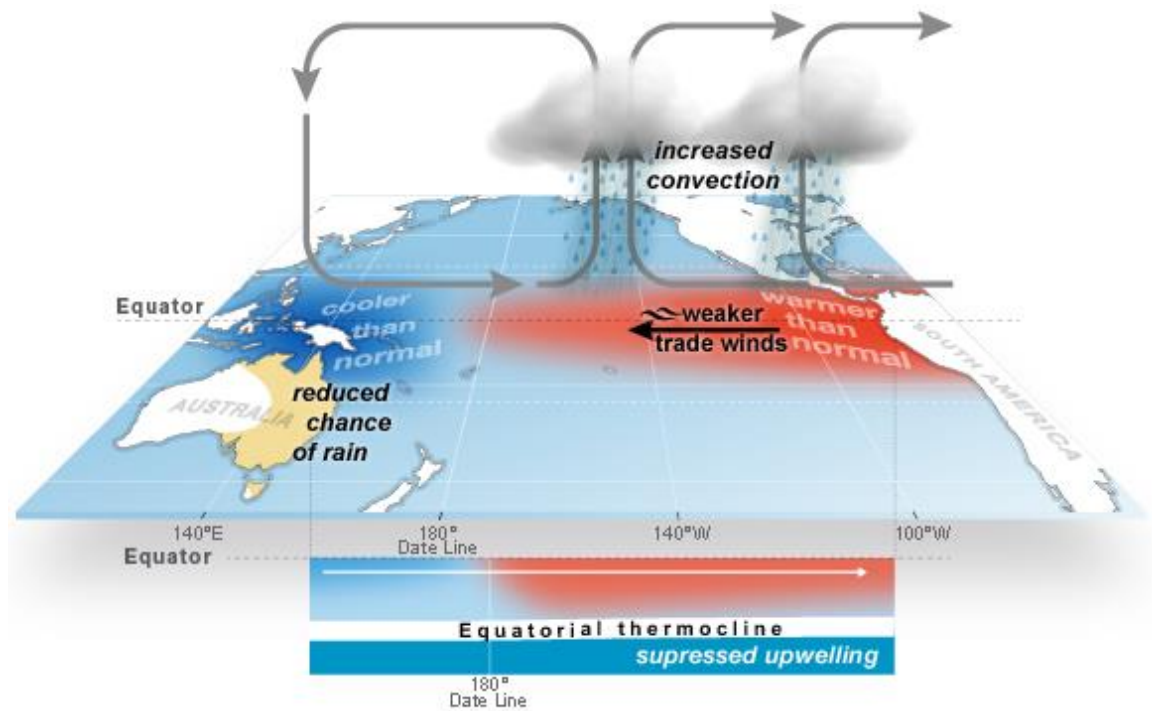
SAM is a climate mode that refers to the latitudinal movement of the southern westerly winds dominating the mid to high latitudes of the Southern Hemisphere (Hendon et al., 2007; Meneghini et al., 2007). The westerly winds, or westerlies, are the prevailing winds in the mid-latitudes, and are particularly dominant in the Southern Hemisphere. SAM has a significant influence on the climate of southern Australia (**Fig. 3.8**). During positive SAM phases, the westerlies contract polewards, thus reducing their strength and enhancing high-pressure systems over southern Australia. During negative SAM phases, the westerlies

expand equatorwards increasing the frequency of storm tracks and low-pressure systems over southern Australia (**Fig. 3.9**).

The IOD refers to shifts in average SSTs in the tropical Indian Ocean and has a significant influence on the precipitation and temperature patterns of large parts of western, southern and eastern Australia (Smith et al., 2000b; Ashok et al., 2003a; Ummenhofer et al., 2008; Cai et al., 2011). It is defined by three phases: positive, neutral, and negative (**Fig. 3.10**). During positive IOD phases, the westerlies are weakened resulting in a shift of warmer waters towards Africa. In Australia, this phase is generally represented by higher temperatures and reduced rainfall. Negative IOD phases are characterised by increased westerlies, and ultimately result in warmer SSTs northwest of Australia and thus increased rainfall (Ummenhofer et al., 2008). During neutral IOD phases there is no significant influence on the climates of Australia. These climate modes all have significant influences on the climate of the Nullarbor region, and Australia more broadly under present conditions. However, there are problems with applying climate modes such as these to the distant past, as will be discussed further in **Chapter 5**.

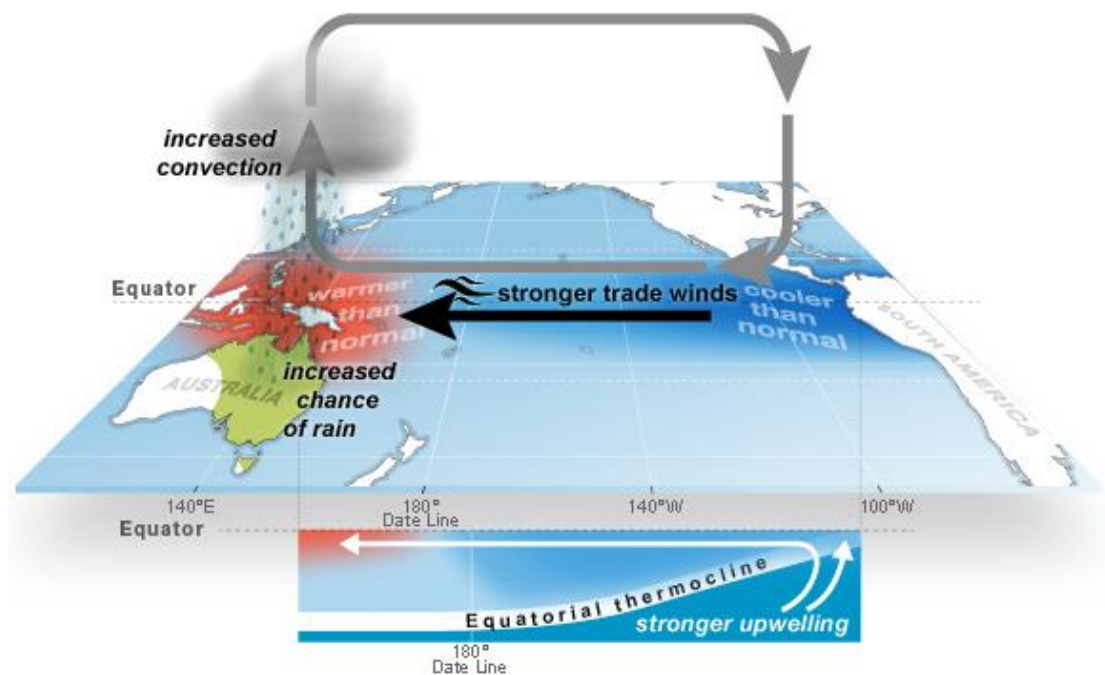
The subtropical jet stream also has a significant influence on precipitation in Australia, including the Nullarbor region, largely due to its role in the production of the northwest cloud bands (Wright, 1997; Gallant et al., 2007). These cloud bands develop as a result of interactions between the warm SSTs of the Indian Ocean and the high winds and trajectories of the jet stream. Large proportions of winter and spring rainfall in parts of western and central Australia have previously been identified to be a result of these north-west cloud bands (Simmonds, 1990; Wright, 1997; Murphy and Timbal, 2008). The subtropical jet stream is controlled by global atmospheric circulation patterns and is thus liable to vary in relation to expansions or contractions of the Hadley cell, by which an expansion of the Hadley cell results in a southward shift in the jet stream, results in decreased northern cloud band (NCB) sourced precipitation to the Nullarbor region (Wright, 1997).

Parts of north, west and eastern Australia fall within one of the global tropical cyclone zones (Klingaman et al., 2013). The cyclone season of Australia occurs between November and April and is associated with strong winds and heavy rainfall. The frequency and extent of tropical cyclones is strongly influenced by ENSO, with La Niña conditions increasing the frequency of cyclones making landfall in Australia (Folland, 2002; Risbey et al., 2009b; Klingaman et al., 2013). The locations of these cyclone zones, also referred to as mid-latitudinal storm tracks (Klingaman et al., 2013), are strongly influenced by Hadley circulation, and are therefore likely to shift equatorwards or polewards with the contraction or expansion of the Hadley cell respectively (Chen and Held, 2007).



El Niño–Southern Oscillation (ENSO): **El Niño**

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El Niño–Southern Oscillation (ENSO): **La Niña**

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Fig. 3.6 – Key characteristics of El Niño (top) and La Niña (bottom) phases and their overall influence on Australian climate. Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

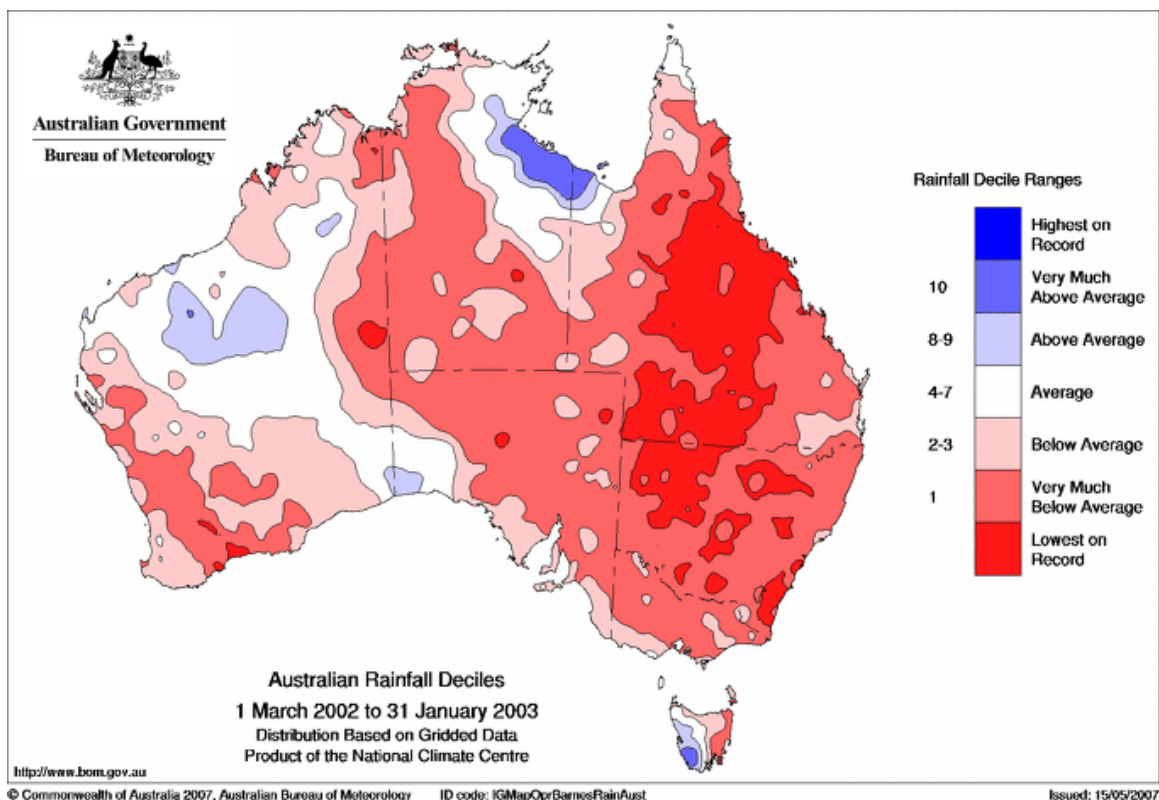
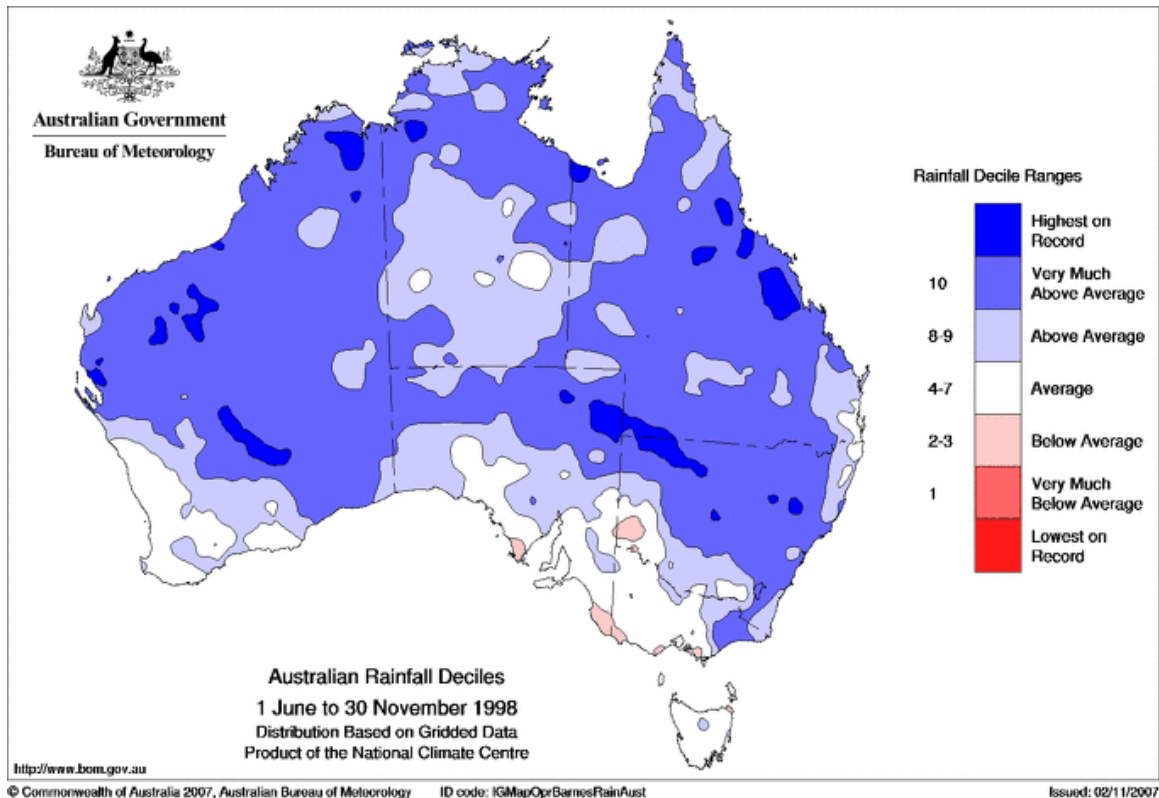


Fig. 3.7 – Average rainfall across Australia during periods of La Niña (top) and El Niño (bottom) conditions. Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

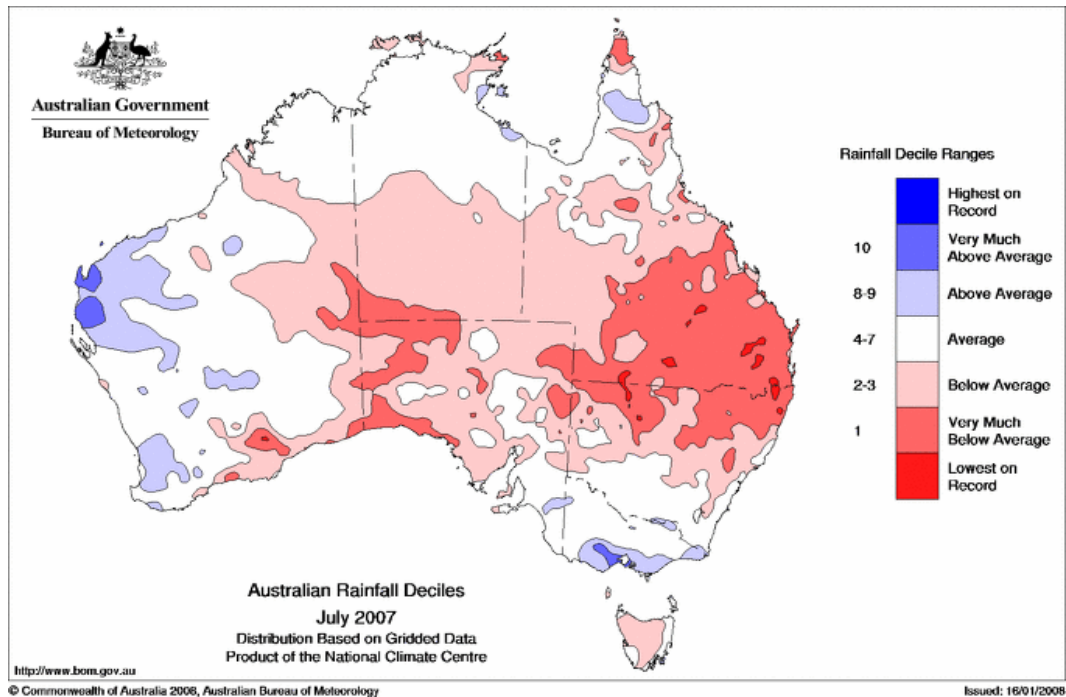


Fig. 3.8 – Summer rainfall (compared to average annual rainfall) under negative Southern Annual Mode conditions. Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

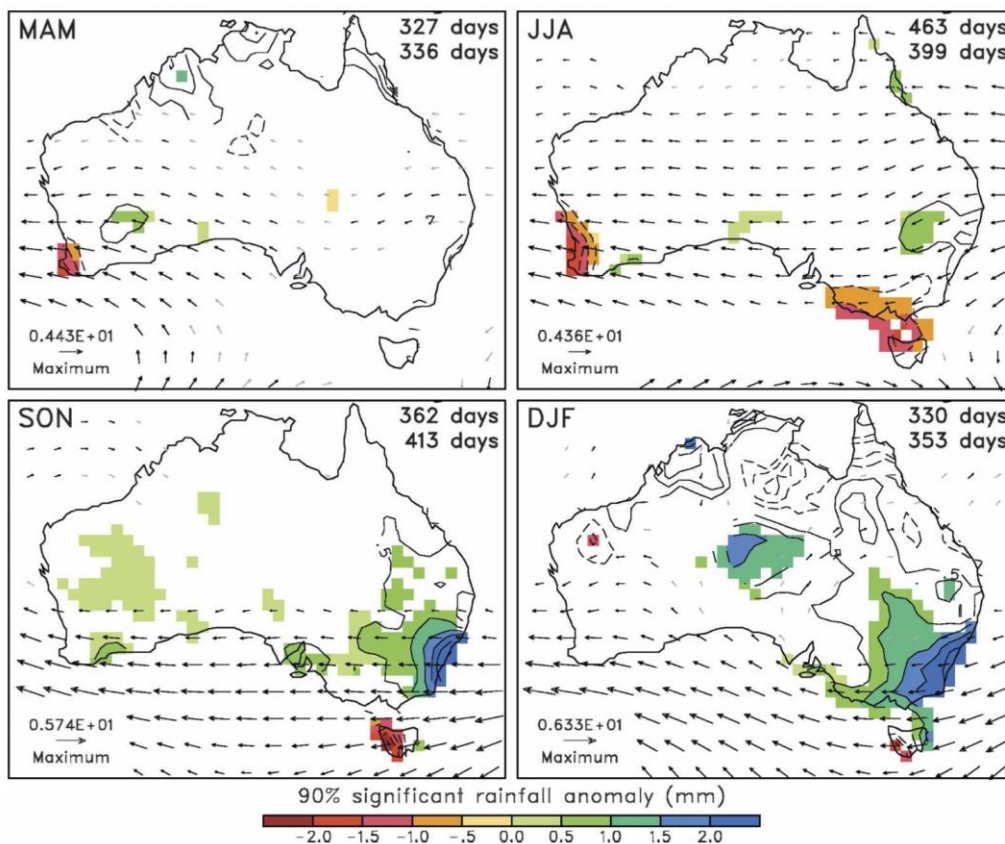
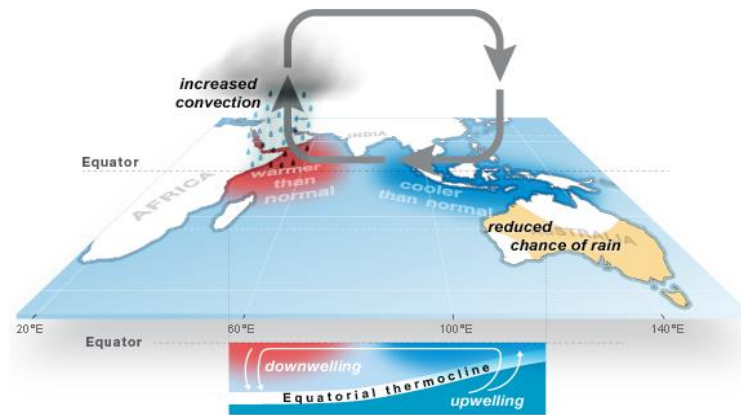
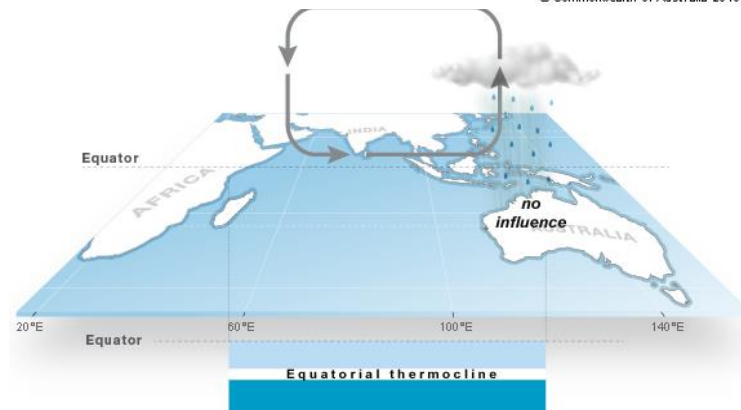


Fig. 3.9 – Composite daily rainfall maps for positive Southern Annual Mode conditions based on season (autumn top left, winter top right, spring bottom left, summer bottom right). Source: Hendon et al. (2007).

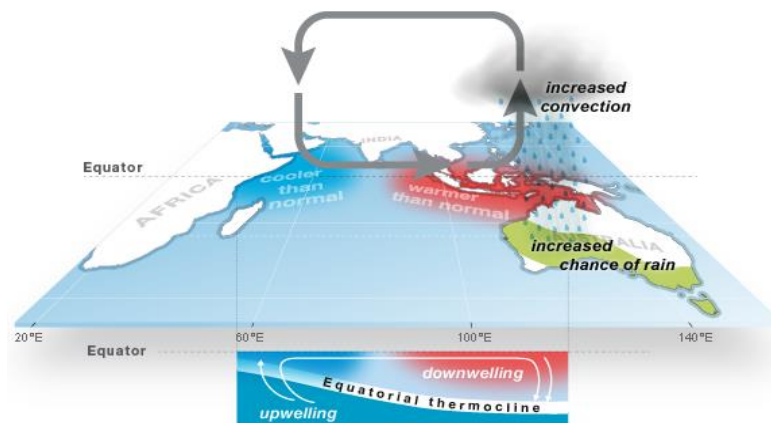


Indian Ocean Dipole (IOD): **Positive phase**

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Indian Ocean Dipole (IOD): **Neutral phase**



Indian Ocean Dipole (IOD): **Negative phase**

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Fig. 3.10 – Characteristic conditions of the positive (top), neutral (middle) and negative (bottom) phases of the Indian Ocean Dipole. Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

These cyclone systems commonly make landfall over northwest Australia, however the tail end of these systems can penetrate southern Australia, including the Nullarbor region (**Fig. 3.11**). It is important to consider the potential influences of variations in ENSO and Hadley circulation on the pathways of tropical cyclones and how this may influence the Nullarbor region.

Under modern conditions, the Nullarbor is sparsely vegetated and largely treeless, dominated by a shrub steppe vegetation regime (Gillieson et al., 1996). However, some coastal regions support taller shrubs, and small eucalypts and acacias (Miller and James, 2012). While it has been argued that due to the modern arid climate of the Nullarbor region there are no calcium carbonate speleothems actively growing at present, and few speleothems in the region more generally (Burnett et al., 2013), our field work has noted some active drips and a few active speleothems in some caves.

3.4.2. Past Conditions

The current understanding of Pliocene climates has been discussed more generally in Chapter 2. From the abundance of literature regarding Pliocene climates, it is possible to extract some details and understanding of the Nullarbor region more specifically. For example, models suggest increased temperatures of approximately 3-4 °C (Salzmann et al., 2013), with a mean annual precipitation of between 320 - 875 mm (Brierley et al., 2009; Sniderman et al., 2016). The notion that the Nullarbor Plain once had a significantly wetter climate is further

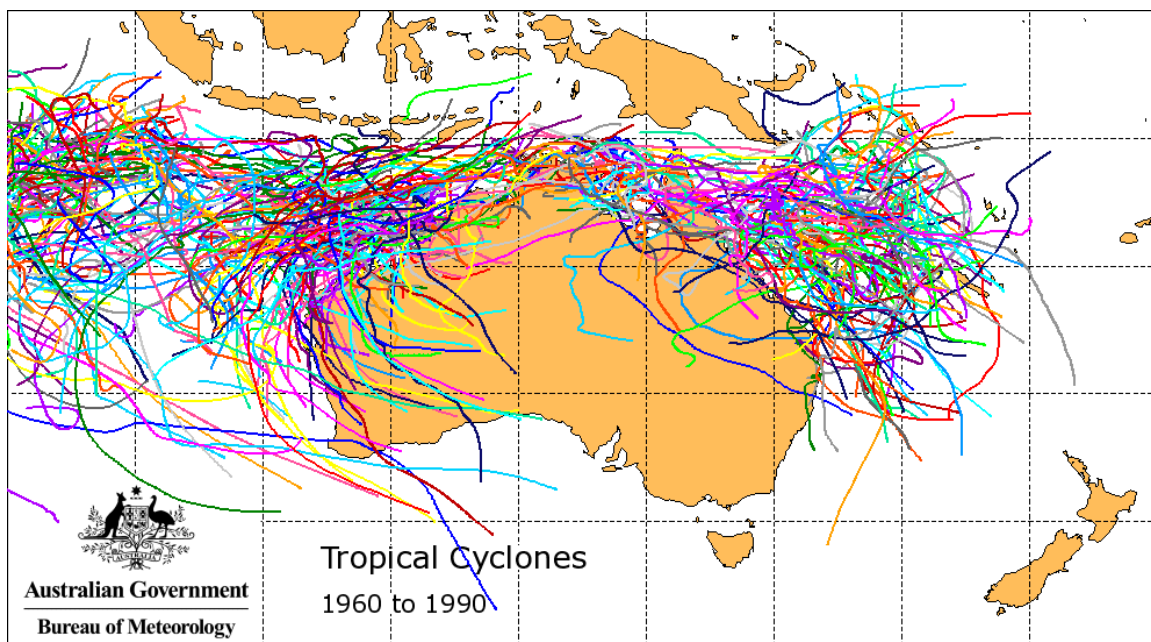


Fig. 3.11 – Composite map of tropical cyclone tracks around Australia between 1960 and 1990. Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

supported by evidence for ancient river channels in the northern parts, hypothesised to be relicts from the wetter and warmer climates of the Pliocene (Webb and James, 2006).

Both vegetation reconstruction models and speleothem pollen data have indicated that during the Pliocene the region was dominated by grassland vegetation regimes, compared to the desert vegetation regime seen at present (Salzmann et al., 2008; Sniderman et al., 2016). Pollen reconstructions have also identified the presence of vegetation types such as Myrtaceae, Proteaceae and Doryanthaceae in the Nullarbor region during the Pliocene (Sniderman et al., 2016). These communities are today associated with regions exposed to moist climates and high summer rainfall, such as eastern Australia (Groves, 1994), thus supporting suggestions of higher precipitation regimes in the Nullarbor region during much of the Pliocene. The evidence for denser vegetation and higher rainfall regimes in the past are supported by an increase in speleothem growth in the Nullarbor region noted during this period (Woodhead, 2019), as these conditions are more favourable for speleothem growth.

3.5. Sample Selection and Preparation

Fieldwork conducted in April 2014 focused on obtaining individual long stalagmites (>1 m in height), along with short stalagmites of <1 m in height for comparative purposes. In all speleothem studies it is recommended that replicate samples from similar geographical positions and corresponding time periods be studied. The purpose of this is to verify the information and interpretations of a given sample, and to reduce the potential that a sample is producing anomalous results that are not representative of the mean climate state at the time of growth. Following sawing and visual observations for evidence of internal dissolution of these stalagmites, two speleothems (BT and M2) were selected from cave 370 ('Matilda') based on their length (BT is approximately 2 m), distinct laminations, and lack of dissolution features (e.g. **Fig. 3.12**). Both speleothems have the distinctively dark colouration evident in several Nullarbor speleothems, which is attributed to their particularly high organic contents (Caldwell et al., 1982; Blyth et al., 2010; Sniderman et al., 2016).

Additional analyses were conducted on a variety of speleothems from other locations on the Nullarbor (**Fig. 3.13**). These were selected from the larger Nullarbor archive of speleothems on the basis of preliminary dating that placed them within the MPWP, and secondly due to their well-preserved nature (i.e. no evidence of dissolution). Analyses of these additional stalagmites corroborated interpretations from the data obtained from the primary samples. Their principal

purpose was for additional fluid-inclusion and clumped-isotope analyses in order to obtain palaeotemperatures from a wide variety of MPWP-dated speleothems. This is especially significant due to the novel nature of these techniques as the increased verification of the temperatures produced for the MPWP allows for better determination of the reliability of the given techniques. The full list of speleothem used in this study and the caves from which they were obtained is presented in **Table 3.1**.

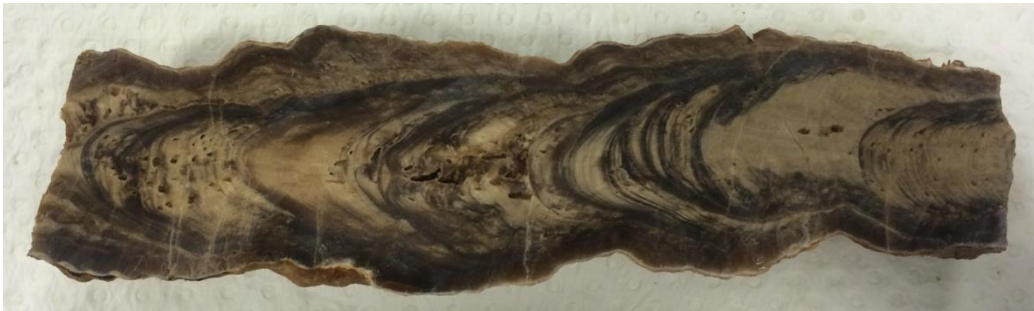


Fig. 3.12 – An example of the internal dissolution present in certain Nullarbor speleothems from Webb’s cave: sample 132-14-8.

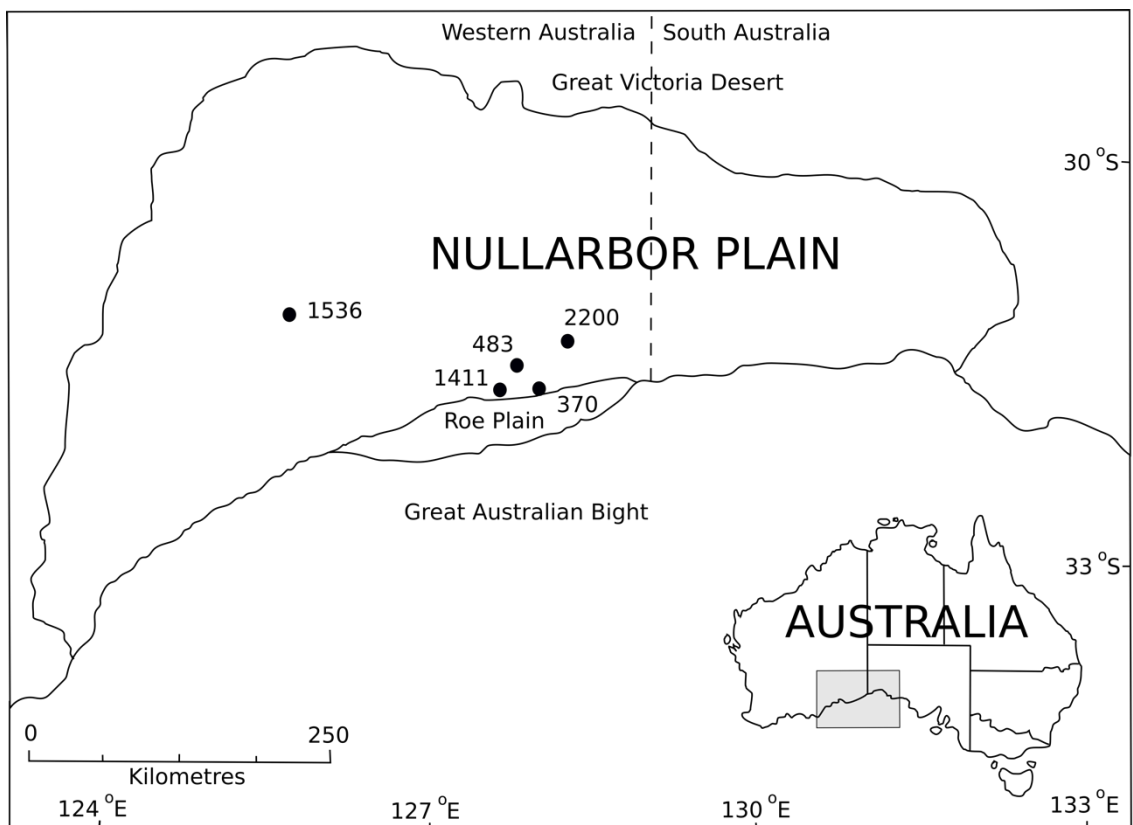


Fig. 3.13 – Locations of the caves from which speleothems have been used in this study, and position within Australia (inset). The numbers represent the formal catalogue codes for each of the caves; Matilda cave, from which the primary samples were obtained, is shown as ‘370’. Further information on each of the caves and the samples obtained from them is presented in **Table 3.1**.

Table 3.1 – All samples used in this study, the caves from which they were obtained, and geographical location.

Sample Name	Cave Name	Cave Catalogue No.	Cave Latitude	Cave Longitude
1411-6	Sentinel	1411	-31.86	127.58
1536-11	Flaker's Rest	1536	-31.09	125.76
2200-14b	Leaena's Breath	2200	-31.43	128.14
2200-4	Leaena's Breath	2200	-31.43	128.14
370-12	Matilda	370	-31.82	127.78
370-7	Matilda	370	-31.82	127.78
BT	Matilda	370	-31.82	127.78
FIA	Flaker's Rest	1536	-31.09	125.76
FIB	Hurricane Hole	483	-31.71	127.66
FIC	Flaker's Rest	1536	-31.09	125.76
FID	Matilda	370	-31.82	127.78
FIF	Sentinel	1411	-31.86	127.58
M2	Matilda	370	-31.82	127.78

Once the speleothems were returned to The University of Melbourne visual observations of the probable growth directions were made, and markings made to approximate the position of the central growth axis. This transect was used to saw the speleothem into two halves. During these investigations no obvious signs of recrystallisation or growth hiatuses were evident. Speleothems were then set in a clear casting resin to provide additional support to the sample, thus reducing the chance of breakages along planes of weaknesses, and to increase the stability of the speleothem during drilling. The setting of the speleothem in resin was conducted over several days, with the resin being added in small increments to avoid the possibility of the exothermic reaction damaging the sample. Once set in resin, the surface of speleothems was polished by hand using hand laps to remove sawing marks and increase the visibility of growth laminae.

4. Dating Pliocene Speleothems

4.1. Background

Geochronology is one of the fundamental tools of palaeoclimate research (Harmon, 1992; Bourdon et al., 2003). The widely accepted and preferred method for establishing age models for speleothems is U-series dating (Fairchild and Baker, 2012), with few alternative methods capable of producing equally accurate or precise chronologies (Drysdale et al., 2012b). The first applications of U-series dating to speleothems occurred in the 1960's to 1980's (Harmon et al., 1977; Ford et al., 1981; Harmon, 1992) and the method subsequently formed the mainstay of speleothem palaeoclimate studies. The continued uptake of the method has been aided by on-going technological advances since the mid-1980s, which have both increased the precision and accuracy of dates obtained and decreased the initial sample size requirements (Drysdale et al., 2012b). Despite the widespread use of U-series dating in speleothems, however, the method is limited to the last ~500 kyr (Richards and Dorale, 2003; Zhao et al., 2009). Recent developments in U-Pb dating methods have addressed this limitation, offering the possibility of extending the dating of speleothems back many millions of years (Richards et al., 1998; Woodhead et al., 2006), thus significantly expanding the scope of speleothem research. At present the oldest published speleothem age derived by U-Pb dating is of 289 ± 0.68 Ma (Woodhead et al., 2010), exemplifying the extent of opportunity presented by this new method.

4.1.1. Basis of Method

The U-Pb technique is based upon the quantification of the radiogenic lead isotopes ^{206}Pb and ^{207}Pb , and their respective parent uranium isotopes, ^{238}U and ^{235}U (**Fig. 4.1**). In their pioneering paper, Richards et al. (1998) first described the application of the U-Pb dating method to speleothems of Quaternary age and older. Following this publication, there have been a variety of improvements to the method and a subsequent rapid increase in the number of publications in this area.

There are several requirements in order the U-Pb dating method to be successful (Woodhead and Pickering, 2012). Primarily, it is essential that the speleothem calcite has not undergone processes of diagenesis or recrystallisation i.e. that the system has to remain closed after formation (Richards and Dorale, 2003). Processes of diagenesis have been shown to impact both U and Pb, with U being a particularly mobile element, such that notable irregularities in the isochron become evident where diagenetic alteration has occurred (Jones et al., 1995).

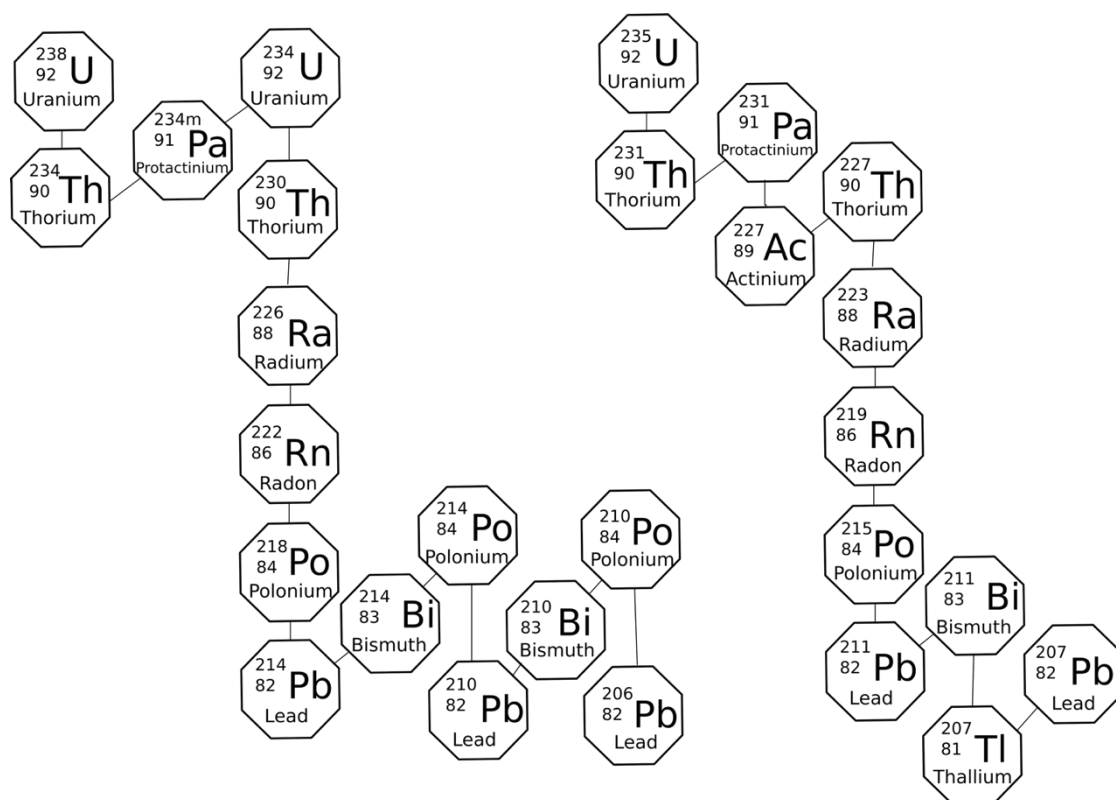


Fig. 4.1 – Decay chains of U isotopes used in U-Pb dating (U^{235} and U^{238}).

Samples must also contain sufficient U for analysis, with preferred concentrations of >0.5 ppm, and have low concentrations of so-called ‘common Pb’ – Pb incorporated into the crystal lattice at the time of its formation (Woodhead et al., 2006). Preliminary analyses of the sample by either phosphor imaging (Pickering et al., 2010) or laser ablation trace element analysis (Woodhead et al., 2012) allows for assessment of the suitability of a sample for U-Pb analyses. The advantage of conducting trace element analysis is that it also provides insight into potential transport mechanisms of any common Pb occurring within the sample (Woodhead et al., 2012). Ideally, all Pb within a sample should originate from the *in situ* decay of U (radiogenic Pb); however it is also generally the case that common Pb is also incorporated into a speleothem as detrital material (e.g. clays) or complexed with certain oxides, e.g. as uranyl-phosphate complexes (Borsato et al., 2007; Fairchild and Treble, 2009a). To successfully date a sample, it is generally necessary to obtain a range of radiogenic/common Pb ratios in order to form an

isochron. This is achieved through the individual analysis of multiple samples along individual growth layers.

4.1.2. Problems Associated with Method

Despite the enormous potential of the U-Pb technique, there are still several problems that may be encountered that complicate its use. For samples beyond the range of U-series methods it is often not possible to determine the initial state of disequilibrium in the U-series decay chain, in particular the original $^{234}\text{U}/^{238}\text{U}$ ratio. Corrections for these initial disequilibrium effects remain essential and contribute greatly to overall uncertainties (Woodhead et al., 2006).

While Pb generally exhibits low variability within single speleothems or between multiple speleothems from the same cave (Woodhead and Pickering, 2012), its concentrations can be highly variable both within, and between samples (Woodhead et al., 2012). If samples or sections of samples exhibit particularly high Pb concentrations, much of this Pb is likely to be largely composed of common Pb as opposed to radiogenic Pb. The proportion of common Pb to that resulting from the radioactive decay of U is a critical factor determining the potential precision of ages that can be acquired from a given sample (Woodhead et al., 2012). Significant potential problems also arise from the presence of variable common Pb compositions (multiple common Pb components). At present, little is known about the processes by which common Pb is incorporated into speleothems (Woodhead et al., 2006). Although not a particularly common problem, it is known that in speleothems in which fluid-inclusions densities are substantially high, to the degree that crystal growth has been impeded, the levels of common Pb can be problematic as the inclusions provide an alternative pathway for the incorporation of Pb (Woodhead et al., 2006).

U is very commonly variably distributed throughout individual speleothems and as such, pre-screening is essential to identify materials of suspected low U concentrations prior to determining sampling locations (Woodhead and Pickering, 2012). As with all U-based geochronology techniques, it is possible for the U concentrations to be too low for accurate and precise dates to be obtained (Drysdales et al., 2012b). As such, a primary consideration prior to obtaining dates from a speleothem is that the concentration and distribution of U and Pb within the sample should be determined (Woodhead and Pickering, 2012). Speleothems containing high U and low Pb contents, where the Pb concentrations at the time of formation are negligible, are ideal for dating by the U-Pb method as any subsequently measured Pb can then be accurately assumed to be a result of radioactive decay of the U parent isotopes (Woodhead et al., 2012).

Another significant issue with the U-Pb method is that, while age uncertainties of 1-2% are readily attainable (Bajo et al., 2012), with speleothems of great antiquity this is not adequate for the development of internal chronologies (Woodhead et al., 2010). Although such uncertainties are similar to those of the U-Th method, beyond a certain limit, the error becomes increasingly significant relative to the length of time recorded within a given speleothem (Woodhead and Pickering, 2012).

4.2. Methods

4.2.1. Sampling Procedure

Dating focussed on the two speleothems identified for primary study (see **section 3.5**). For the preliminary dating analysis of speleothem BT, a total of five locations were identified. Upon visual examination no obvious growth hiatuses were identified; therefore sampling locations were at approximately equal intervals along the length of the stalagmite (**Fig. 4.2**). Sampling was performed using a hand-held dental drill with a 1 mm drill bit to obtain small aliquots of calcite of approximately 50-100 mg each, with locations relative to the central growth axis noted for future reference (**Fig. 4.3**). Only four of these samples were used in the initial dating analyses, due to the preparation procedure and number of subsamples requires from each layer. Due to the large and overlapping errors, subsequent dating focused on the top and base sections of the stalagmite in attempts to resolve top and bottom ages for the sample (**Fig. 4.2**), and the fifth sample from the centre of the speleothem was omitted. For speleothem M2, a single location was identified for preliminary analyses, followed by additional locations along the length of the sample in an attempt to reduce age uncertainties and to test for the presence of a long growth hiatus (**Fig. 4.4**). Again, there were no obvious growth hiatuses to determine sampling locations.



Fig. 4.2 – U-Pb dating sampling locations in speleothem BT: preliminary dates in red, subsequent dates in yellow.

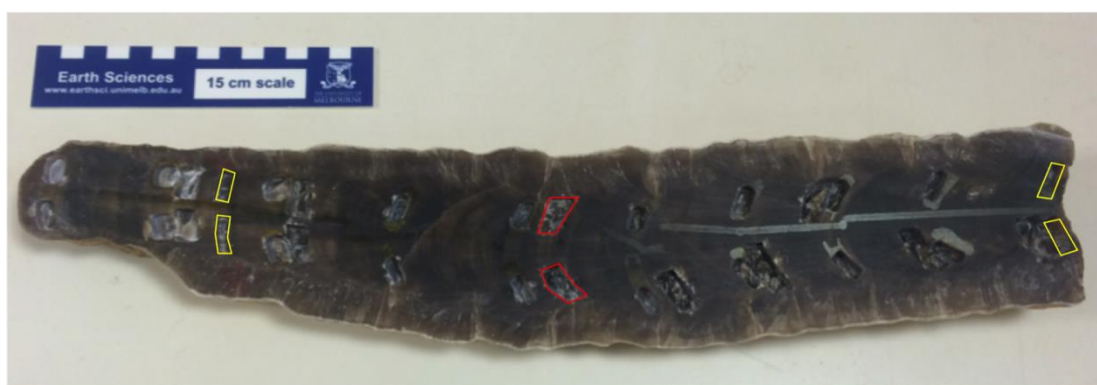


Fig. 4.3 – U-Pb dating sampling locations in speleothem M2: preliminary dates in red, subsequent dates in yellow.

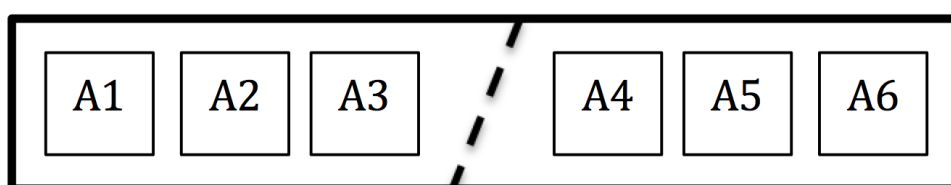


Fig. 4.4 – U-Pb dating sampling placement along individual layers of a speleothem.

For the additional speleothems analysed, preliminary dating had previously been conducted placing each samples' growth within the MPWP. For the purposes of the analyses and interpretations required for this study, these preliminary dates were deemed adequate and no further dating was undertaken on these materials.

4.2.2. Sample Preparation and Analyses

U-Pb geochronology was undertaken at The University of Melbourne following the procedures outlined in Woodhead et al. (2006) and Woodhead et al. (2012). Each solid sample aliquot was cleaned in diluted HCl and rinsed using ultra clean water two times before being left overnight to dry. Samples were then weighed before being completely dissolved in HCl and having artificial isotopic tracers of ^{233}U and ^{205}Pb added. Samples were then weighed again, refluxed and dried on a hot plate.

U and Pb were separated using conventional ion-exchange procedures. To undertake Pb chemistry, columns were prepared by filling with anion exchange resin (AG 1X-8), then cleaned using 6N HCl, and finally conditioned with 0.6 molar HBr. Samples were then dissolved in 0.6 molar HBr and poured into individual columns. The columns were rinsed with HBr to remove matrix components and

finally Pb was eluted into clean beakers with 6N HCl; sample vials were then placed onto the hot plate to dry.

For U separation, columns were prepared with ion specific exchange resin (TRU-Spec) and cleaned with an HCl/HF mixture. Each sample was then dissolved in 3M HNO₃ prior to loading onto individual columns. Columns were then rinsed with 3M HNO₃ and then 3M HCl to remove matrix components prior to elution of the purified U cut with HCl/HF mix. Samples were then placed onto the hot plate to dry.

After sample preparation and extraction of U and Pb, samples were run on a Nu Plasma mass spectrometer with attached DSN-100 desolvation unit equipped with a Glass Expansion Opal Mist nebuliser. Prior to U measurement, 1ml of 2% HNO₃ is added to each sample vial, and 0.7ml of 2% HNO₃ for Pb measurement. Dissolved samples were then measured together with a series of reference materials to allow monitoring of, and corrections for varying instrumental effects. Once reduced, the data are represented on a Tera-Wasserburg Concordia diagram, as recommended by Richards et al. (1998), Woodhead et al. (2006), and Woodhead et al. (2012). This is preferable to the use of the conventional Concordia diagram as it overcomes the need for common-Pb corrections and provides greater resolution for samples only a few million years in age (Woodhead et al., 2012). The raw data must also be corrected for disequilibrium effects following this process.

4.3. Results and Discussion

4.3.1. U and Pb Concentrations

The U-Pb dating results of the individual growth layers of BT are presented in **Table 4.1**. The concentrations of U in speleothem BT range between 0.56 and 0.96 ppm, with an average concentration of 0.72 ppm. The concentrations of Pb range between 0.93 and 4.93 ppb, with an average concentration of 2.06 ppb. The U-Pb results of the individual growth layers of M2 are presented in **Table 4.2**. For this sample the concentrations of U range between 0.42 and 0.65 ppm, with an average concentration of 0.53 ppm. The concentrations of Pb range between 0.91 and 2.87 ppb, with an average concentration of 1.54 ppb. The dating results of samples acquired prior to this study (Woodhead et al., 2018) are presented in **Table 4.3**. Within this collection of speleothems, the concentrations of U range between 0.34 and 4.13 ppm, with an average concentration of 0.95 ppm. These values are similar to those evident in the entire Nullarbor collection, which has an average of 1.11 ppm (Woodhead et al., 2019).

As previously discussed, the variability in both U and Pb concentrations may result from a number of factors prior to speleothem deposition. However, all

dating samples for both BT and M2 displayed $^{207}\text{Pb}/^{206}\text{Pb}$ intercepts on the Tera-Wasserburg Concordia within error or one another, thus indicating relative stability of common Pb input throughout speleothem growth.

4.3.2. Accepted Ages

The single aliquot U-Pb dating method as described by (Woodhead et al., 2012) was not applicable to the samples in this study, thus isochron ages were calculated for both speleothem BT (**Fig. 4.5**), and speleothem M2 (**Fig. 4.6**). The development of isochrons is advantageous as they can also be used to suggest the likelihood of processes of diagenesis in the speleothems. Where carbonates are subject to diagenetic alteration the isochrons tend to become discordant due to the preferential removal of U and potential for incorporation of additional Pb (Jones et al., 1995). Vitally, the concordant nature of the isochrons developed from both speleothems BT and M2 indicate that processes of diagenetic alteration are unlikely to have occurred, therefore confirming their suitability for preserving palaeoclimatic signals.

This thesis is the first to investigate the possibility of using U-Pb dating to obtain internal chronologies from Pliocene-age speleothems. Consequently, dating focused on speleothem BT, primarily due to its length of approximately 2 m. Despite the dating of 31 aliquots from 4 distinct layers across the length of the sample, all allocated ages proved to be within error of one another (**Fig. 4.7**), thus confirming their reliability, but also making construction of an internal chronology impossible. In further attempts to derive top and bottom ages for the sample, the two uppermost and lowermost layers were subjected to further analyses through assuming two (rather than four) individual layers and developing further isochron ages accordingly (**Table 4.1**). The anchored ages were used as final dates for the sample. Using all dates obtained produces a final weighted-average age with 95% confidence of 3.17 ± 0.13 Ma for speleothem BT, placing it within the MPWP.

From the constraints of the ages and their errors, combined with the structure of speleothem growth (i.e. the top must be younger than the base), it is possible to restrict the likely growth period of the sample to the period from 3.28 Ma to 3.08 Ma (**Fig. 4.7**). It must be noted that this maximum growth period should be treated with caution as it makes the key assumption that the principles of Gaussian distribution hold true despite the relatively small dataset. However, it potentially provides useful insight into the growth span of the speleothem and is therefore presented here with this caveat in mind. The error restricted maximum growth period produced for speleothem BT is 200 ka, with a minimum growth rate of 0.00972 mm/yr. This suggests a significantly slower growth rate in comparison to average modelled and measured speleothem growth rates globally (**Table 4.4**).

Table 4.1. – All U-Pb data from speleothem BT, the location of the samples within the speleothem is indicated by the approximate depth from top (cm). For the top and base of the speleothem, from which two subsequent layers were analysed, the ages are presented by individual layer, and in terms of combined and anchored ages.

Sample Name	Depth from Top (cm)	Weight (mg)	U ppb	Pb ppb	$^{238}\text{U}/^{206}\text{Pb}$	% err	$^{207}\text{Pb}/^{206}\text{Pb}$	% err	corr. coef.	Age/error (Ma)	Combined Age (Ma)	Anchored Age (Ma)
BT1.1	0	65.61	558.20	2.865	564.81	4.32	0.62	1.99	-0.999	3.33 ±0.21	3.337 ±0.152	3.208 ±0.132
BT1.2		51.98	569.82	2.082	754.32	7.14	0.54	4.82	-1.000			
BT1.3		118.27	570.50	1.622	879.73	3.69	0.50	3.02	-0.977			
BT1.4		80.26	563.96	1.583	899.40	5.57	0.49	4.84	-1.000			
BT1.5		51.30	556.60	1.490	966.39	9.49	0.46	9.26	-1.000			
BTD 1.4	5	94.39	567.50	1.803	814.95	4.30	0.52	3.19	-0.993	3.31 ±0.16		
BTD 1.3		95.68	576.76	1.620	892.77	4.56	0.49	3.84	-0.994			
BTD 1.1		149.61	563.95	2.025	733.17	2.49	0.56	1.55	-0.978			
BTD 1.2*		169.99	581.41	1.562	931.74	2.70	0.51	2.06	-0.977			
BT22.1	60	64.87	857.28	1.989	1023.41	5.16	0.45	5.34	-1.000	3.11 ±0.15	-	-
BT22.2		57.91	900.99	2.456	929.47	5.00	0.49	4.34	-1.000			
BT22.3		101.44	955.12	2.957	814.80	2.37	0.52	1.75	-0.989			
BT22.4		39.51	949.06	2.711	901.51	6.74	0.49	5.67	-1.000			
BT22.5*		84.79	888.80	2.292	957.09	3.56	0.48	3.12	-1.000			
BT22.6		75.57	867.58	2.142	971.39	4.16	0.46	3.98	-1.000			
BT34.1	95	42.71	883.91	2.112	1023.15	7.60	0.44	8.19	-1.000	3.23 ±0.27	-	-
BT34.2		77.69	877.49	4.926	513.35	2.11	0.64	0.88	-0.997			
BT34.3		59.63	883.40	4.590	548.46	2.92	0.62	1.37	-0.999			
BT34.4		62.26	867.80	3.486	676.06	3.53	0.57	2.16	-0.978			
BT34.5		87.90	865.35	2.702	814.23	3.01	0.52	2.23	-0.995			
BT34.6		80.96	851.29	2.055	989.38	4.03	0.47	3.84	-0.999			
BTD 2.2	190	74.63	621.08	1.548	981.79	5.98	0.46	5.95	-0.980	3.01 ±0.18		
BTD 2.4		64.18	615.01	1.420	1042.78	7.48	0.43	8.29	-0.974			
BTD 2.3		77.05	630.30	0.925	1412.11	8.17	0.32	15.29	-0.998			
BTD 2.1		54.99	617.02	1.609	971.60	8.06	0.46	7.78	-0.991			
BT50.1	195	52.03	648.02	1.041	1363.75	11.34	0.32	20.86	-1.000	3.10 ±0.16	3.061 ±0.136	3.150 ±0.130
BT50.2		65.53	661.26	0.996	1381.43	8.94	0.31	17.12	-1.000			
BT50.3		40.35	674.31	1.391	1182.18	12.22	0.38	16.79	-0.991			
BT50.4		77.56	704.90	1.521	1073.15	5.51	0.42	6.36	-0.999			
BT50.5		82.86	700.58	1.153	1277.63	6.17	0.35	9.81	-1.000			
BT50.6		69.45	697.25	1.136	1304.72	7.60	0.34	12.76	-0.983			

Table 4.2 – All U-Pb dating data from speleothem M2; the location of the samples within the speleothem is indicated by the approximate depth from top (cm).

Sample Name	Depth from Top (cm)	Weight (mg)	U ppb	Pb ppb	²³⁸ U/ ²⁰⁶ Pb	% err	²⁰⁷ Pb/ ²⁰⁶ Pb	% err	corr. coef.	Age/error (Ma)
M2 2.5	10	53.10	492.47	1.748	910.38	9.78	0.67	3.49	-0.999	No age possible
M2 2.2		65.81	507.96	1.587	849.11	7.14	0.51	5.56	-0.990	
M2 2.4		48.28	535.40	1.161	1190.40	12.92	0.42	14.87	-0.999	
M2 2.1		36.67	490.42	2.868	529.56	8.27	0.65	3.38	-0.998	
M2 2.3		46.70	616.50	1.293	1261.23	12.29	0.45	12.54	-0.999	
M2 1.1	25	68.82	420.27	1.965	617.99	5.99	0.60	3.16	-0.999	3.18 ±0.43
M2 1.2		105.66	447.56	1.454	805.32	4.78	0.52	3.54	-0.999	
M2 1.3		161.05	477.83	1.488	820.21	2.99	0.53	2.16	-0.999	
M2 1.4		235.79	427.46	1.221	864.38	2.41	0.50	1.93	-1.000	
M2 1.5		152.23	419.73	1.393	782.30	3.43	0.53	2.42	-1.000	
M2 3.1	50	128.25	535.24	1.041	1148.34	4.72	0.41	5.79	-0.993	3.24 ±0.11
M2 3.3		65.78	654.02	2.663	690.17	4.53	0.59	2.39	-0.993	
M2 3.4		158.99	643.93	1.346	1080.63	3.01	0.44	3.18	-0.980	
M2 3.2		110.10	636.11	1.007	1303.10	5.24	0.35	8.36	-0.995	
M2 3.5*		102.58	600.16	0.910	1389.02	6.35	0.35	10.09	-0.997	

Table 4.3 – All U-Pb data from additional MPWP speleothems. These data have been obtained from the larger collection of Nullarbor speleothems, (Woodhead, 2019 and unpublished data).

Sample Name	Weight (mg)	U ppb	Pb ppb	$^{238}\text{U} / ^{206}\text{Pb}$	% err	$^{207}\text{Pb} / ^{206}\text{Pb}$	% err	Age/error (Ma)
FID	152.01	691.78	0.650	1668.77	4.45	0.20	15.48	3.20 ±0.11
	144.11	715.15	0.785	1547.37	4.21	0.25	11.31	
	164.49	682.99	1.031	1301.85	3.25	0.34	5.40	
	200.44	698.04	0.563	1761.18	3.53	0.17	15.48	
370-7	93.00	384.81	2.232	487.88	1.91	0.62	0.88	3.17 ±0.14
	139.00	407.81	2.359	485.69	1.20	0.62	0.55	
	89.00	493.27	2.257	591.45	1.89	0.58	1.05	
	145.00	452.40	2.407	519.54	1.11	0.61	0.54	
	103.00	454.83	2.556	497.86	1.49	0.62	0.70	
	68.00	445.85	3.597	366.94	1.70	0.66	0.63	
370-12	81.50	711.44	1.585	1011.81	2.47	0.45	2.61	3.32 ±0.11
	145.49	765.10	0.756	1600.12	4.03	0.21	13.44	
FIB	90.00	1218.35	1.403	1509.23	1.93	0.28	4.28	2.97 ±0.13
	150.53	1326.39	1.299	1647.75	2.32	0.24	6.44	
1411 6	98.10	336.57	0.880	936.86	3.98	0.48	3.52	3.20 ±0.12
	68.20	362.88	0.833	1043.14	5.91	0.44	6.19	
	157.50	340.99	0.870	937.52	2.45	0.48	2.17	
	70.20	354.72	2.211	473.62	2.67	0.66	1.01	
	64.40	376.28	1.056	903.92	5.23	0.50	4.32	
FIF	220.00	449.69	0.913	1081.31	1.53	0.43	1.70	3.26 ±0.13
	179.73	474.70	1.182	965.46	3.17	0.48	2.88	
FIA	73.84	2975.48	3.186	1567.23	1.00	0.28	2.26	2.96 ±0.31
	131.86	2819.99	2.559	1713.65	1.30	0.24	3.62	
FIC	63.11	2356.25	1.504	1751.22	1.65	0.10	13.89	3.50 ±0.40
	119.99	2450.84	2.430	1503.31	1.46	0.22	4.56	
1536-11	57.84	2901.40	2.218	1845.72	1.54	0.19	5.69	2.91 ±0.28
	148.60	2684.33	2.393	1746.04	1.27	0.24	3.62	
2200-4	167.18	3387.12	1.755	1984.15	0.99	0.08	10.72	3.24 ±0.11
	187.38	3537.89	2.243	1852.01	0.80	0.13	4.82	
2200-14b	191.46	4124.72	2.185	1829.31	0.85	0.07	4.15	3.51 ±0.35
	171.37	3878.48	2.169	1843.66	0.79	0.08	7.94	

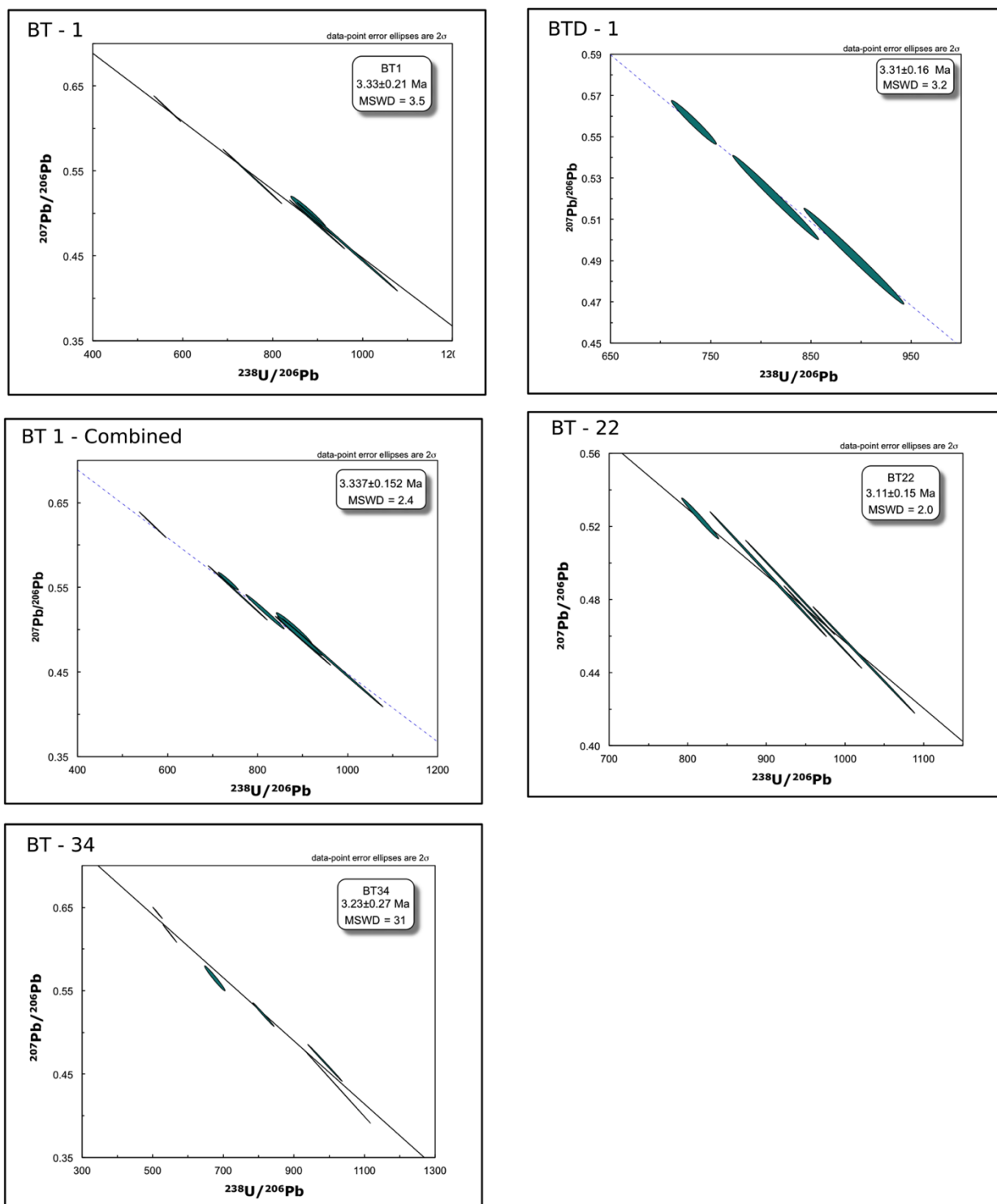


Fig. 4.5 – Isochron ages for speleothem BT. Continued on following page.

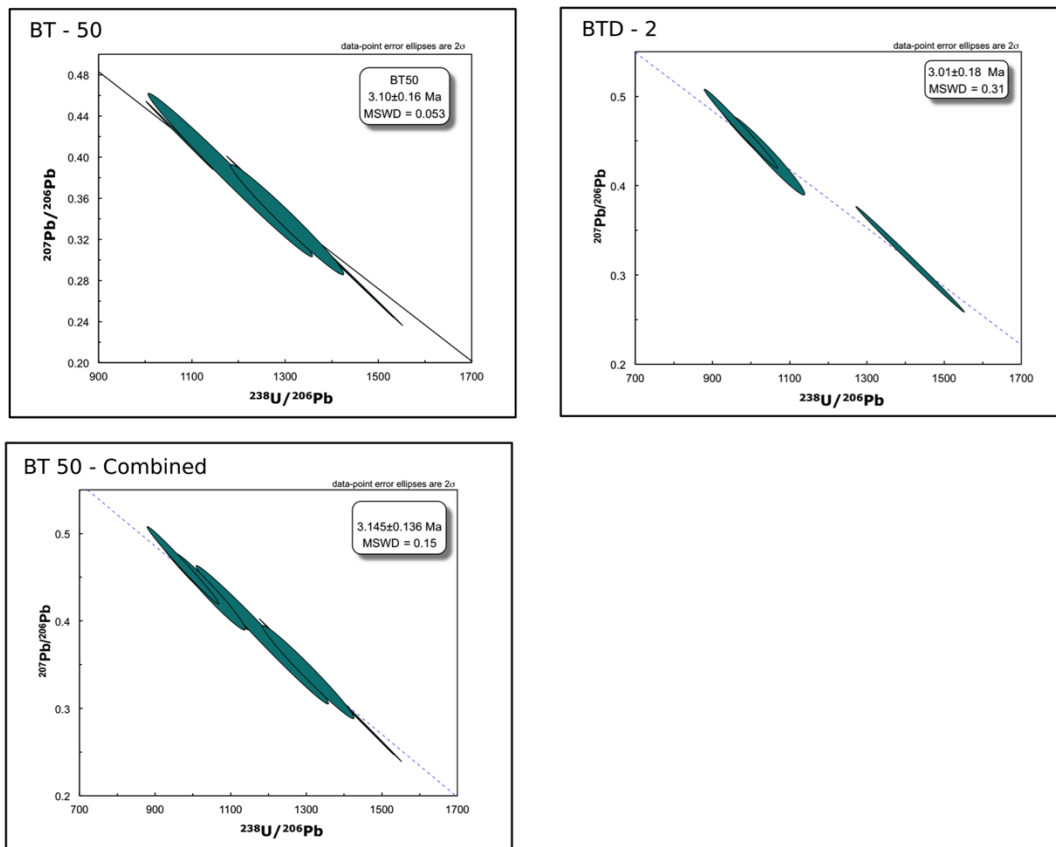


Fig. 4.5 continued – Isochron ages for speleothem BT.

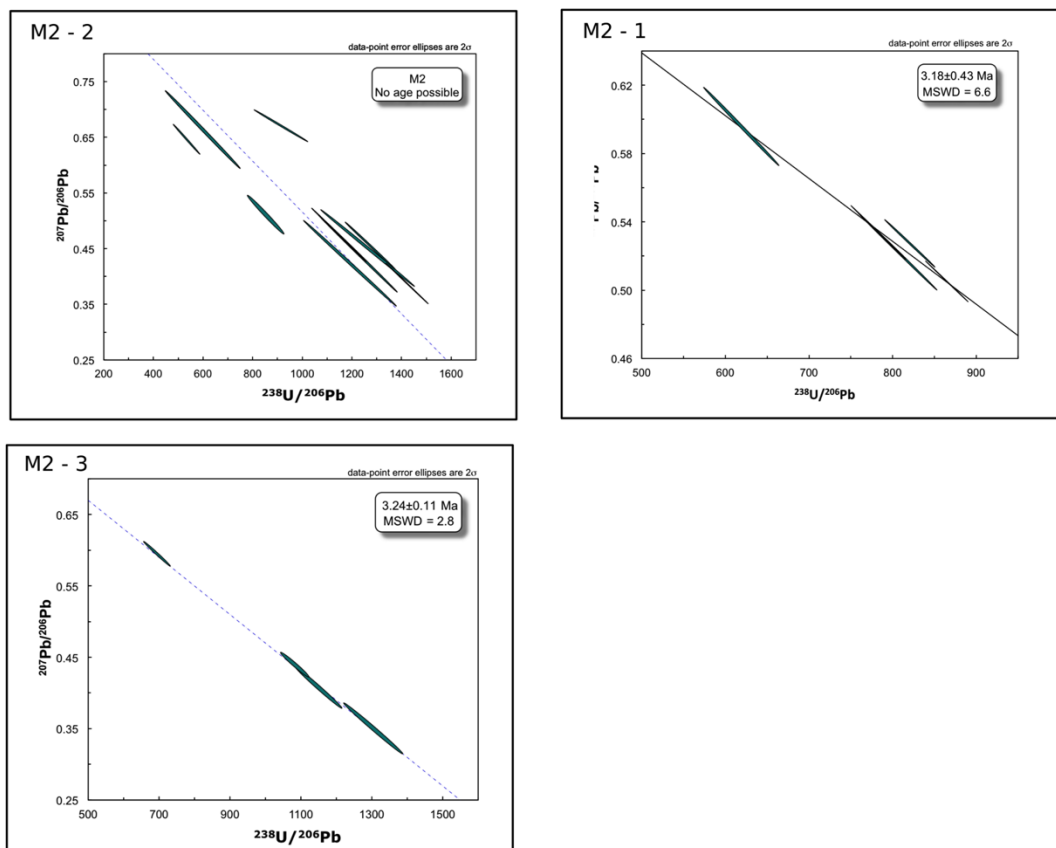


Fig. 4.6 – Isochron ages for speleothem M2.

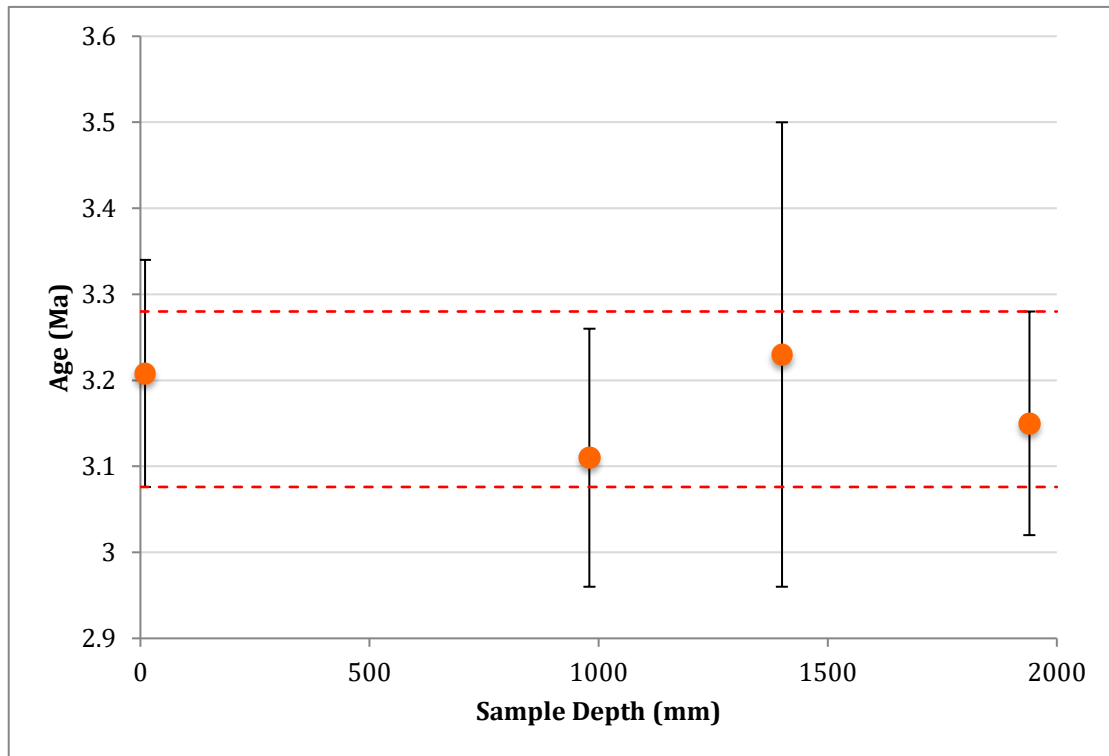


Fig. 4.7 – BT isochron ages and errors, with the associated maximum growth period of the speleothem.

Table 4.4 – Approximate growth rates from a collection of global speleothems for comparison.

Location	Approx. Growth Rate (mm/yr)	Reference
Corchia Cave, Italy	0.005	(Bajo et al., 2012)
Hesheng Cave, China	0.03 – 0.04	(Johnson et al., 2006)
Brown’s Folly Mine, UK	0.05 – 0.23	(Baker et al., 1998)
Nevada, USA	0.007 – 0.03	(Steponaitis et al., 2015)
Grotte de Clmouse, France	0.05	(McMillan et al., 2005)
Nettlebed Cave, New Zealand	0.01 – 0.05	(Hellstrom and McCulloch, 2000)

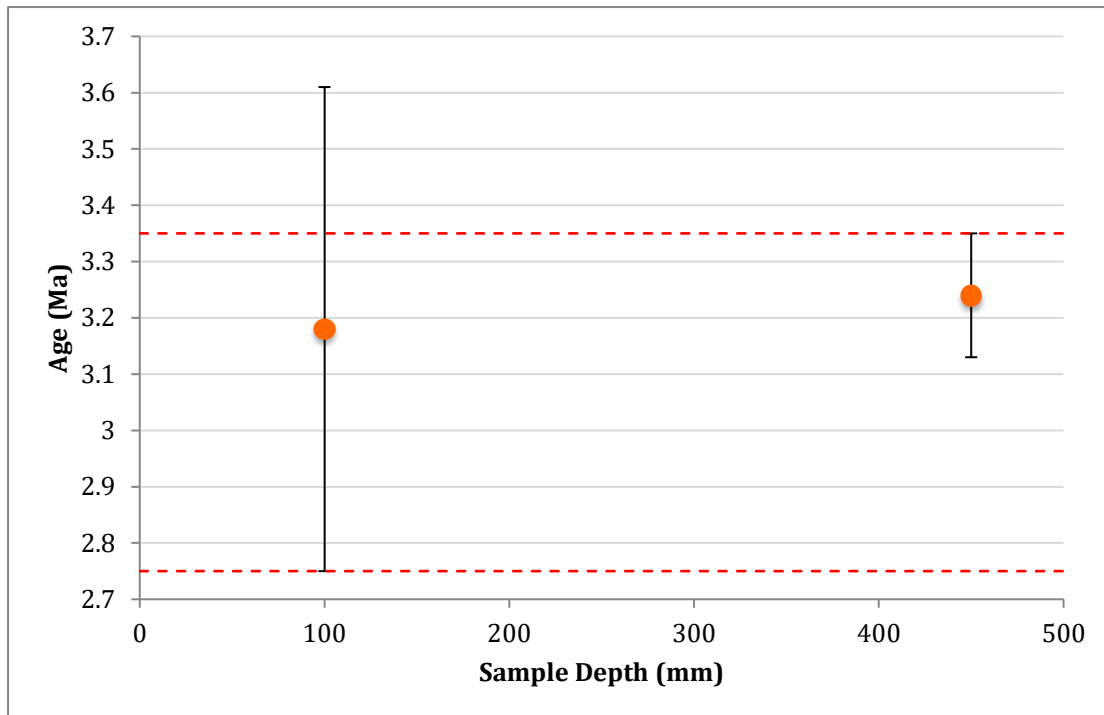


Fig. 4.8 – M2 isochron ages and errors, and the associated maximum growth period for the speleothem.

It is suggested that such a slow growth rate is in fact quite unlikely, and that either the actual growth period lies somewhere within the calculated maximum, or growth hiatuses exist within the speleothem. Due to the difficulties with establishing top and bottom ages, speleothem M2 was less intensively dated with only 15 aliquots from 3 distinct layers. While unknown errors in analysis led to one of these layers producing unrealistic and unreliable ages, from the two remaining dates obtained it is possible to assign the sample a weighted-average age with 95% confidence of 3.24 ± 0.10 Ma.

It is also possible to tentatively restrict the growth period of the sample (with the aforementioned assumption) to the period from 3.35 Ma to 2.75 Ma (**Fig. 4.8**), with a maximum growth period of 600 ka and minimum growth rate of approximately 0.00076 mm/yr, significantly slower than the estimated growth rate of speleothem BT and slower than average speleothem growth rates globally (**Table 4.4**). Again, such a slow growth rate is argued to be unlikely, with the more probable scenario, in the absence of significant growth hiatuses, being a growth period somewhere within the calculated errors. It is not possible to restrict the growth period further within these bounds at this stage. While extensive dating of the samples may have reduced the error somewhat, from the data obtained in this study it was decided that it would not be cost or time

effective to pursue this course of action. As such, ages were accepted as stated above.

4.3.3. Problems Encountered

The most significant problem encountered with the U-Pb dating of these samples results from their antiquity and the current limitations of the method. At present, as demonstrated by this study, it is not possible to derive internal chronologies from samples of substantial antiquity with relatively low U abundance, since the uncertainties associated with any given age determination often exceed the likely growth period of most speleothems. This is a recognised difficulty associated with the dating of more ancient speleothems. This hindrance in the development of more precise ages in samples of antiquity is something that may only be improved by further investigation and understanding of factors such as common Pb estimates and disequilibria effects within speleothems (Woodhead and Pickering, 2012; Engel et al., 2019).

4.3.4. Further Research Required

4.3.4.1. Advancing U-Pb Dating of Ancient Samples

The continued development of the U-Pb method should be recognised as one of the main goals of speleothem palaeoclimate research, as should the development of more robust time series for speleothems of greater antiquity (Fairchild and Baker, 2012).

Further reducing the errors associated with U-Pb dating should be a primary focus of future research. To achieve this, it is vital that a better understanding of the systematics of U and Pb relationships within speleothems is developed. This will improve the efficiency of both sampling and calibration practices within the method, thus allowing for reductions in the uncertainties of ages produced. To date, there has been little discussion regarding the development of U-Pb speleothem age models (Bajo et al., 2012); as improvements to the U-Pb method allow for reduced errors, further investigation into more sophisticated methods for developing age-depth models will also become increasingly important (Schölz et al., 2012). Additionally, there are new *in situ* methods, which have the potential to advance the U-Pb dating of speleothems and should be explored further (Coogan et al., 2016; Woodhead and Petrus, 2019).

4.3.4.2. Alternative Approaches to Internal Chronologies

Unfortunately, due to time constraints, it was not possible within the scope of this study to fully explore alternative approaches to developing an

internal chronology for speleothems BT and M2. However, there are other methodologies that may have applications in this regard where U-Pb dating alone is insufficient. Various types of annual laminae may be present within speleothems (Baker et al., 2008), although lamina counting alone may be misleading where sporadic multi-year events influence speleothem layering (Shen et al., 2013). To date, this approach has largely been utilised through comparisons with radiometric ages or known event horizons – e.g. tourist use (Treble et al., 2003), volcanic ash markers (Jamieson et al., 2015) – or through investigations of modern growth rates and intensive cave monitoring (Baker et al., 2008). None of these criteria can be reliably applied in this study due to the antiquity of the samples and the inability to relate data to the U-Pb ages achieved. As such, the counting of laminae through petrography, fluorescence (Baker et al., 1993; Baker et al., 2008) or trace element methods (Smith et al., 2009) was not undertaken for this purpose. For significant advances in the development of internal chronologies for more ancient samples, it is suggested here that alternative approaches to verifying the annual nature of laminae present within speleothems becomes a focus of future research.

4.4. Conclusions

The U-Pb dating undertaken in this thesis has shown that at present it is not viable to obtain a climate time-series from Pliocene speleothems, and that advances in the U-Pb method are required to achieve this. However, the isochrons produced provide sufficient evidence that these speleothems have not undergone significant processes of diagenesis, and therefore have the potential to have preserved palaeoclimatic signals. Although internal chronologies could not be developed within the scope of this study, the dating undertaken adequately places the speleothems BT and M2 within the MPWP (3.29 – 2.97 Ma), with weighted-average ages of 3.17 ± 0.17 Ma and 3.24 ± 0.10 Ma respectively. Similarly, the additional samples used in this study have previously been dated and placed within the MPWP. With confidence that the samples are within this time period, it is still possible to use the data to infer large-scale climatic conditions and influences during the Pliocene. Despite not being able to produce a climatic time-series, this study still provides unique and important insights into the climate of the MPWP more generally. As such, the unique palaeoclimate information produced continues to address several of the significant gaps in palaeoclimate research and offers essential information for the development of future climate models.

5. Modern Precipitation Isotope Analysis

5.1. Background

The dominant influence on oxygen isotope variations in speleothems is the isotopic composition of the precipitation that falls above the cave (McDermott, 2004; Lachniet, 2009). To provide a basis upon which to interpret the oxygen isotope variations in the Pliocene Nullarbor speleothems, and thus the palaeoprecipitation from which they derive, it is useful as a first-order approach to understand the factors that drive isotopic variations of modern precipitation in the Nullarbor region. Modern precipitation studies are particularly applicable in this case, when approaching the suggestions of model outputs that tropical influences were likely a key driver in the difference between Pliocene and modern climates (Lawrence et al., 2006; Haywood et al., 2013). In consideration of this, a thorough understanding of the key factors driving $\delta^{18}\text{O}$ variations in modern precipitation in the Nullarbor region is of great importance to allow the most reliable interpretations of Pliocene precipitation.

5.1.1. Influences on Precipitation Isotope Values

The isotopic composition of precipitation is influenced by a number of factors (Dansgaard, 1964; Rozanski et al., 1993; Callow et al., 2014); however,

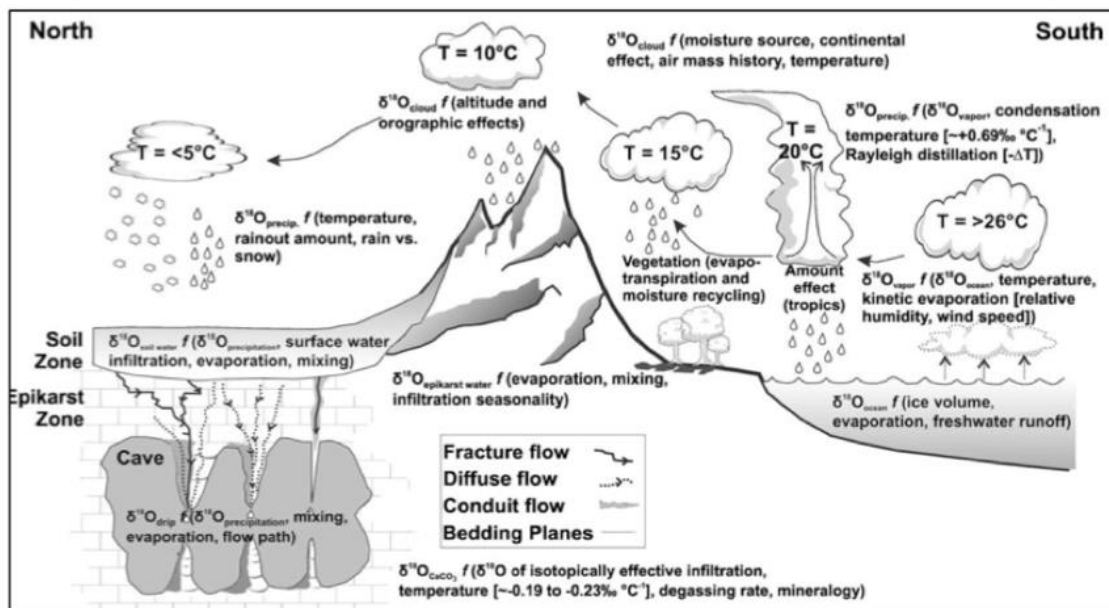


Fig. 5.1 – Potential primary influences on $\delta^{18}\text{O}$ variations prior to speleothem formation. Source: Lachniet, (2009).

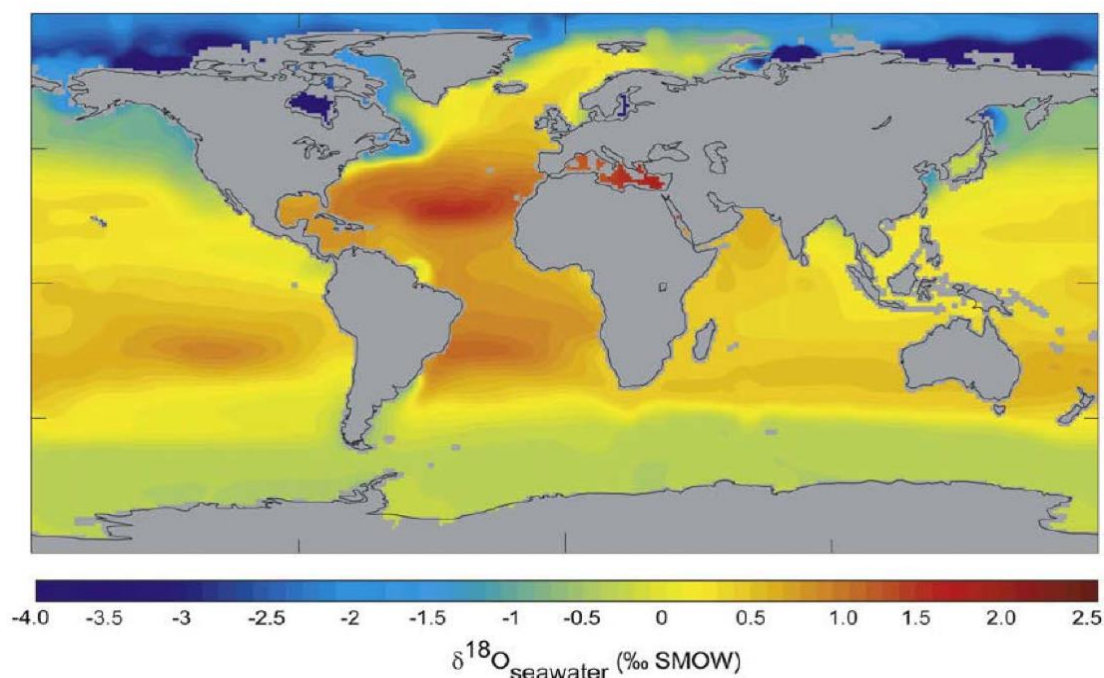


Fig. 5.2 - The simulated global modern $\delta^{18}\text{O}$ values of the ocean. Source: LeGrande and Schmidt, (2006).

the degree of influence of each differs between locations (Bowen and Revenaugh, 2003). In the Nullarbor region, there are several potential influences on the $\delta^{18}\text{O}$ composition of precipitation (**Fig. 5.1**). A sound understanding of each is essential to the accurate interpretation of the $\delta^{18}\text{O}$ signals preserved in speleothems (Dayem et al., 2010). The drivers of modern precipitation patterns, as discussed in Chapter 3, are also highly influential on the $\delta^{18}\text{O}$ variations observed in precipitation and should therefore be given due consideration.

Precipitation moisture source is one of the significant controls on the isotopic signal of local precipitation (Rozanski et al., 1993; Hoffmann et al., 1998; Treble et al., 2005b; Barras and Simmonds, 2008). The global pattern of ocean $\delta^{18}\text{O}$ values (**Fig. 5.2**) is attributed to geographic variations in factors including ocean salinity, rainout over the ocean, ocean and atmospheric circulation patterns, and terrestrial freshwater inputs (Lachniet, 2009). Sea-surface temperatures (SSTs) at the moisture source are also an important control, as they are a key driver of the fractionation of $^{18}\text{O}/^{16}\text{O}$ between ocean water and vapour. The result of this process is that higher isotope ratios are associated with precipitation sourced from warmer SSTs. Thus, where moisture source is a main driver of the isotopic composition of precipitation at a given location, periods of globally higher SSTs should produce precipitation that is more isotopically enriched; however, this effect may be offset as higher SSTs also correspond to periods of globally lower ice volumes, which in turn results in an overall isotopic depletion of ocean water. Despite the potential for the SST effect

to be buffered, the combined influence of ocean water $\delta^{18}\text{O}$ composition and SST variation results in moisture source as a key control on isotopic variation in global precipitation.

The so-called 'amount effect' is the process by which the isotopic ratio in rainwater becomes increasingly depleted as precipitation amount increases. This results from the preferential condensation of ^{18}O to the remaining water vapour in the air mass, which becomes increasingly ^{18}O depleted. Therefore, as a precipitation event from a given cloud mass progresses, the residual $\delta^{18}\text{O}$ signature of the precipitation becomes more and more depleted. While this effect is most evident in tropical locations associated with monsoons and deep-convective thunderstorms (Wang et al., 2001), it has also been well-documented in the extra-tropics (Bar-Matthews et al., 2003; Treble et al., 2005a).

The 'continental effect' is the process by which the isotopic composition of precipitation depletes with increased distance from the ocean (Dansgaard, 1964; Clark and Fritz, 1997; Winnick et al., 2014). This is due to the progressive rainout of ^{18}O leading to increasingly lower ratios along the air-mass trajectory. Even in regions with high levels of moisture uptake, the air mass will become increasingly depleted the further inland it travels because the isotopic composition of this uptake moisture will be inherently depleted in comparison to the initial moisture source (Winnick et al., 2014). As a result of this effect, coastal precipitation is more likely to reflect isotopic values closest to that of its oceanic moisture source.

While the influences discussed so far are those most likely to impact the isotopic composition of precipitation in the Nullarbor region, it is also important to note that there are several other variables that can influence precipitation isotopic values more generally and/or over longer timescales (**Fig. 5.1**). The altitude effect is a process by which $\delta^{18}\text{O}$ values become increasingly depleted with increasing altitude. This can be explained by a combination of changing temperature, and increased rainout as the air mass passes over an orographic barrier (Poage and Chamberlain, 2001; Lachniet, 2009). More generally, temperature influences the $\delta^{18}\text{O}$ of precipitation in several ways. Firstly, precipitation within an air mass is dependent on its temperature falling sufficiently for 100% humidity to be attained, thus allowing for the condensation of water vapour. As such, the level of reduction in temperature determines the amount of moisture condensed (Dansgaard, 1964; Fricke and O'Neil, 1999). Secondly, and on a global scale, average temperatures influence the $\delta^{18}\text{O}$ of precipitation through an ice-volume effect. During colder periods, when ice volumes are substantially higher, the ocean will have a significantly more

enriched isotopic signature. This is a result of ^{16}O enriched precipitation being incorporated into and stored in ice sheets and other substantial ice masses (White, 2015). During interglacial periods, when significant portions of global ice melt, the isotopically-depleted water is returned to the ocean, and thus the precipitation will carry the overall depleted isotopic signature of the ocean.

Modern drivers of precipitation variation are relatively well understood, allowing us to interpolate these processes to explain past conditions. Models have suggested that a weakened (contracted) Hadley Circulation and the resultant expanded tropical warm pool would have brought warmer temperatures during the Pliocene (Brierley et al., 2009). This is supported by evidence of higher precipitation in the Nullarbor region during the Pliocene (Sniderman et al., 2016); a strengthened (expanded) Hadley Circulation would see a poleward shift in mid-latitude storm tracks (Yin et al 2005), potentially bringing significantly more tropically sourced rainfall to the region, including increase frequency of cyclones. It must be noted, however, that in models of future climate focused on mid-latitude storms, there is some disagreement on the impact of an expanded Hadley circulation, with some suggesting reduced rainfall in southern Australia due to changes in storm tracks (Bengtsson et al., 2006). While models of future climates under strengthened Hadley circulation are uncertain (Sniderman et al., 2019), current evidence from the Nullarbor clearly indicates increased precipitation during the Pliocene.

As previously discussed, under modern climate conditions there are significant relationships between precipitation and specific climate modes, such as the Indian Ocean Dipole, the Southern Annular Mode, and the ENSO. For example, El Niño has been shown to imprint a strong signal on the isotopes of precipitation (Jouzel et al 2000). However, when attempting to interpret and understand past climates, especially the distant past (i.e. the Pliocene), these climate modes may not have existed, and there is the potential for them to be masked by other controls on $\delta^{18}\text{O}$ variation. As such, it is not reliable to estimate the prevalence of such systems during the Pliocene based on modern precipitation alone. Therefore, these climate modes will not be discussed further in this chapter, but rather will be revisited alongside the complete dataset of this thesis in **Chapter 8**.

5.1.2. Back Trajectories

When analysing modern precipitation, interpretation of the major drivers of isotopic variation can be achieved by comparing the isotopic values of individual precipitation events with their moisture source region as determined by back-trajectory analysis (Barras and Simmonds, 2009; Callow et al., 2014).

Back trajectories are estimates of the transport pathway of an air mass (Fleming et al., 2012), and have been used for several decades since their development in the 1940s (Petterssen, 1940). Pioneering work using back trajectories involved sourcing regions of atmospheric pollution (Fox and Ludwick, 1976; Ashbaugh et al., 1985). Since then, they have been widely used to identify numerous characteristics related to precipitation over various spatial and temporal scales, with one of the most common current applications being determining the origin of air masses (Fleming et al., 2012).

Back trajectories are calculated using a number of meteorological variables, dependent on the model being used (Pfahl and Wernli, 2008; Fleming et al., 2012; Stein et al., 2015). The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model is one of the most commonly used atmospheric transportation models in climate studies (Stein et al., 2015). The HYSPLIT model produces data on both horizontal and vertical coordinates on an hourly basis for a given air mass, in order to produce a detailed model of its likely pathway. (Baldini et al., 2010). In addition, a multitude of variables including temperature, rainfall amount, and relative humidity, are calculated on an hourly basis, yielding information on the processes associated with precipitation events that may influence isotopic values, including moisture source, rainout and transport patterns (Aggarwal, 2004).

5.1.3. Synoptic Systems

In addition to the features that can be analysed using back trajectories, the study of synoptic climatology can also assist in the interpretation of modern precipitation variability. It is possible to determine potential small-scale synoptic controls on precipitation as well as information regarding the large-scale circulation and structure of the atmosphere from the isotopic composition of precipitation (Barras and Simmonds, 2008). The study and classification of synoptic systems has been an area of much interest in climatology since the pioneering research in 1950s (Lamb, 1950; Lamb, 1972). There is significant empirical evidence that synoptic systems affect modern precipitation $\delta^{18}\text{O}$ (Treble et al., 2005b; Hope et al., 2006; Barras and Simmonds, 2008; Barras and Simmonds, 2009). Each synoptic system is characterised by a number of different features, including barometric pressure, wind speed and direction, temperature and humidity (Whitaker, 2010). Thus, the identification of the synoptic system provides a good summary of the multiple factors characterising a given precipitation event. The isotopic signature of a given precipitation event is influenced not only by the prevailing synoptic conditions, but also by local convective and evaporative processes (Barras and Simmonds, 2009).

The main synoptic systems influencing the Nullarbor are low-pressure cells, cold fronts, and the advection of moisture across the continent sourced from the tropics (IOCI, 2012). Low-pressure systems are generally associated with cloud, rain and strong winds, whereas high-pressure systems are generally associated with fine weather and light winds. Cold fronts occur when a cold air mass approaches and undercuts a warmer air mass, which commonly triggers cloud formation and precipitation.

5.1.4. Applications to Palaeoclimate Studies

Modern rainfall analyses have been used to interpret variations in the $\delta^{18}\text{O}$ in palaeoclimate archives, including speleothems (Mattey et al., 2008; Dayem et al., 2010; Baker et al., 2014). These can then be used to identify significant palaeoclimate changes based on our understanding of these systems under modern conditions (Poage and Chamberlain, 2001; Johnson and Ingram, 2004; Dayem et al., 2010). However, our ability to apply modern precipitation analyses to the interpretation of palaeoprecipitation is based on two key assumptions. The first of these is that the basic mechanisms by which $\delta^{18}\text{O}$ is fractionated and transported were no different in the past despite potential differences in boundary conditions (Dayem et al., 2010). While specific isotopic values may vary temporally, the general principles of isotopic variation dictate that the systematic variations in the signatures from given synoptic systems and/or moisture sources will remain the same. Therefore, by identifying how these variables are reflected in modern precipitation $\delta^{18}\text{O}$ values, it is possible to identify the most dominant synoptic conditions or moisture sources for periods of particularly enriched/depleted isotopic values in the past.

A secondary key assumption is that the instrumental data collected are representative of events or synoptic conditions that occurred in the target time period (in this case, the Pliocene). While it is likely that modern synoptic systems behaved somewhat differently to Pliocene ones (e.g. Haywood et al., 2013; Zhang et al., 2013), it is reasonable to assume that the range of weather systems we see today would have been present, but occurring with frequencies. It is the change of dominance in these systems that we aim to identify through our understanding of the isotopic variations of modern precipitation. The analyses of back trajectories can be particularly useful in this regard as they produce data on several of the factors that influence the $\delta^{18}\text{O}$ values of precipitation (Treble et al., 2005b; Barras and Simmonds, 2008), such as moisture source and continental effects. Such relationships can be vital for assessing the dominant influences of precipitation $\delta^{18}\text{O}$ at a given location. Similarly, synoptic typing can be very useful in identifying the signatures of predominant systems influencing the $\delta^{18}\text{O}$

values of modern precipitation. Relationships between particular $\delta^{18}\text{O}$ signatures and the overall characteristics of a given synoptic type can highlight larger-scale changes in palaeoprecipitation from palaeodata. Therefore, in the context of assisting with interpretations of the precipitation of the Nullarbor region during the Pliocene, the analysis of modern precipitation is vital.

5.2. Methods

5.2.1. Site Selection and Sample Collection

A total of six relatively well-distributed sites surrounding the Nullarbor cave locations were selected for the collection of modern rainfall samples (**Fig. 5.3**). Personnel at these sites, which are part of the Bureau of Meteorology (BoM) volunteer rain-gauging network, were contacted and requested for assistance with this study. Rainfall collection was conducted for twenty-four months in order to cover two complete annual cycles.

All the necessary equipment and collection protocols were provided for each site, and samples returned to The University of Melbourne for analysis at approximately six-month intervals. As each site was already registered with the BoM, those conducting the daily rainfall readings were asked to transfer any

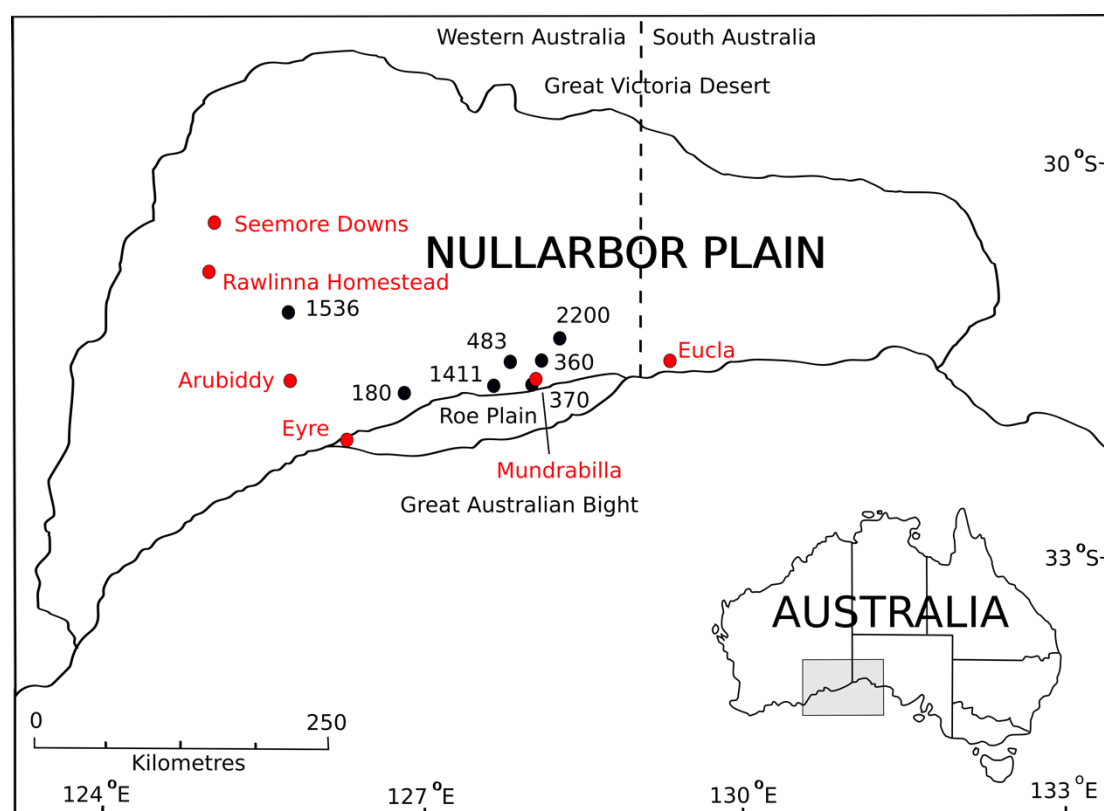


Fig. 5.3 - Locations of rainfall collection sites (red) and cave sites from which speleothems used in this study were obtained (black) on the Nullarbor Plain, position within Australia inset.

rainfall from the gauge into a collection vial, which was labelled with the site code, date of rainfall event, and precipitation amount. All samples were refrigerated after collection until they were sent to The University of Melbourne for isotopic analysis.

5.2.2. Sample Analysis

Samples where only trace volumes (<0.1 mm rainfall amounts) were recorded were excluded from analysis due to the potential for isotopic exchange with the vial headspace when not completely filled with water. Upon return to the lab, all other samples were transferred from the collection vials into 2 ml measurement vials. Filtering using a 0.45 μm filter and luer-lock syringe attachment was carried out to expel any particles (e.g. dust). Samples and standards were placed in set positions in the sampling rack. Three in-house standards ('lake', 'snow', and 'woolies') and two international reference materials ('V-SMOW', and 'GISP'), all with known isotopic values, were used.

Analyses were conducted in 'high-precision mode' on a Picarro cavity-ringing down L2120 isotope analyser at The University of Melbourne. To reduce any memory effects, the injection needle was rinsed three times each in deionised water and 1-methyl-2-pyrrolidinone between each analysis. For each rainfall sample measurement, six separate aliquots of 0.10 μl were injected into the vaporiser for isotopic composition measurement. To completely eliminate memory effects, data from the first three injected aliquots were discarded. Data reduction was conducted using an Excel macro, developed in-house. During this process, data from aliquots four to six were averaged; in cases where the standard deviation exceeded 0.1‰ for $\delta^{18}\text{O}$ or 0.5‰ for δD , the sample was reanalysed. The standards were also checked for potential drift throughout the run of 54 samples; no drift was ever recorded. The standard deviation of the woolies standard was used to estimate the external reproducibility. Sample data were then calibrated to the V-SMOW scale, using batch-specific log-linear fits, then expressed in per mille (‰) on the V-SMOW scale.

5.2.3. Rainfall Data Organisation and Additional Data Collection

Metadata for each rainfall event at the individual sites were compiled, including rainfall date, rainfall amount, season, and average surface temperature, to complement the measured $\delta^{18}\text{O}$, δD , and the calculated *d-excess* (defined by Dansgaard, 1964). The latter represents the level of deviation from the GMWL, largely reflecting the level of kinetic fractionation that has occurred during non-equilibrium processes such as evaporation (Jouzel et al., 2000). Average surface temperature was calculated using daily temperature data obtained from the BoM

online database for the station at Eyre (**Appendix 1**). This temperature represents the average of the maximum temperature of the day preceding the rainfall event and the minimum temperature of the day of the rainfall event, the most commonly applied method in similar studies (Treble et al., 2005a; Treble et al., 2005b). The *d-excess* was calculated using the following equation:

$$d = \delta D - (8 \times \delta^{18}\text{O})$$

where *d* is *d-excess* and the constant 8 is derived from the global meteoric water line (GMWL) equation.

Analysis of the isotopic results was undertaken in a number of stages involving the strategic selection of certain datasets for further analyses. Further analysis involved the collection of plots of Australia and surrounding oceans depicting daily composites of anomalous conditions of precipitable water (**Fig. 5.4D**), outgoing long-wave radiation (**Fig. 5.4B**) and sea-level pressure (**Fig. 5.4C**), as well as synoptic charts and back trajectories. Composites were obtained for the day of, and the day before, each rainfall event at an analysis barometric level of 1000 mb. The majority of daily composites were obtained online from the National Oceanic and Atmospheric Administration (NOAA) website, provided by the Physical Sciences Division of the Earth System Research Laboratory sector¹. In addition, composites were obtained for the day before rainfall events at analysis levels of 1000 mb and 500 mb for the variable of geopotential height (**Fig. 5.4A**): 1000 mb represents processes occurring at ground level, and 500 mb approximates the middle of the troposphere where the majority of circulation, potential precipitation and storm tracks are likely to form (Yarnal et al., 2001). Positive sea-level pressure anomalies represent higher-than-average atmospheric pressures, whereas the negative values represent lower-than-average pressures. Positive outgoing long-wave radiation (OLR) anomalies represent lower-than-average cloud cover (i.e. particularly dry air parcels), whereas negative anomalies represent higher-than-average cloud cover. Positive anomalies in precipitable water represent above-average moisture availability, whereas negative anomalies represent lower-than-average moisture availability (i.e. dry conditions). Positive anomalies in geopotential height represent higher-than-average pressure conditions, whereas the negative anomalies represent lower-than-average pressure conditions. To assist the identification of moisture source and potential air-mass interactions, archived composite weather maps

¹ www.esrl.noaa.gov/psd/data/composites/day/

were also obtained online through the BoM. For each rainfall event, three weather maps covering a 24-hour period were analysed (**Fig. 5.5**).

A limitation of this method is the level of subjectivity involved in classifying moisture sources (Frakes and Yarnal, 1997; Yarnal et al., 2001). To some extent, this is overcome by the inclusion of modelled back-trajectory analyses. While these also have their limitations and should not be relied upon solely, their combined use along with other climate data compensates for the limitations of the individual methods. Back trajectory analyses were also undertaken for each selected event. The online version of the HYSPLIT model (Draxler and Hess, 1998) was used for all analyses. The optional inputs followed the principal procedures of similar studies such as (Baldini et al., 2010) and (Breitenbach et al., 2010). Precise GPS coordinates of each site were used (**Table 5.1**), and a standardised time of 01:00 am (UTC) was used for each given rain day to represent the constant collection time (09:00 am AWST) of all rainfall samples. The key inputs for all trajectories were selected as a total run time of 72 hours at 3000 m and 1000 m a.m.s.l., thus producing two air-mass pathways for the three days leading to the set rainfall time (**Fig. 5.6**). Back trajectories were run at these levels because 1000 m a.s.l. represents near-surface processes and 3000 m a.s.l. is the approximate level at which precipitation is typically generated (Theobald and McGowan 2016). By combining these data, events were then assigned to one of four moisture sources – Southern Ocean (SO - code 1), northern cloud band – Southern Ocean interactions (CB/SO - code 2), tropical (T - code 3), and Tasman influenced (TI - code 4). Samples were identified as SO sourced where all maps and trajectories indicate that the sole moisture source for the rainfall event was the Southern Ocean (e.g. **Fig. 5.7**). Events where the cloud cover and/or precipitable water suggest that there is also a potential northwest moisture source, which may have influenced the rainfall (e.g. **Fig. 5.8**), were classified as CB/SO. Events identified as T are sourced entirely from the northwest sector of the Australian tropics (e.g. **Fig. 5.9**). Where there is potential influence of moisture sources from the Tasman Sea (e.g. **Fig. 5.10**), events were classified as TI. Whilst subclasses exist within these categories, it was not deemed necessary within the aims of this study to subdivide further into minor moisture sources. This conclusion was based upon the overarching aim to apply the information gained from the modern precipitation studies to the speleothem-based palaeoclimate record.

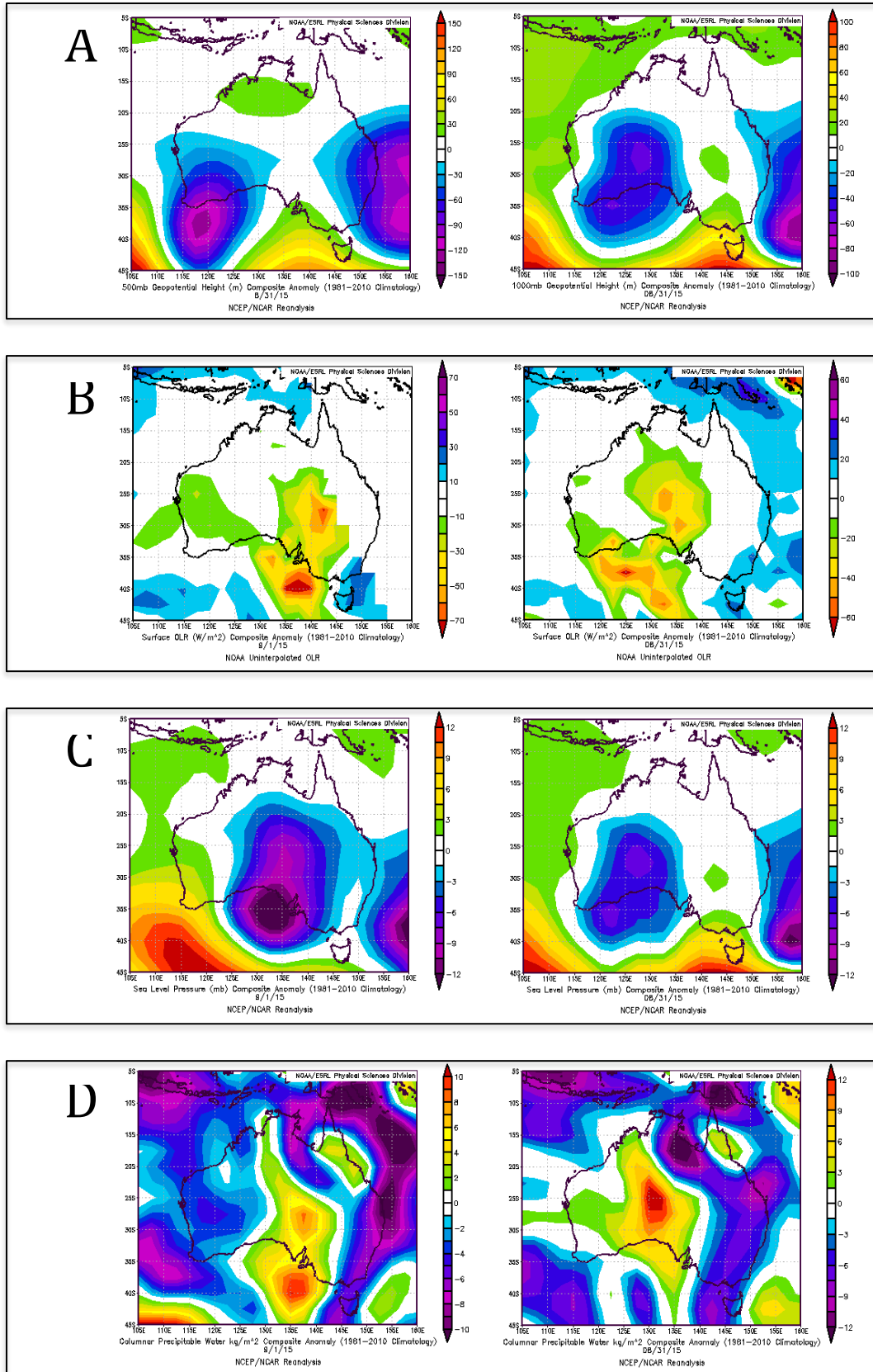


Fig. 5.4 – Examples of NOAA daily composites for geopotential height (A), outgoing long-wave radiation (B), sea level pressure (C), and anomalous condition of precipitable water (D), used for allocating moisture sources to precipitation events. Images on the left represent the day before the rainfall collection day; the images on the right represent the day of sample collection. Source: National Oceanic and Atmospheric Administration (www.ready.noaa.gov/).

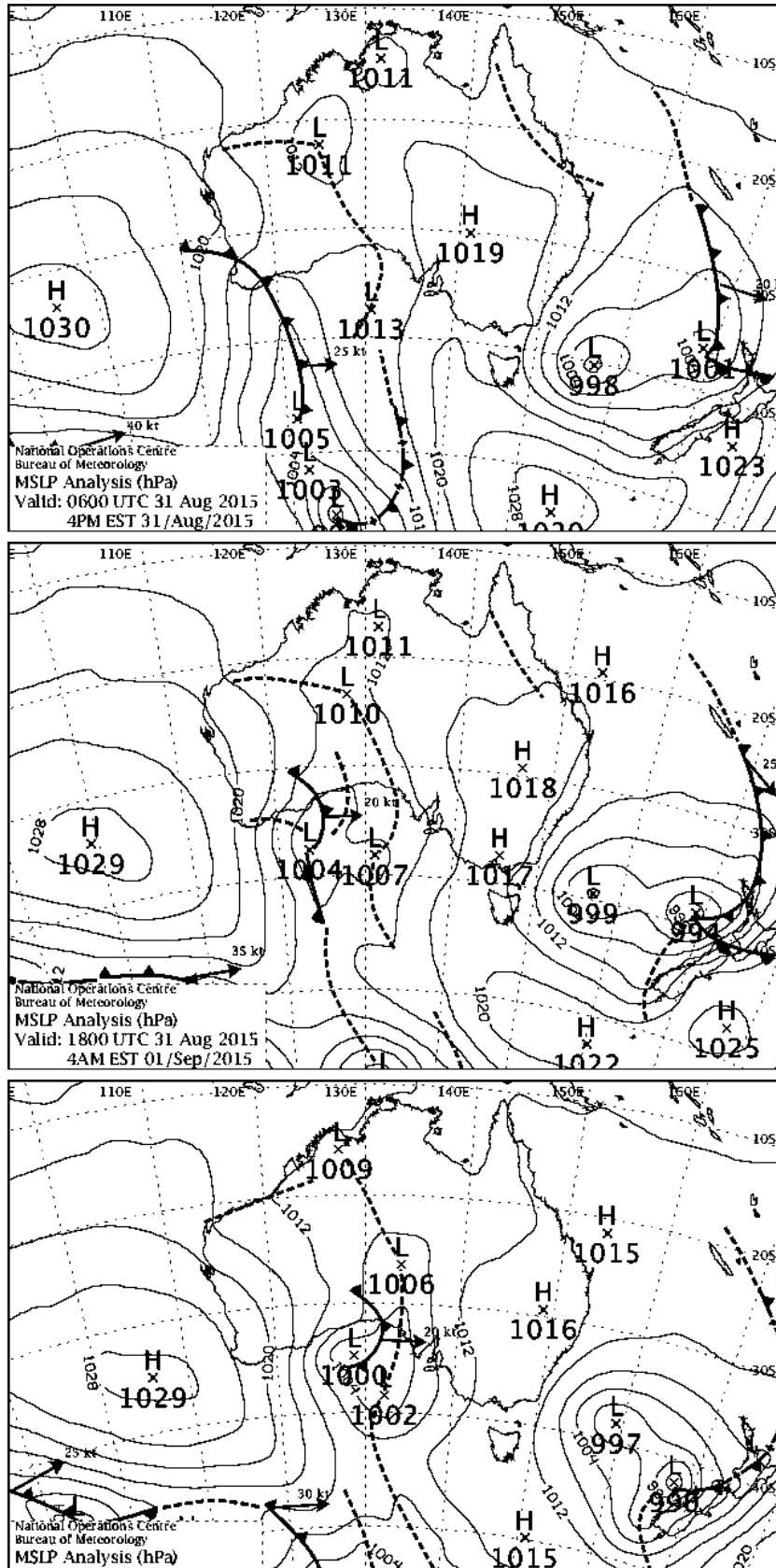


Fig. 5.5 - Examples of the composite weather maps obtained for each precipitation event to cover a 24-hour period around rainfall sample collection (12 hours prior collection - top, time of collection - middle, 12 hours after collection - bottom). Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

Table 5.1 – GPS coordinates used for the back-trajectory analyses of all rainfall collection sites.

Site Name	Site Code	GPS Coordinates	
Eucla	EUC	31.68 S	128.90 E
Eyre	EYR	32.25 S	126.30 E
Rawlinna Depot/ Homestead	RAW	31.04 S	125.22 E
Arubiddy	ARU	31.81 S	125.93 E
Seemore Downs	SED	30.74 S	125.29 E
Mundrabilla Station	MUN	31.84 S	127.86 E

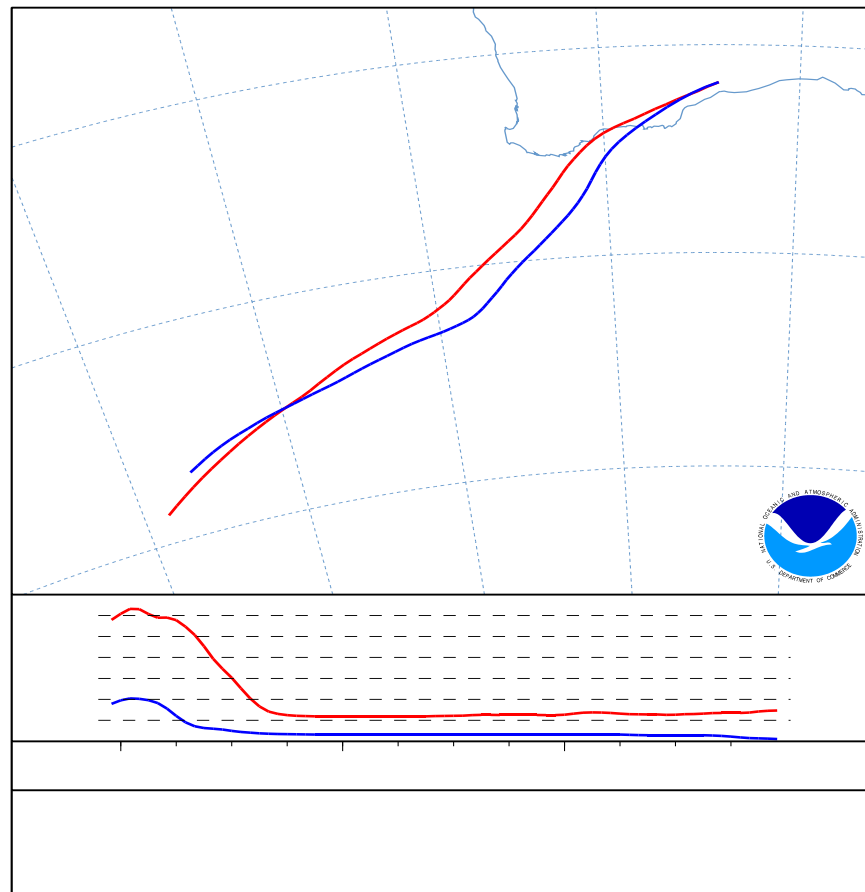


Fig. 5.6 – An example of the back-trajectory output data used for allocating moisture sources to each precipitation event. Source: National Oceanic and Atmospheric Administration (www.ready.noaa.gov/HYSPLIT).

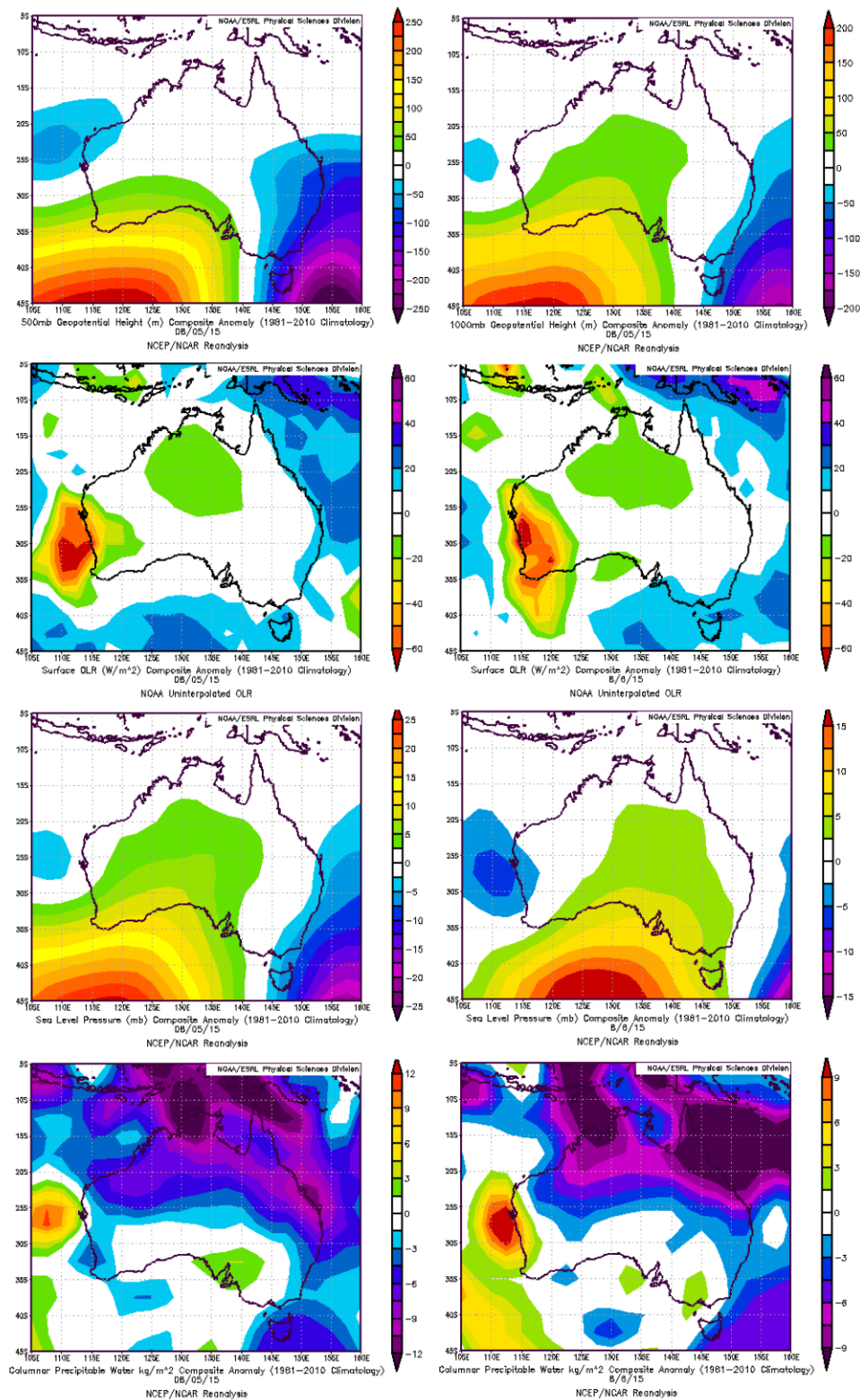
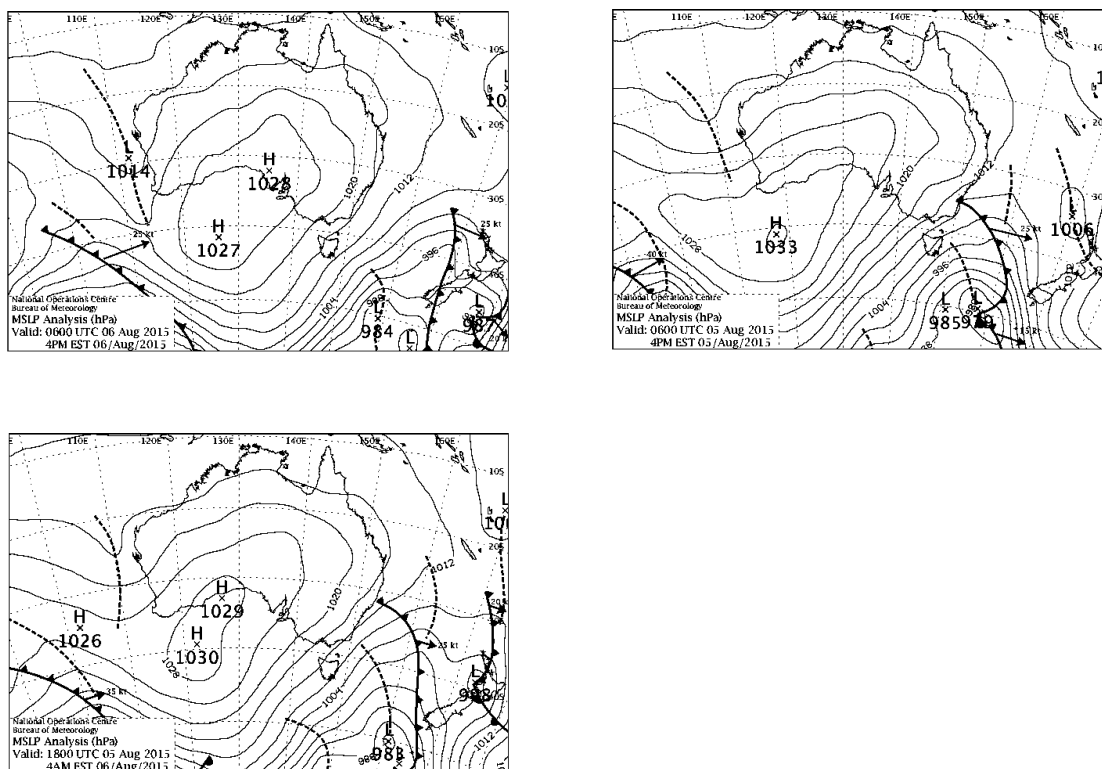


Fig. 5.7 – An example of the daily composite maps indicating a precipitation event sourced from the Southern Ocean. Each pair of composite maps shows (from top to bottom) the conditions of geopotential height at 500mb (left) and 1000 mb (right), and outgoing long-wave radiation, sea-level pressure, and anomalous condition of precipitable water, respectively, the day before (left), and day of each rainfall event (right). Source: National Oceanic and Atmospheric Administration (www.ready.noaa.gov/). Continued on following page.



NOAA HYSPLIT MODEL
Backward trajectories ending at 0100 UTC 06 Aug 15
GDAS Meteorological Data

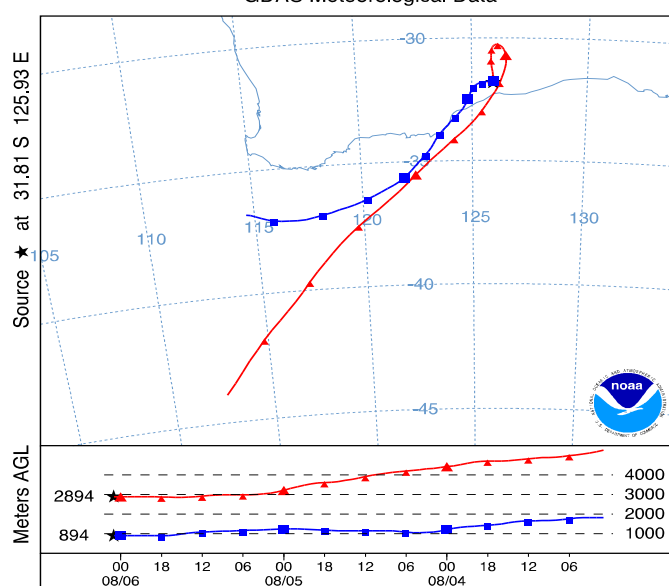


Fig. 5.7.cont. – An example of the daily composite maps and back-trajectory maps indicating a precipitation event sourced from the Southern Ocean. The daily composite weather maps track the 24-hour period leading up to the precipitation event and represent 24 hours prior to, 12 hours prior to, and the time of sample collection. The back-trajectory map indicated the modelled path of the rainfall events in the 72 hours leading up to the precipitation event collection, at altitudes of 3000m asl (red), and 1000m asl (blue). Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/) and National Oceanic and Atmospheric Administration (www.ready.noaa.gov/HYSPLIT).

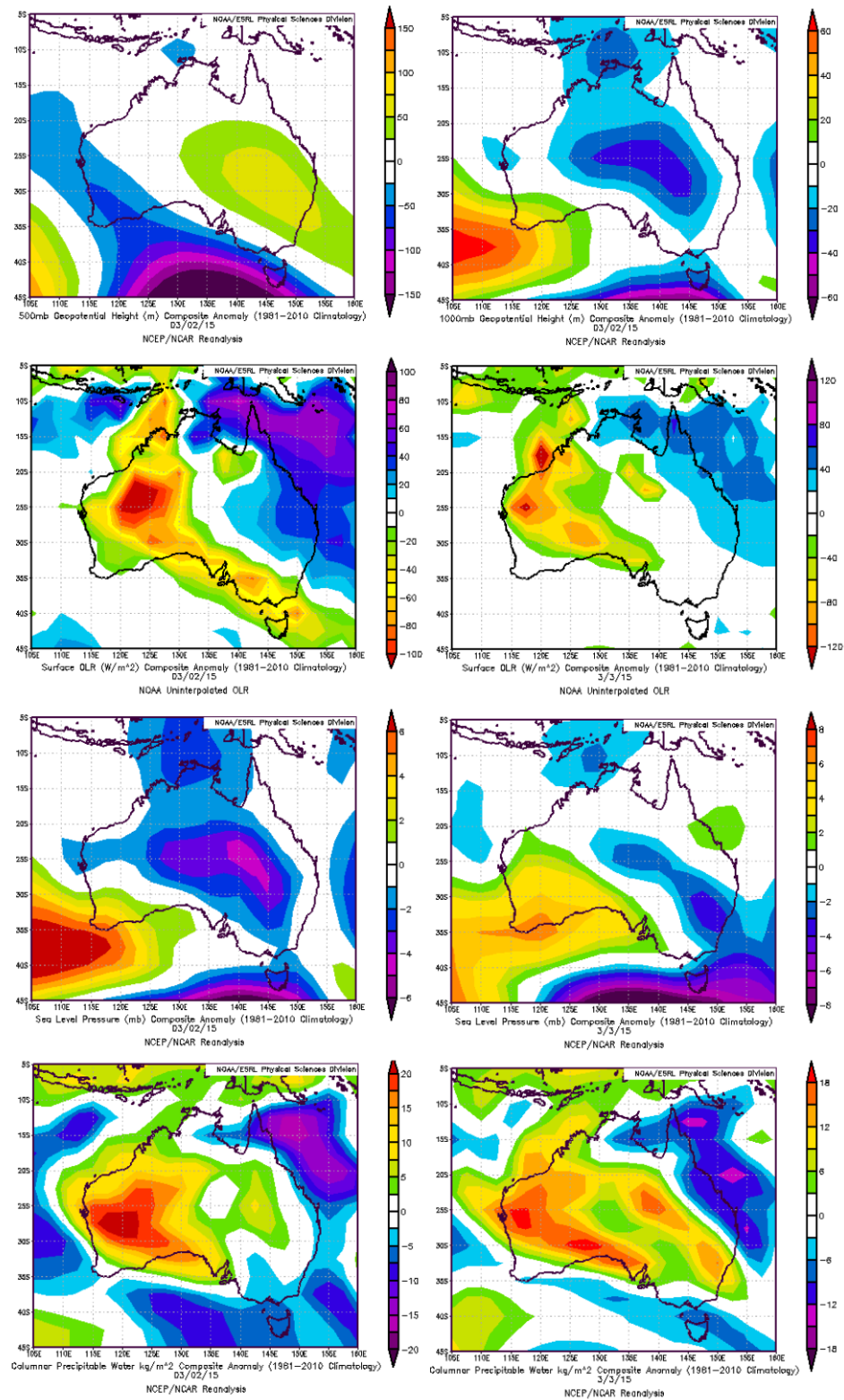
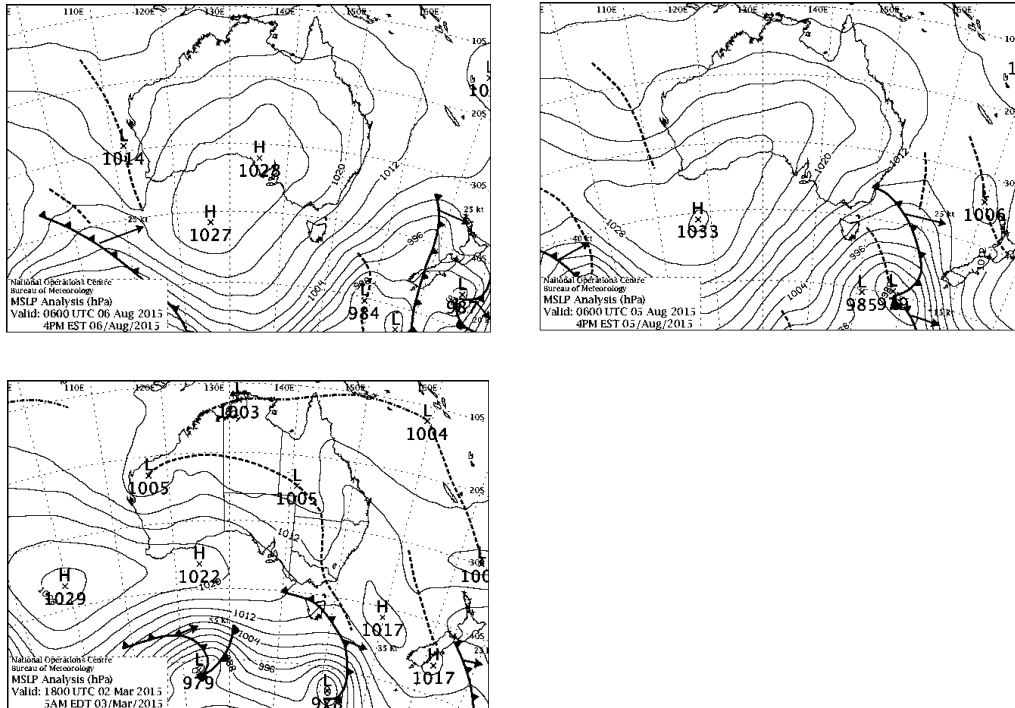


Fig. 5.8 – An example of the daily composite maps indicating a precipitation event with northern cloud band and Southern Ocean interactions. Each pair of composite maps shows (from top to bottom) the conditions of geopotential height at 500mb (left) and 1000 mb (right), and outgoing long-wave radiation, sea-level pressure, and anomalous condition of precipitable water, respectively, the day before (left), and day of each rainfall event (right). Source: National Oceanic and Atmospheric Administration (www.ready.noaa.gov/). Continued on following page.



NOAA HYSPLIT MODEL
Backward trajectories ending at 0100 UTC 03 Mar 15
GDAS Meteorological Data

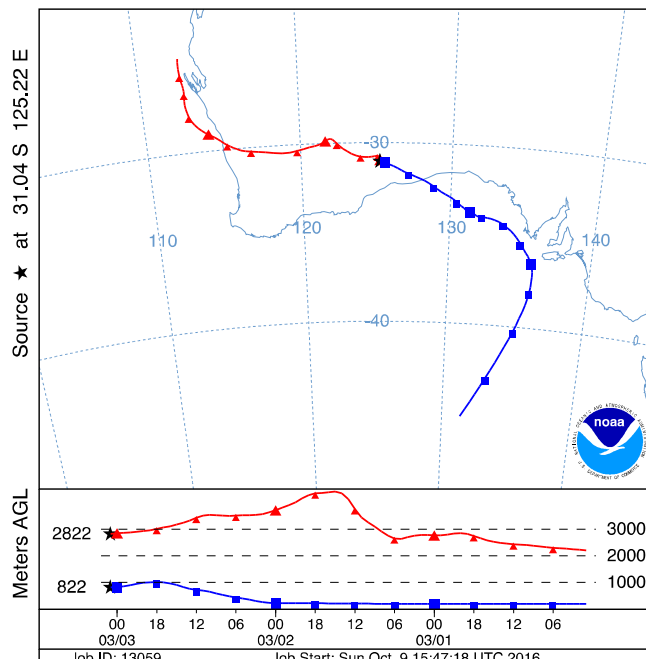


Fig. 5.8.cont. – An example of the daily composite maps and back-trajectory maps indicating a precipitation event with northern cloud band and Southern Ocean interactions. The daily composite weather maps track the 24-hour period leading up to the precipitation event and represent 24 hours prior to, 12 hours prior to, and the time of sample collection. The back-trajectory map indicated the modelled path of the rainfall events in the 72 hours leading up to the precipitation event collection, at altitudes of 3000m asl (red), and 1000m asl (blue). Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/) and National Oceanic and Atmospheric Administration (www.ready.noaa.gov/HYSPLIT).

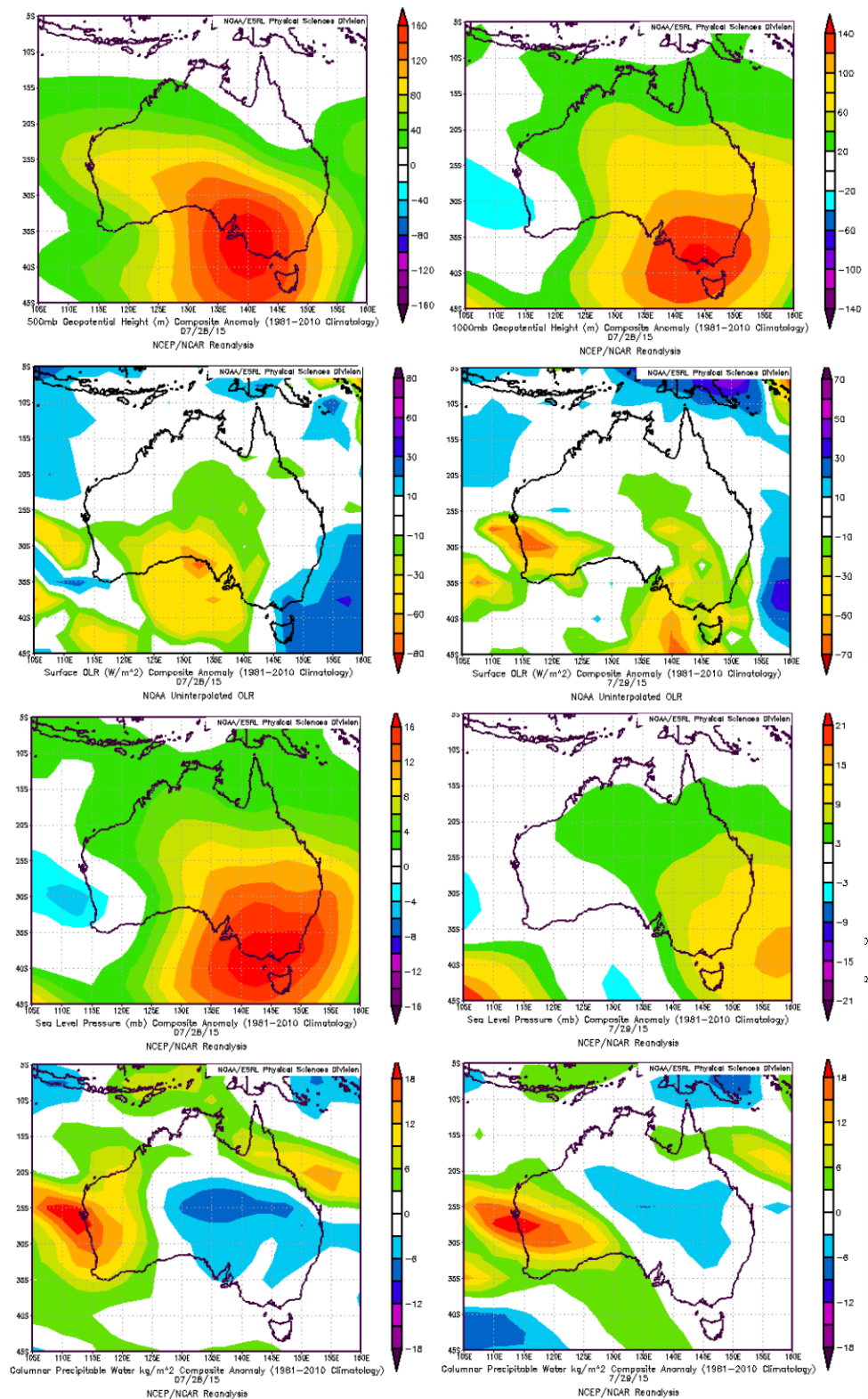
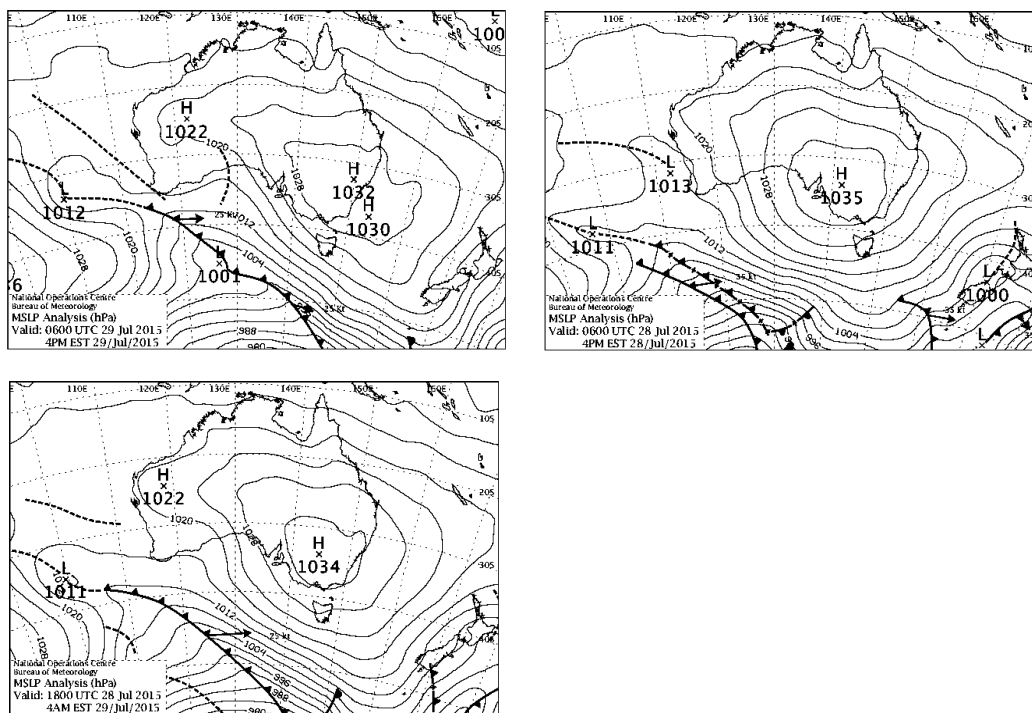


Fig. 5.9 – An example of the daily composite maps indicating a precipitation event sourced from the tropics. Each pair of composite maps shows (from top to bottom) the conditions of geopotential height at 500mb (left) and 1000 mb (right), and outgoing long-wave radiation, sea-level pressure, and anomalous condition of precipitable water, respectively, the day before (left), and day of each rainfall event (right). Source: National Oceanic and Atmospheric Administration (www.ready.noaa.gov/). Continued on following page.



NOAA HYSPLIT MODEL
Backward trajectories ending at 0100 UTC 29 Jul 15
GDAS Meteorological Data

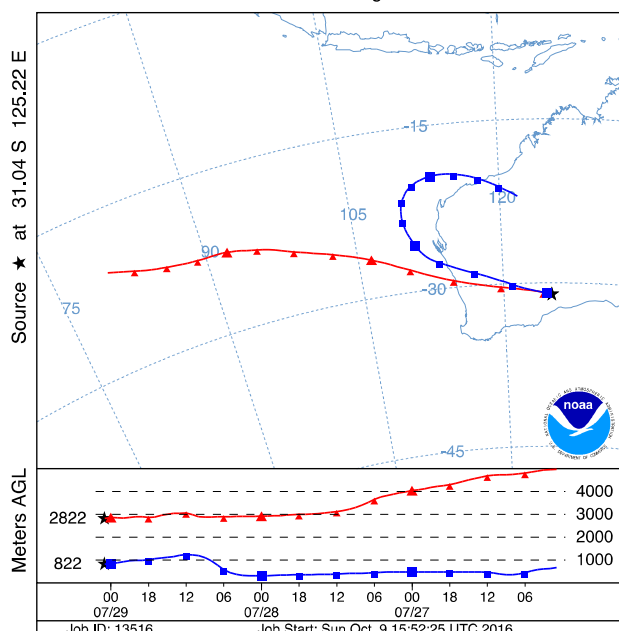


Fig. 5.9.cont. – An example of the daily composite maps and back-trajectory maps indicating a precipitation event sourced from the tropics. The daily composite weather maps track the 24-hour period leading up to the precipitation event and represent 24 hours prior to, 12 hours prior to, and the time of sample collection. The back-trajectory map indicated the modelled path of the rainfall events in the 72 hours leading up to the precipitation event collection, at altitudes of 3000m asl (red), and 1000m asl (blue). Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/) and National Oceanic and Atmospheric Administration (www.ready.noaa.gov/HYSPLIT).

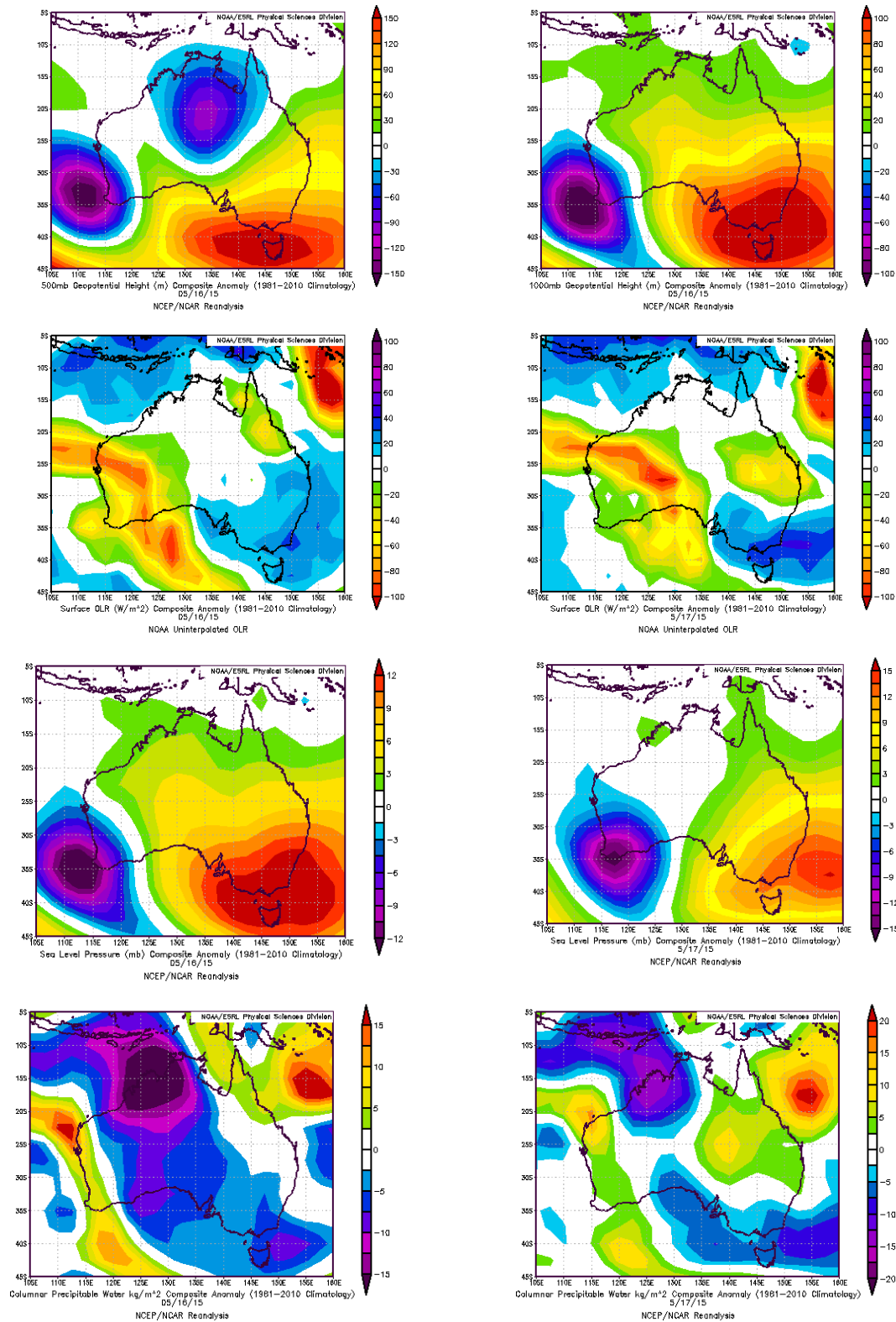
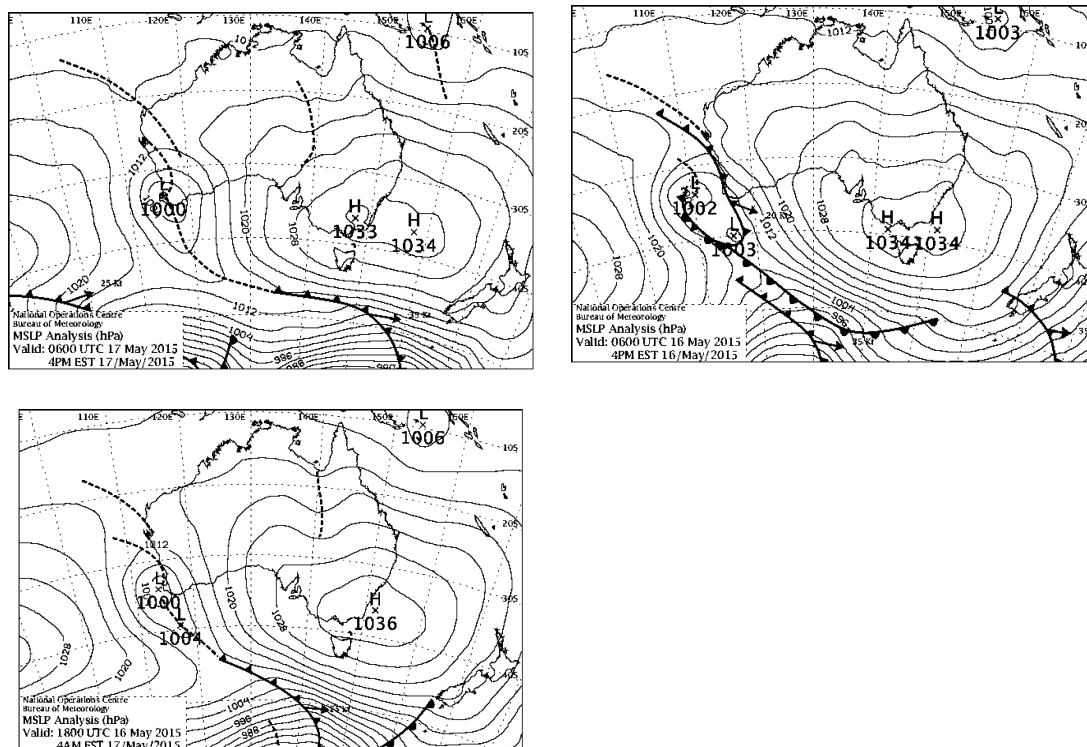


Fig. 5.10 – An example of the daily composite maps indicating a precipitation event sourced from the Tasman Sea. Each pair of composite maps shows (from top to bottom) the conditions of geopotential height at 500mb (left) and 1000 mb (right), and outgoing long-wave radiation, sea-level pressure, and anomalous condition of precipitable water, respectively, the day before (left), and day of each rainfall event (right). Source: National Oceanic and Atmospheric Administration (www.ready.noaa.gov/). Continued on following page.



NOAA HYSPLIT MODEL
Backward trajectories ending at 0100 UTC 17 May 15
GDAS Meteorological Data

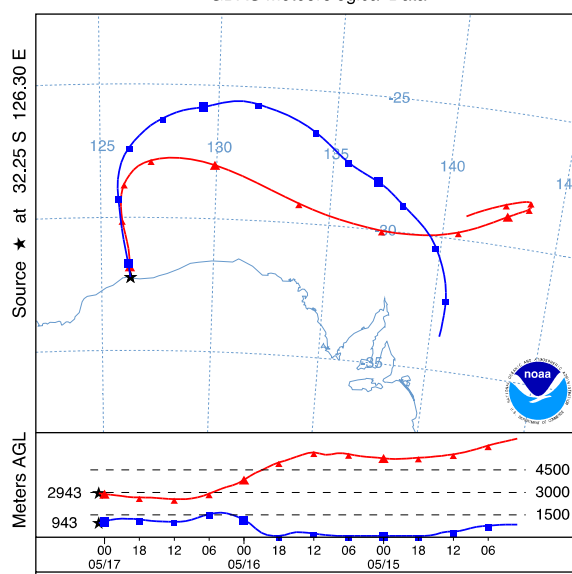


Fig. 5.10.cont. – An example of the daily composite maps and back-trajectory maps indicating a precipitation event sourced from the Tasman Sea. The daily composite weather maps track the 24-hour period leading up to the precipitation event and represent 24 hours prior to, 12 hours prior to, and the time of sample collection. The back-trajectory map indicated the modelled path of the rainfall events in the 72 hours leading up to the precipitation event collection, at altitudes of 3000m asl (red), and 1000m asl (blue). Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/) and National Oceanic and Atmospheric Administration (www.ready.noaa.gov/HYSPLIT).

Additionally, due to the sampling resolution applied to the speleothems in this study, it would not be possible to resolve smaller-scale $\delta^{18}\text{O}$ variations of moisture source subclasses. As such, the focus is placed on the aforementioned four 'major' moisture sources in order to produce a basic understanding of the precipitation source-isotope patterns at a scale applicable to the larger aims of this thesis.

5.2.4. Data Analyses

Within the scope of this study it was deemed unnecessary to analyse and classify moisture sources for all rainfall events. This conclusion was reached, because while the complete dataset is useful for identifying overall seasonal trends, it is only the drivers of the most depleted and enriched $\delta^{18}\text{O}$ values that can be applied to the palaeodata of this study. It is the changing dominance of these drivers that will be causing the shifts evident in the speleothem $\delta^{18}\text{O}$ values, and as such it is these drivers, which must be investigated. In a higher-resolution study, where annual and subannual signals are evident, it may be of interest to investigate the complete dataset, however, due to the dating restrictions of these Pliocene speleothems, such detail is not applicable to the interpretations. As such, rainfall data were stratified to best represent 'extreme' events that portray key relationships between $\delta^{18}\text{O}$ and the numerous potentially influential factors (e.g. rainfall amount, moisture source, season). Several approaches were taken to stratifying the data to ensure a broader overview of the key influences and drivers on $\delta^{18}\text{O}$. Initially, data were stratified by rainfall amount, with a total of twelve events selected from each site for analysis: the six events of highest rainfall amounts, and the six events of lowest rainfall amounts. This approach was chosen primarily in order to identify and patterns between moisture source and synoptic systems and rainfall amount.

This is an important factor to consider, as it is the higher rainfall amounts that are going to have the biggest impact on the $\delta^{18}\text{O}$ values represented in speleothems. Therefore, if there is a significant pattern in the synoptic conditions resulting in large precipitation events, this will be an important consideration in the interpretation of the palaeodata. Each of the aforementioned composite map types (**Fig. 5.4**) were utilised in attributing individual rainfall events to their most likely original moisture source. The variables of sea-level pressure and geopotential height were used to observe the path of air masses over time, and together indicate the presence of pressure anomalies.

Accordingly, both can be used to track the movement of these systems over vertical, latitudinal, longitudinal and temporal scales. Similarly, the OLR and precipitable water variables allow analyses over the same four scales. However, they are only indicative of the level of cloud cover and availability of moisture, respectively.

The combined analyses of the composite maps and weather maps allows interpretation of the pathways of the air parcels from which the rainfall of a given event has followed; this, in turn, resolves the provenance of the precipitation. This interpretation can then be verified through the use of the back-trajectory analyses for each event. As it is possible that multiple air parcels are interacting, or that one air parcel has lost the majority of its available moisture through rainout prior to its arrival at the collection site, it is important to consider the collection of composite map types and back trajectories alongside one another. If there are multiple moisture sources or there is considerable rainout prior to a given precipitation event, it can often be distinguished through the comparison of the back-trajectory analysis with all of the composite data maps but may be missed through the use of back-trajectory analyses alone.

Among the most commonly used statistical method for quantifying correlations is the Pearson product moment correlation coefficient:

$$r = \frac{N\sum xy - (\sum x)(\sum y)}{\sqrt{[N\sum x^2 - (\sum x)^2][N\sum y^2 - (\sum y)^2]}}$$

where *cov* is the covariance and σ is the standard deviation. This is the measure of linear dependence between two variables. This is frequently used in both modern precipitation studies and in speleothem-focussed precipitation studies (e.g. Treble et al., 2005a; Treble et al., 2005b; Orland et al., 2014; Mutz et al., 2016). The statistical significance of the *r* values was calculated using the ‘table of critical values of *r*’. For nominally classified data where the Pearson product correlation coefficient is not applicable, Pearson’s Chi-square tests were used to test either homogeneity or independence according to the hypothesis being tested. Data were organised into contingency tables and the CHISQ.TEST function of Excel used to calculate *p*-values. The function first calculates the χ^2 statistic using the following equation:

$$\chi^2 = \sum_{i=1}^r \sum_{j=1}^c \frac{(A_{ij} - E_{ij})^2}{E_{ij}}$$

where r is the number of rows, c is the number of columns, A is the actual frequency, and E is the expected frequency. The CHISQ.TEST function then uses the result of the χ^2 statistic with the appropriate number of degrees of freedom to produce a p -value. All p -values <0.05 are deemed statistically significant.

These were used to assess correlations between various factors influencing $\delta^{18}\text{O}$. Values of probability were derived from the calculated degrees of freedom for each statistical test. To allow for direct comparisons with moisture source by the Chi-squared analyses, as well as to allow the stratification of the data, $\delta^{18}\text{O}$ and rainfall amount were categorised. $\delta^{18}\text{O}$ was divided into three groups: enriched (13.38 to -1.06), intermediate (-1.05 to -2.56), and depleted (-2.57 to -10.72). Rainfall amount was also divided into three groups: high (4.3 to 52 mm), moderate (1.3 to 4.2 mm) and low (0.1 to 1.2 mm). The categories of both $\delta^{18}\text{O}$ and rainfall amount were allocated based on the complete dataset; it was organised by $\delta^{18}\text{O}$ and rainfall amount respectively and divided into groups containing approximately 33% of the data (189 ± 5). The upper and lowermost values of each grouping were used to assign values to the groups of enriched, intermediate and low for $\delta^{18}\text{O}$, and high, moderate and low for rainfall amount. Additionally, season was used a proxy for temperature and used for both Chi-squared statistics and stratified data analyses.

5.2.5. Approach to Site Comparison Analysis

In order to compare variations in $\delta^{18}\text{O}$ across the six different rainfall sites, an additional series of analyses were undertaken as follows. Initially, individual rainfall days for which collections occurred across a minimum of four sites were identified, irrespective of the sites over which the rainfall events occurred. The rainfall amounts at each site were summed to provide total rainfall amounts for each of these rain days. Results were then stratified by total rainfall amount, and the ten days with highest rainfall amount were selected for further analyses. The highest rainfall amounts were selected in order to better identify any patterns of rainout along the air mass trajectories between the sites. Once the ten events had been identified each event was investigated individually. Consideration was given to $\delta^{18}\text{O}$, rainfall amount, and moisture source, and analysed with respect to the location of each site and the projected moisture source and trajectory of each event. The primary purpose of this analysis was to identify any influence of the 'amount effect' on the weighted average $\delta^{18}\text{O}$ of event precipitation. This was achieved through identifying any systematic variability in $\delta^{18}\text{O}$ dependent on the site location and moisture pathway. These additional analyses were undertaken as such an influence could have potential

implications on the $\delta^{18}\text{O}$ signal subsequently preserved within a speleothem in the region, thus influencing interpretations of palaeoprecipitation.

In addition to allowing study of $\delta^{18}\text{O}$ variation in precipitation across the Nullarbor Plain, this series of analyses also provided an opportunity for assessing the validity of back-trajectory analyses. In order to do this, individual analyses were conducted for each site. This allows assessment of the consistency of multiple back trajectories from relatively closely spaced locations for individual precipitation events for which identical or very similar moisture pathways would be expected.

5.2.6. Stratification for Palaeoprecipitation Analyses

The overall goal of the modern precipitation analyses is to assist interpretations of palaeoprecipitation via the $\delta^{18}\text{O}$ of the speleothem calcite. To best achieve this goal, an additional level of analysis was undertaken, which considers the context of cave hydrology and speleothem $\delta^{18}\text{O}$. This is of importance as not all precipitation during an event will reach the cave and contribute to speleothem $\delta^{18}\text{O}$. The proportion of total precipitation that reaches the cave ('effective recharge'), is determined by a number of factors, including rainfall amount, evapotranspiration, and antecedent rainfall. In order to account for this, a minimum precipitation amount for effective recharge was calculated for this stage of analysis. In order to calculate a value for minimum precipitation amount, a number of steps were taken. Firstly, it was necessary to find an approximate modern geographic analogue for modelled Pliocene temperature and precipitation. These modelled estimates of temperature (**Fig. 2.3**) and precipitation (**Fig. 2.4**) were presented in **Chapter 2** and used to identify mean annual temperatures in the region of approximately 3-4 °C warmer than the present day, alongside approximately 700 mm higher annual rainfall. These constraints were used to define candidate regions within Australia based on modern average precipitation (**Fig. 5.11**) and temperature (**Fig. 5.12**). The selection criteria included a rainfall amount similar to estimates for the Pliocene, but average temperatures higher than the modelled 3-4 °C temperature increase on the modern-day Nullarbor. A higher temperature was required in order to produce a conservative estimate of the proportion of rainfall that would hypothetically reach the cave systems. By increasing the annual temperature while maintaining the same annual precipitation, a higher potential evapotranspiration value is produced. This reflects on the theoretical minimum precipitation amount required to infiltrate into the cave.

Due to uncertainties in the precise rainfall amounts and seasonal temperatures of the Pliocene, it was decided that palaeodata interpretations

would be more reliable if a relatively extreme minimum rainfall amount was chosen for this stage of analyses. As such, temperatures approximately 5 °C higher than the modelled Pliocene temperatures, were investigated; this allows for a higher evapotranspiration rate reducing the precipitation percolating into the cave system, thus giving insight into the precipitation amounts that would have almost certainly resulted in speleothem growth. Broome, northwest Australia, was selected as an appropriate analogue for the purposes of this study with 700 mm more annual rainfall than the Nullarbor region and temperatures approximately 6-9 °C higher.

Data regarding average annual actual evapotranspiration and average annual number of rain days per year for Broome were obtained (**Fig. 5.13** and **Fig. 5.14**), and these data used to calculate average rainfall amount per event that has the potential to reach a cave and result in speleothem growth:

$$\frac{(\text{rainfall amount} - \text{evapotranspiration})}{\text{number of rain days}}$$

$$\frac{(1000 - 500)}{40}$$

Evapotranspiration was selected over pan evaporation as it has been established that there is not a clear, well-understood relationship between potential evaporation (of which pan evaporation is an observed estimate) and actual evapotranspiration (Murphy and Timbal, 2008). As such, it is suggested that actual evapotranspiration is a more reliable estimate for determining what proportion of precipitation could plausibly reach a cave system. For the extreme minimum precipitation amount, a cut-off daily value of 12.5 mm was calculated; rainfall amounts below this were excluded for this subset of data. Due to the limited number of events with a rainfall amount greater than 12.5 mm, there were no individual site analyses for this stage of analysis. Instead, the most enriched and depleted 30% of this sample selection were identified for moisture source classification.

Due to the overarching aim of assisting palaeoprecipitation interpretations, it was not deemed necessary to calculate such a minimum value at a monthly resolution, because the speleothem palaeo data are highly unlikely to preserve individual recharge events due to mixing within the overlying aquifer. As such, this minimum value of 12.5 mm was calculated at an annual resolution.

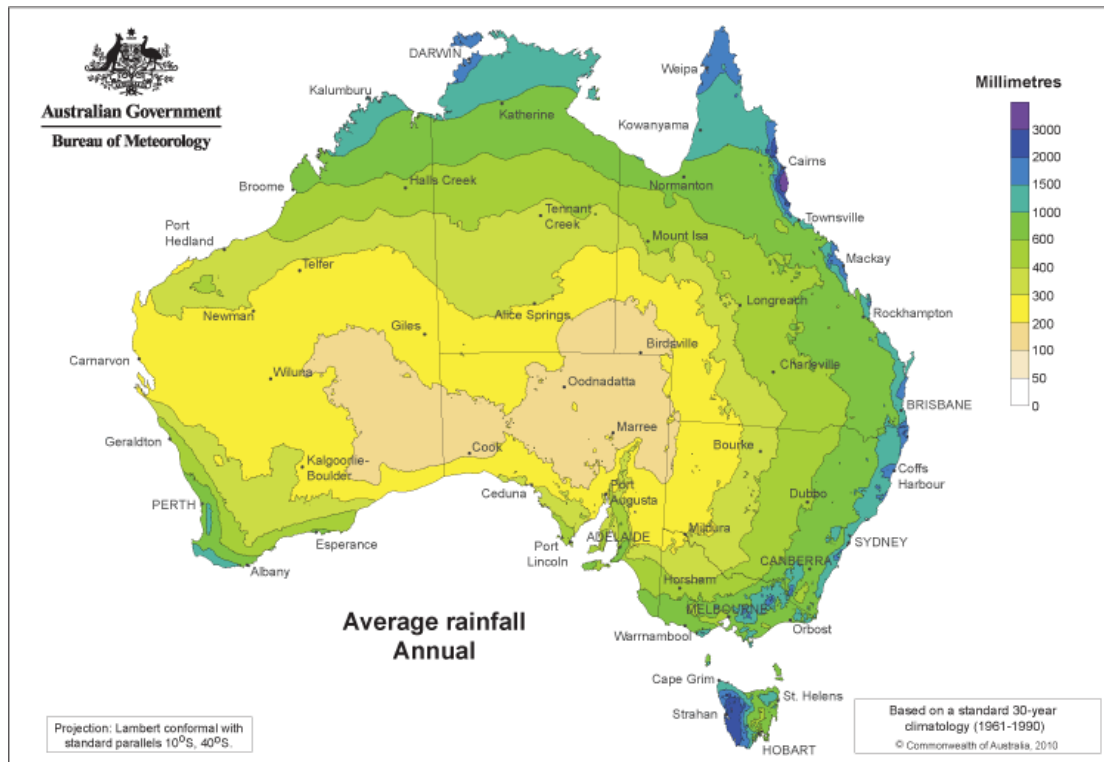


Fig. 5.11 – Average annual precipitation in Australia based on a 30-year measurement period between 1961 and 1990. Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

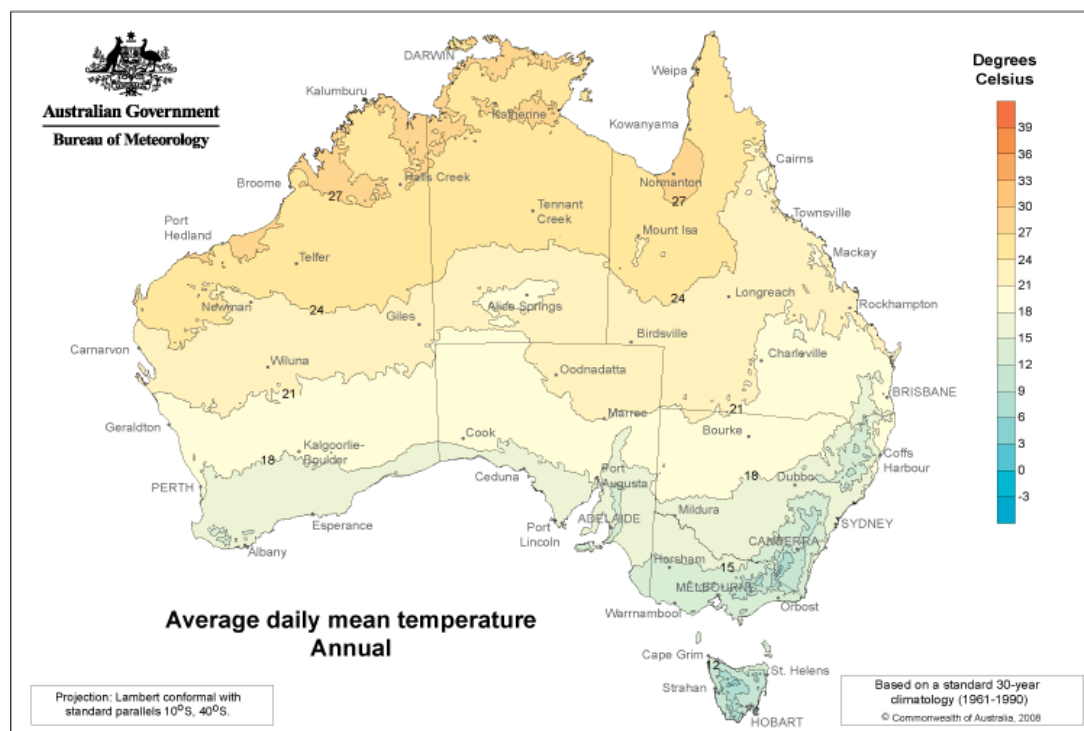


Fig. 5.12 – Average daily mean temperature in Australia as based on a 30-year climatology from 1961 to 1990. Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

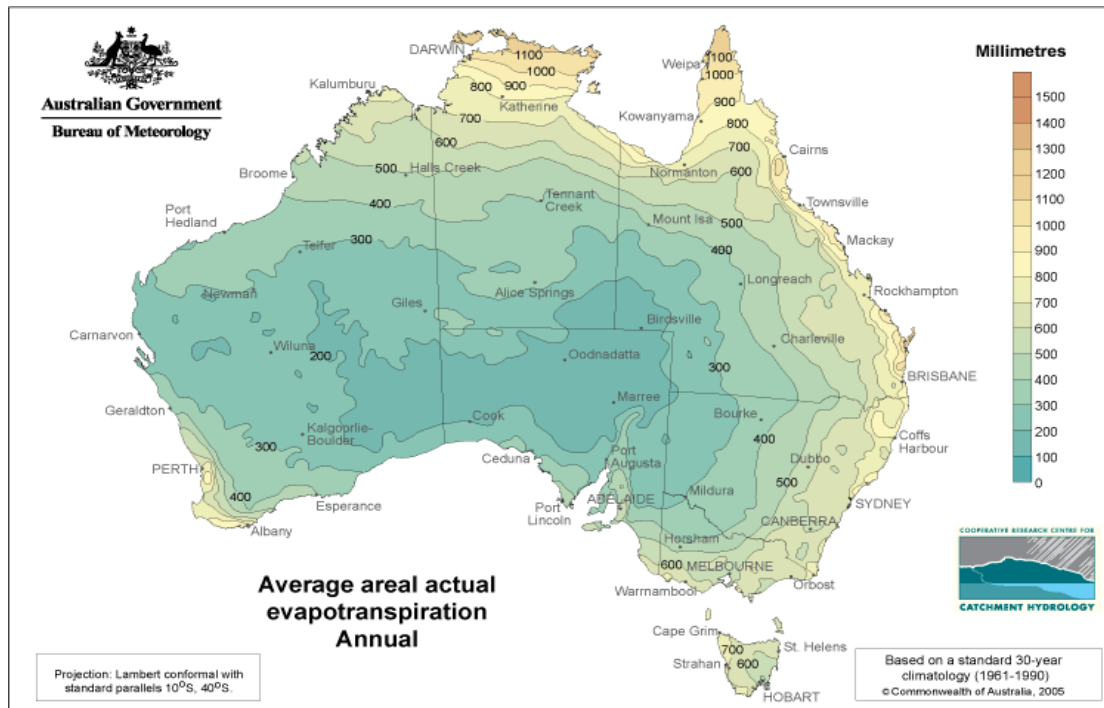


Fig. 5.13 – Average annual evapotranspiration in Australia as based on a 30-year climatology from 1961 to 1990. Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

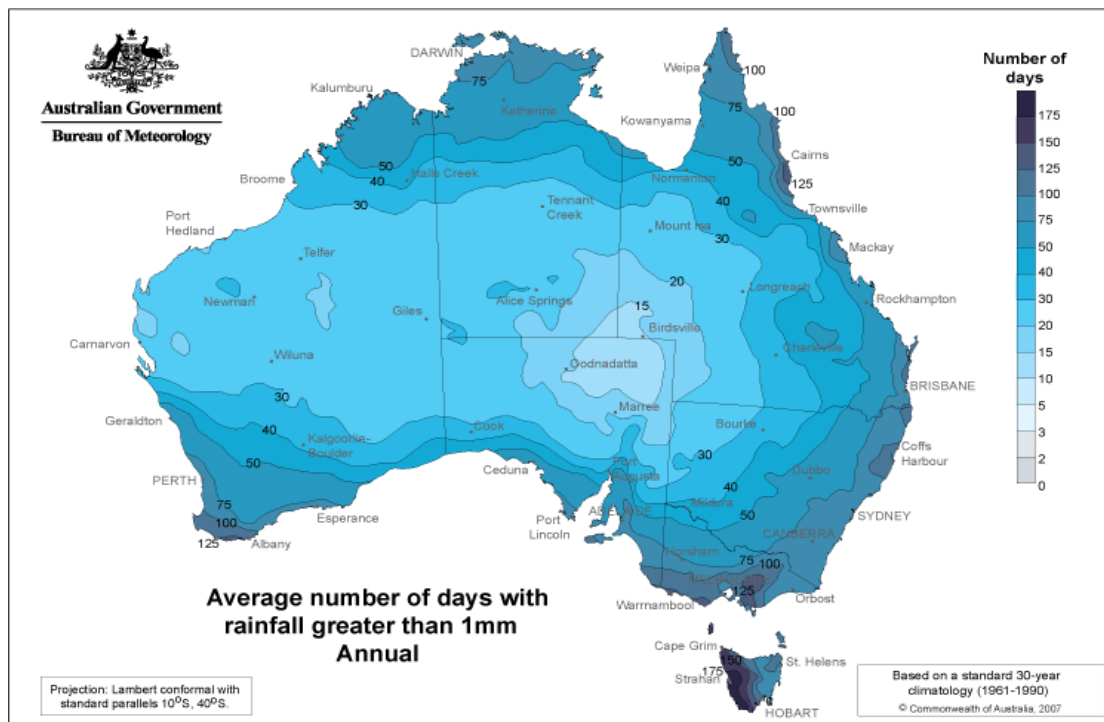


Fig. 5.14 – Average number of rain days per year in Australia as based on a 30-year dataset from 1961 to 1990. Source: Australian Bureau of Meteorology (www.bom.gov.au/climate/).

This method completely excludes all smaller rainfall amounts and therefore is not reflective of frequent low-amount precipitation events that may be represented in a speleothem. This is accepted as there would be severe vadose-zone mixing of the isotopic signal from these smaller events, therefore, without a significant understanding of the complex precipitation pathways into the cave and mixing dynamics it would not be possible to decipher the $\delta^{18}\text{O}$ signals of these events regardless.

5.3. Stable Isotope Results

A total of 568 rainfall events were collected and used for stable isotope analyses (**Appendix 2**); 33 from Arubiddy (ARU), 158 from Eucla (EUC), 175 from Eyre (EYR), 67 from Mundrabilla (MUN), 102 from Rawlinna Homestead (RAW), and 33 from Seemore Downs (SED). Similar ranges and amount-weighted averages of $\delta^{18}\text{O}$ and δD occur at each site (**Table 5.2**), with a total range across all sites of -10.72 ‰ to 13.38 ‰ for $\delta^{18}\text{O}$ and -70.53 ‰ to 67.00 ‰ for δD . The site that deviates most from the all site ranges is ARU; it is argued that this is an artefact of the fewer samples from this location, and the seasonal bias of the samples obtained. The values from all rainfall events at all sites have been used to calculate individual LMWLs for each site (**Fig. 5.15**); these have been combined to derive a regional meteoric water line for the Nullarbor Plain, which will be used for future analyses (**Fig. 5.16**). The equation for this line is:

$$\delta\text{D} = 5.6587(\delta^{18}\text{O}) + 4.70$$

compared to the global meteoric water line:

$$\delta\text{D} = 8(\delta^{18}\text{O}) + 10$$

the local meteoric water line for Perth as calculated by Hughes and Crawford, (2012):

$$\delta\text{D} = 7.33(\delta^{18}\text{O}) + 13$$

the local meteoric water line for Australia developed by Liu et al., (2010):

$$\delta\text{D} = 7.10(\delta^{18}\text{O}) + 8.21$$

and to allow comparisons with a comparatively arid region, the local meteoric water line for Eastern Tianshan, northwest China developed by Pang et al., (2017):

$$\delta D = 7.05(\delta^{18}O) + 0.60$$

These four meteoric water lines are presented in **Fig. 5.17**. Deviations from the GMWL are to be expected due to variations in atmospheric circulation patterns, processes of evaporation and regional water sources (Liu et al., 2009). Of these lines, the most closely related to the LMWL developed in this study is that of Pang et al. (2011), suggesting a possible consistency of this LMWL with other arid locations. With this in mind it was compared to other arid and semi-arid locations within Australia (Hughes and Crawford, 2012), (Gammons et al., 2006), and (Mayr et al., 2007). It was found that that the closest relation was to the LMWL for Perth of (Hughes and Crawford, 2012), suggesting a relatively consistent deviation from the GMWL of arid sites across Australia. This is to be expected as similar moisture sources and atmospheric circulation patterns would be driving the isotopic variation of precipitation in geographically close locations.

Table 5.2 – Minimum, maximum and amount-weighted mean values for each site and for all sites combined.

		All Sites	ARU	EUC	EYR	MUN	RAW	SED
$\delta^{18}O$ (VSMOW ‰)	Highest	10.61	-0.91	8.41	5.40	3.90	10.61	6.43
	Lowest	-10.72	-7.47	-10.25	-10.00	-9.66	-10.72	-9.83
	Average	-3.57	-2.95	-3.44	-3.29	-4.58	-3.69	-3.90
δD (VSMOW ‰)	Highest	67.00	12.80	47.48	38.13	23.80	67.00	50.56
	Lowest	-70.50	-40.77	-61.26	-66.89	-68.70	-70.50	-62.90
	Average	-16.35	-15.12	-14.40	-13.94	-21.48	-18.19	-20.75
d-excess	Highest	29.15	23.97	24.68	27.71	29.15	22.60	23.74
	Lowest	-39.19	-0.67	-39.19	-29.83	-5.31	-25.59	-35.55
	Average	10.30	8.51	13.10	9.42	10.90	8.16	10.48
Rainfall Amount	Highest	52.0	52.0	42.0	40.6	31.0	35.4	47.0
	Lowest	0.1	0.5	0.1	0.1	0.2	0.2	0.8
	Average	4.6	6.5	4.2	4.3	4.6	4.6	6.7

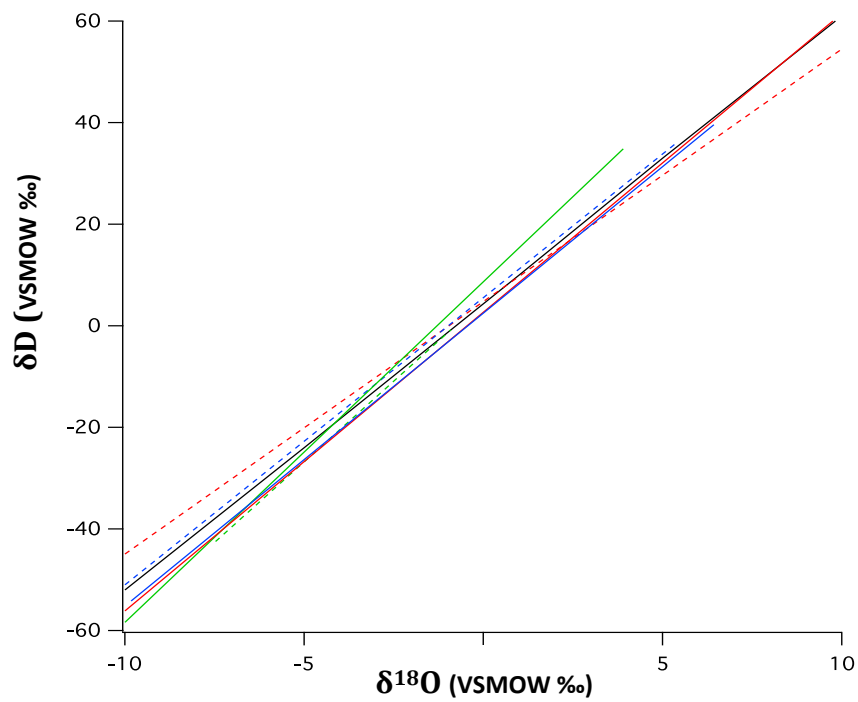


Fig. 5.15 - A comparison of the LMWLs developed for each site (see Appendix 2 for data used to derive LMWLs). Solid green line - MUN, solid blue line - SED, dashed blue line - EYR, solid red line - RAW, dashed red line - EUC, dashed green line - ARU, solid black line - combined site dataset.

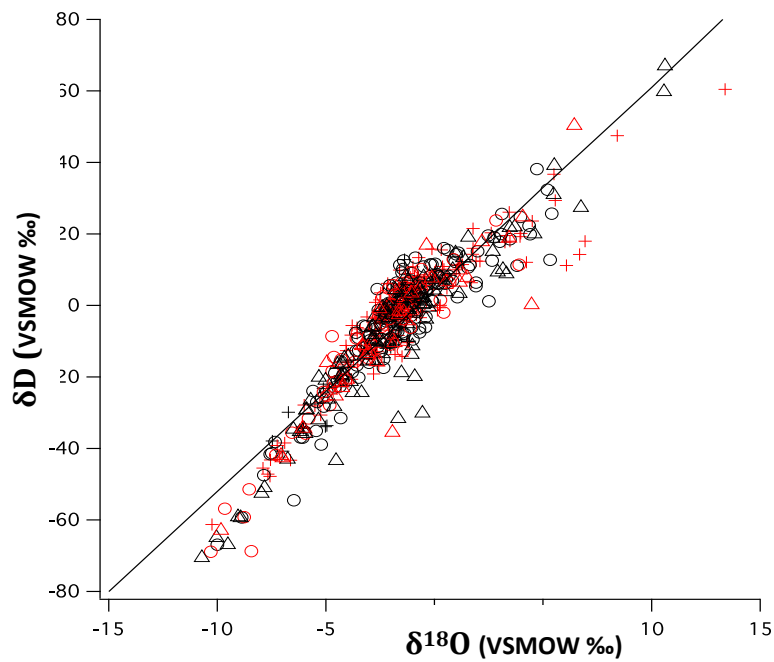


Fig. 5.16 - The LMWL from the combined site dataset. Markers display data from individual sites: black cross - ARU, red cross - EUC, black triangle - RAW, red triangle - SED, black circle - EYR, red circle - MUN.

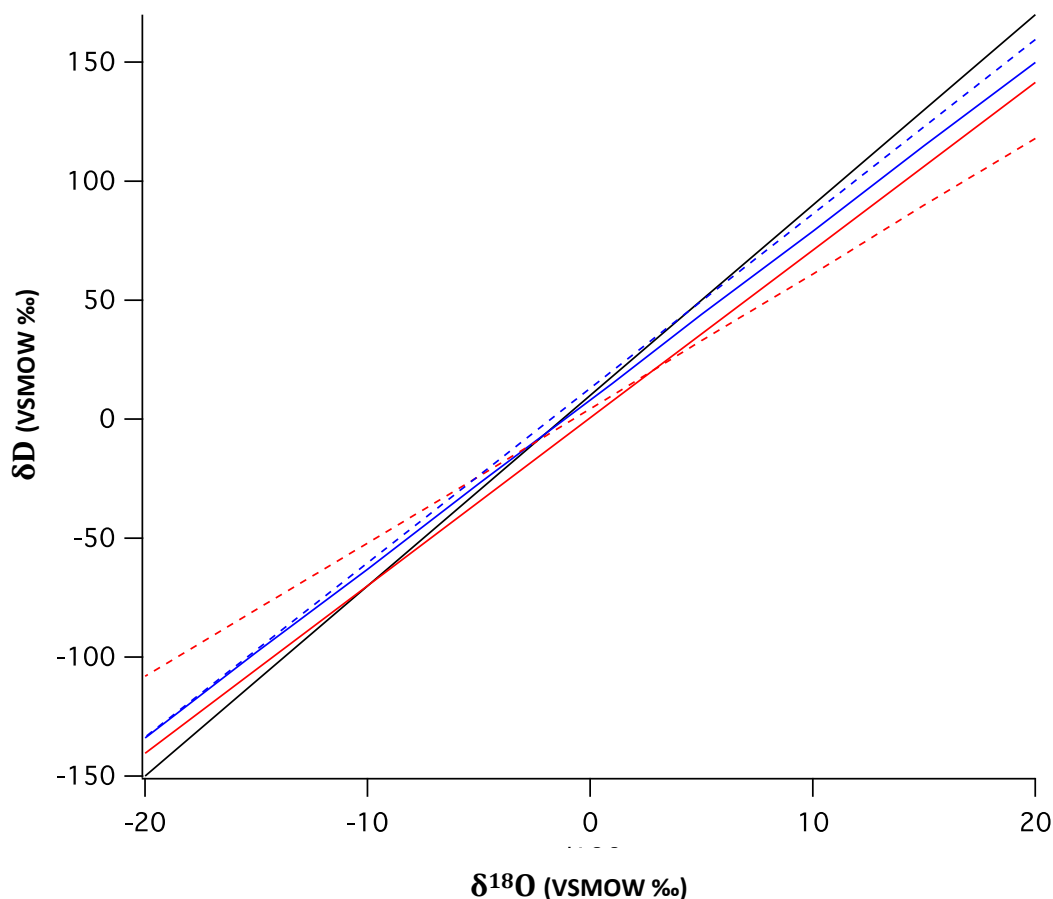


Fig. 5.17 – A comparison of four meteoric water lines: GMWL (solid black line), Nullarbor Plain LMWL derived from combined site precipitation dataset (dashed red line), Australia’s LMWL as defined by Lui et al., 2010 (solid blue line), the LMWL for Perth as defined by Hughes and Crawford, 2012 (dashed blue line), and the LMWL from eastern Tianshan as defined by Pang et al., 2017 (solid red line).

There are notable variations in average $\delta^{18}\text{O}$ and δD values across the seasons over the two-year period of collection (**Fig. 5.18**), evident in the complete datasets of all sites individually as well as overall amount-weighted averaged values (**Table 5.3**). There are also evident seasonal variations in rainfall amount, whereby the majority of precipitation occurs during the winter months (**Fig. 5.19**). This suggests there may be a seasonal signal in both rainfall amount and $\delta^{18}\text{O}$, similar to the seasonal relationship found in studies in Western Australia (Hope, 2006; Hope et al., 2006). However, further analyses are required to assist with further interpretations and disentangle the numerous potential influencing factors of variations in $\delta^{18}\text{O}$.

5.4. Investigation of Back Trajectory Reliability

To assess the reliability of the analyses, the back trajectories generated for each rainfall event in the additional site comparison analyses (to follow in

section 5.7) were compared. Similarities exist between the back trajectories for individual sites (Table 5.4). However, the level of variability evident suggests that back trajectories alone should not be relied upon for identifying moisture sources and pathways of a given rainfall event. This is evident as for some rainfall events there are variations between the different sites, with different moisture sources and pathways being identified (e.g. Fig. 5.20). The conclusion is further supported by the appearance of variability in rainfall amounts and isotopic compositions on rainfall days where the general moisture source and pathway were identified as the same at each site (e.g. Fig. 5.21). While further investigation into the causes of such variability and the consequences for future research are beyond the scope of this study, this preliminary analysis highlights the need for caution in using back-trajectory analyses alone in such studies. It also justifies the use of additional proxies for identifying moisture sources, as applied in this study.

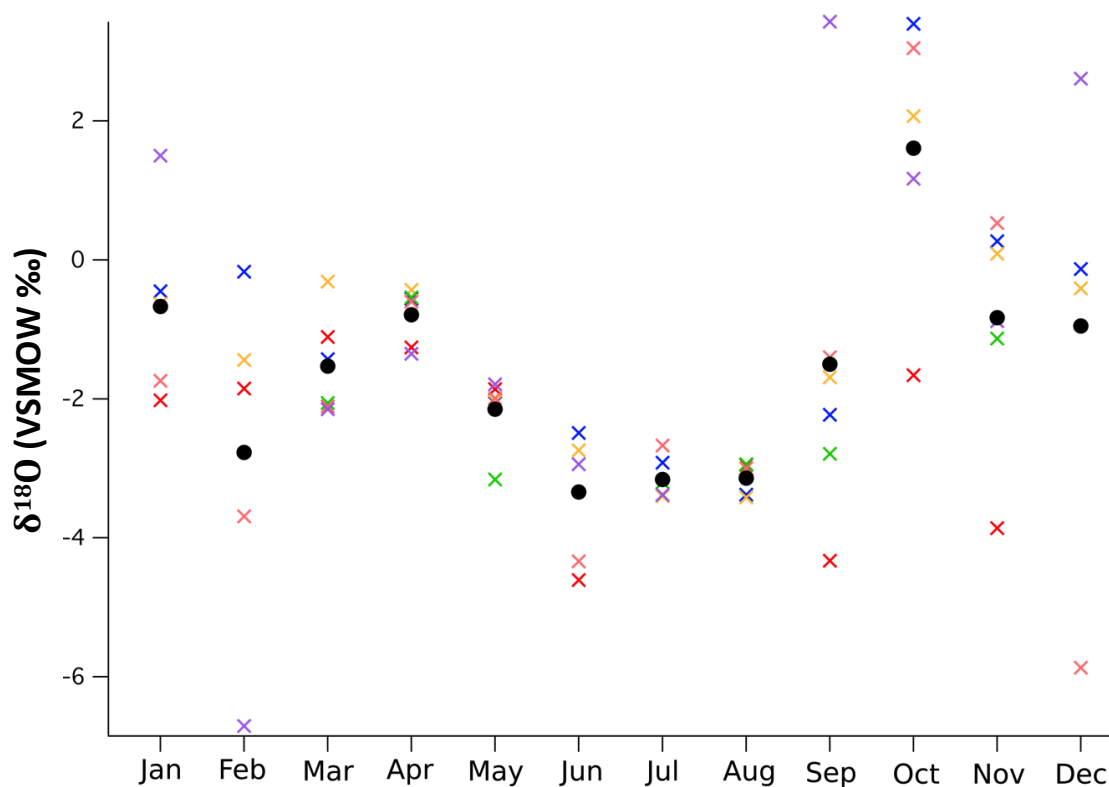


Fig. 5.18 – Monthly average $\delta^{18}\text{O}$ data for each individual site marked by crosses (ARU – red, EUC – blue, EYR – orange, MUN – green, RAW – pink, SED – purple), and for the combined dataset of all sites (black circles).

Table 5.3 – Monthly and seasonal (shaded grey) average values of rainfall amount, $\delta^{18}\text{O}$, δD , d-excess, and temperature for each individual rainfall collection site.

Site	Month / Season	No. of Samples	Average Rainfall Amount (mm)	Average $\delta^{18}\text{O}$ (VSMOW ‰)	Average δD (VSMOW ‰)	Average d-excess	Average Temp (°C)
ARU	January	1	2.0	-2.02	-11.81	4.35	19.3
ARU	February	4	6.7	-1.90	-10.20	4.60	26.7
ARU	March	1	3.0	-1.10	4.80	13.60	16.1
ARU	April	5	5.5	-1.30	1.60	11.70	19.4
ARU	May	2	2.8	-1.90	-10.30	4.50	18.6
ARU	June	2	2.5	-4.60	-26.40	10.50	13.4
ARU	July	8	4.9	-3.40	-13.30	13.90	14.2
ARU	August	4	17.1	-3.00	-17.60	6.00	15.5
ARU	September	3	4.7	-4.30	-22.30	12.30	14.8
ARU	October	1	4.0	-1.70	-7.10	6.30	18.3
ARU	November	3	8.7	-3.90	-24.50	6.40	20.0
ARU	December	0	-	-	-	-	-
ARU	Spring	7	6.3	-3.70	-21.10	8.90	17.5
ARU	Summer	5	5.5	-1.90	-10.60	4.60	24.8
ARU	Autumn	8	4.5	-1.40	-1.00	10.20	18.8
ARU	Winter	14	8.1	-3.40	-16.40	11.20	14.5
EUC	January	8	2.5	-0.40	1.80	5.30	20.5
EUC	February	9	6.8	-0.20	-0.90	0.50	24.4
EUC	March	17	3.2	-1.40	-0.50	11.00	19.5
EUC	April	12	4.4	-0.60	2.10	6.60	18.3
EUC	May	26	4.6	-2.10	-7.80	8.70	16.1
EUC	June	14	4.1	-2.50	-5.70	14.10	12.7
EUC	July	20	2.6	-2.90	-7.20	16.10	11.9
EUC	August	12	6.7	-3.40	-11.10	15.90	11.2
EUC	September	11	2.2	-2.20	-5.80	12.10	14.3
EUC	October	9	2.8	3.40	21.80	-5.30	21.3
EUC	November	11	6.8	0.30	5.30	3.10	19.3
EUC	December	9	3.9	-0.10	3.50	4.50	23.2
EUC	Spring	31	4.0	0.30	6.20	3.80	18.1
EUC	Summer	26	4.5	-0.20	1.40	3.40	22.8
EUC	Autumn	55	4.0	-1.60	-3.60	8.80	17.6
EUC	Winter	44	4.1	-2.90	-7.80	15.50	12.0
EYR	January	9	2.4	-0.60	2.50	7.60	20.1
EYR	February	6	12.3	-1.40	-8.90	2.70	27.2

EYR	March	17	3.1	-0.30	4.60	7.10	20.0
EYR	April	23	1.6	-0.40	2.40	5.90	19.7
EYR	May	26	3.8	-2.00	-8.00	8.40	15.8
EYR	June	17	4.2	-2.70	-6.50	15.50	12.9
EYR	July	19	5.1	-3.40	-10.80	16.40	12.8
EYR	August	16	4.6	-3.40	-15.00	12.40	13.2
EYR	September	12	5.2	-1.70	-2.50	11.10	15.4
EYR	October	9	1.5	2.10	14.60	-2.00	20.9
EYR	November	13	8.3	0.10	6.80	6.10	21.2
EYR	December	8	5.9	-0.40	1.40	4.70	23.9
EYR	Spring	34	5.4	0.00	5.60	5.70	19.1
EYR	Summer	23	6.2	-0.80	-0.80	5.30	23.3
EYR	Autumn	66	2.8	-1.00	-1.10	7.20	18.2
EYR	Winter	52	4.7	-3.20	-10.70	14.90	13.0
MUN	January	0	-	-	-	-	-
MUN	February	0	-	-	-	-	-
MUN	March	4	4.5	-2.10	-3.60	12.90	20.6
MUN	April	3	5.0	-0.50	-2.80	1.60	23.1
MUN	May	8	5.0	-3.20	-15.00	10.20	15.7
MUN	June	16	2.6	-2.90	-12.10	11.40	14.7
MUN	July	20	6.0	-3.20	-10.60	15.00	11.6
MUN	August	13	4.3	-2.90	-11.10	12.50	13.2
MUN	September	1	3.4	-2.80	-5.60	16.70	16.3
MUN	October	0	-	-	-	-	-
MUN	November	2	10.1	-1.10	4.80	13.80	17.7
MUN	December	0	-	-	-	-	-
MUN	Spring	3	7.9	-1.70	1.30	14.80	17.2
MUN	Summer	0	-	-	-	-	-
MUN	Autumn	15	4.9	-2.30	-9.50	9.20	18.5
MUN	Winter	49	4.4	-3.00	-11.20	13.20	13.0
RAW	January	7	2.8	-1.70	-7.20	6.70	24.0
RAW	February	6	9.4	-3.70	-18.30	11.20	24.7
RAW	March	13	6.6	-2.10	-8.40	8.50	20.6
RAW	April	8	4.3	-0.60	-4.00	0.90	21.5
RAW	May	8	3.0	-2.00	-16.50	-0.60	17.7
RAW	June	7	2.3	-4.30	-22.00	12.70	13.3
RAW	July	21	2.7	-2.70	-9.60	11.80	13.0
RAW	August	9	4.5	-3.00	-19.70	4.30	14.3
RAW	September	3	4.3	-1.40	-1.60	9.60	15.9
RAW	October	3	3.1	3.10	23.50	-0.90	22.3
RAW	November	15	6.9	0.50	6.90	2.70	22.2

RAW	December	2	10.9	-5.90	-37.40	9.60	24.2
RAW	Spring	21	6.0	0.60	8.00	3.10	21.3
RAW	Summer	15	6.5	-3.10	-15.70	8.90	24.3
RAW	Autumn	29	5.0	-1.70	-9.40	3.90	20.1
RAW	Winter	37	3.1	-3.10	-14.40	10.10	13.4
SED	January	1	6.0	1.50	7.80	-4.20	21.5
SED	February	3	9.4	-6.70	-39.60	14.10	28.2
SED	March	7	10.5	-2.10	-7.10	10.10	21.4
SED	April	5	5.5	-1.30	-9.50	1.30	21.1
SED	May	2	3.0	-1.80	-19.10	-4.70	15.5
SED	June	2	4.6	-2.90	-15.50	8.00	16.8
SED	July	4	4.6	-3.40	-14.10	12.90	13.2
SED	August	0	-	-	-	-	-
SED	September	1	3.0	3.40	18.80	-8.60	17.5
SED	October	1	6.0	1.20	9.90	0.60	20.0
SED	November	5	5.3	-0.90	4.40	11.40	19.1
SED	December	2	8.1	2.60	15.60	-5.30	27.4
SED	Spring	7	5.1	0.00	7.30	7.00	19.0
SED	Summer	6	8.4	-2.20	-13.30	4.60	26.8
SED	Autumn	14	7.6	-1.80	-9.70	4.80	20.5
SED	Winter	6	4.6	-3.20	-14.60	11.30	14.4

5.5. Exploratory Analyses

Pearson correlations were calculated using the complete dataset in order to identify any relationships between $\delta^{18}\text{O}$, δD , *d-excess*, rainfall amount, and temperature (**Table 5.5**). The critical value required for a significance level of 0.05 within the complete dataset is <0.25. The strongest correlations are between $\delta^{18}\text{O}$ and *d-excess* (**Fig. 5.22**), and δD and *d-excess* (**Fig. 5.23**), with *r* values of 0.92 and -0.70 respectively. These relationships are in agreement with similar modern precipitation studies (Treble et al., 2005b; Barras and Simmonds, 2008; Baldini et al., 2010; Callow et al., 2014), and are caused by the natural correlation of $\delta^{18}\text{O}$ and δD , and their inputs into the calculations of *d-excess*. Temperature and *d-excess* also have a fairly strong negative correlation (**Fig. 5.24**), with an *r* value of -0.50. Temperature and seasonal relationships with *d-excess* have previously been identified in Australia (Guan et al., 2013). However, these relationships have been argued to result from a seasonal difference in dominant moisture sources and synoptic conditions (Guan et al., 2013, therefore

this this will be investigated further alongside other analyses. Beyond this, it is also evident that rainfall amount has a significant negative correlation with $\delta^{18}\text{O}$ (**Fig. 5.25**) and δD (**Fig. 5.26**), with r values of -0.41 for both pairs, thus identifying this as another factor for further investigation. The correlation of -0.41 is comparable to the r value reported in (Treble et al., 2005b), and the correlations between $\delta^{18}\text{O}$ and rainfall amount in other areas of Australia (Barras and Simmonds, 2008; Liu et al., 2010) and globally (Johnson and Ingram, 2004; Baldini et al., 2010). This supports the suggestion that rainfall amount may be a significant influence on precipitation $\delta^{18}\text{O}$ in the Nullarbor region, and southern Australia more generally, and should be considered in further analyses within this study. Initially, the Eucla site was selected for further analyses based on the length of data collection and completeness of the dataset (i.e. the number of missed rainfall events). All rainfall events collected at the Eucla site were first stratified by season, and then by rainfall amount, with the highest and lowest six rainfall amounts being selected for each season. Moisture sources were then assigned for each of these events (**Table 5.6**).

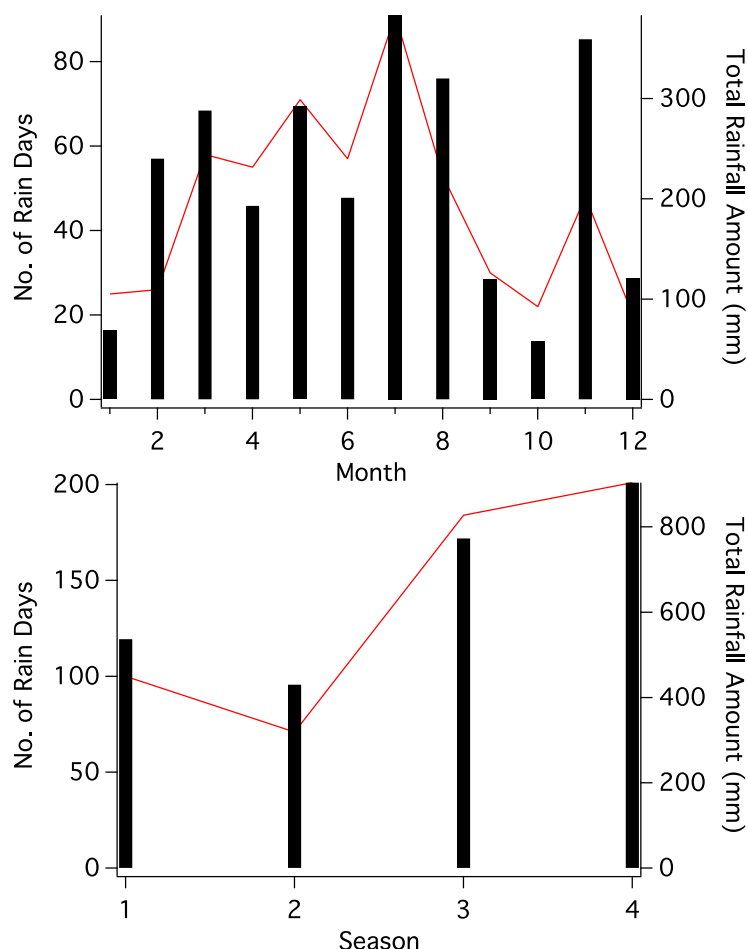


Fig. 5.19 – Monthly (top) and seasonal (bottom) total rainfall amounts and number of rain days for the combined site database. Seasons are represented as 1- spring, 2- summer, 3- autumn, 4- winter.

Table 5.4 – Rainfall events and sites used for the analyses of back-trajectory reliability, and the direction from which the analyses show the moisture source to originate from at both 1000m asl, and 3000m asl.

Site	Date of Event	Trajectory 1000 m asl	Trajectory 3000 m asl
ARU	23/07 /2014	NW	NW
RAW		NW	NW
EYR		NW	NW
SED		NW	NW
MUN		NW	NW
EUC	23/09 /2014	NE	NW
MUN		NE	W
RAW		W	SW
EYR		SW	SW
EUC	14/11 /2014	SW	S
RAW		SW	SW
SED		SW	SW
MUN		S	SW
EYR		SW	SW
SED	15/11 /2014	SW	SW
EYR		W	SW
RAW		SW	SW
EUC		SW	SW
EUC	27/02 /2015	NW	E
ARU		NW	N
EYR		NW	NE
RAW		N	N
SED		N	N
EYR	02/03 /2015	W	W
EUC		N	SW
RAW		N	S
SED		N	S

Site	Date of Event	Trajectory 1000 m asl	Trajectory 3000 m asl
ARU	16/04 /2015	NW	SW
EYR		NW	SW
EUC		NW	SW
RAW		NW	SW
SED		NW	SW
EUC	01/08 /2015	N	NW
MUN		NW	SW
RAW		NW	SW
EYR		NW	SW
ARU		NW	SW
MUN	23/08 /2015	W	SW
RAW		W	SW
EYR		SW	SW
EUC		SW	SW
RAW	03/11 /2015	NW	S
EUC		W	S
ARU		W	S
EYR		NW	NW

This strategy was selected as a way to ensure insight into seasonal variations in $\delta^{18}\text{O}$, and to allow the identification of any correlations with $\delta^{18}\text{O}$ and extreme rainfall amounts (**Table. 5.7**). From these analyses there is an apparent relationship between moisture source and $\delta^{18}\text{O}$, where moisture sourced from Southern Ocean and (NCB) / Southern Ocean interactions yield more depleted $\delta^{18}\text{O}$ values in comparison to the more enriched values evident in precipitation sourced from the tropics and from Tasman influenced moisture sources. This relationship is deemed to be statistically significant, indicating that source is a key influence on the $\delta^{18}\text{O}$ signature of rainfall in the region. Source has commonly been found to be a significant influence on $\delta^{18}\text{O}$ (Barras and Simmonds, 2008; Breitenbach et al., 2010; Callow et al., 2014), and as such is identified as a key factor for further investigation.

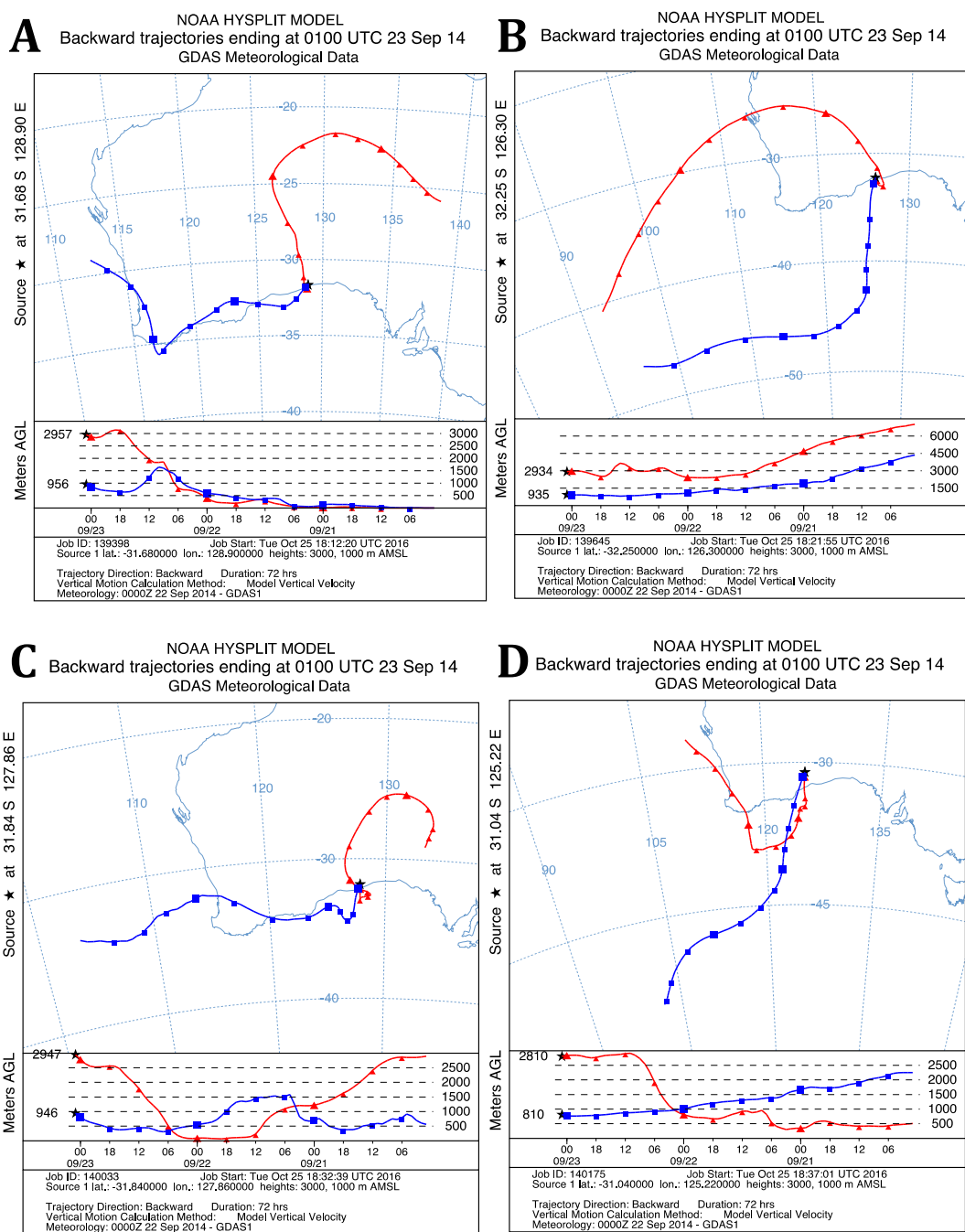


Fig. 5.20 – An example of a single rainfall event (occurring on 23rd September 2014) in which the back-trajectory analyses identify variable moisture sources and pathways at different sites (A- EUC, B- EYR, C- MUN, D- RAW). Generated from National Oceanic and Atmospheric Administration (www.ready.noaa.gov/HYSPLIT).

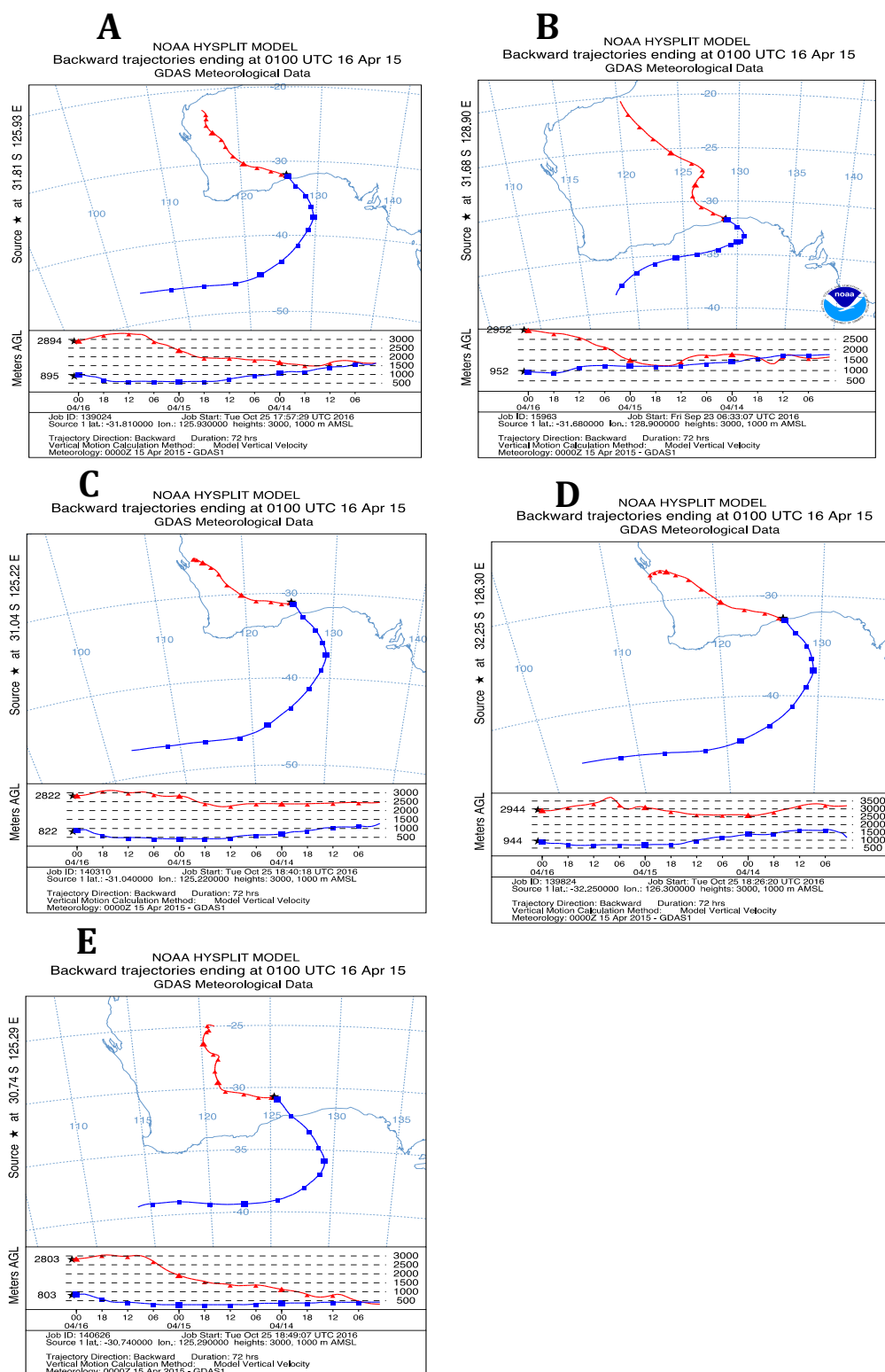


Fig. 5.21 – An example of an individual event (16TH April 2015) in which the back-trajectory analyses identifies a singular moisture source and pathway across multiple sites (A – ARU, B- EUC, C- RAW, D-EYR, E-SED), but where there is significant variation in rainfall amount and/or isotopic composition across the different sites. Generated from National Oceanic and Atmospheric Administration (www.ready.noaa.gov/HYSPLIT).

Table 5.5 – Pearson correlation r -values from the complete dataset.

	$\delta^{18}\text{O}$	δD	d -excess	rain amount
δD	0.92	X	X	X
d -excess	-0.70	-0.37	X	X
rainfall amount	-0.41	-0.41	0.23	X
temperature	0.37	0.21	-0.50	0.05

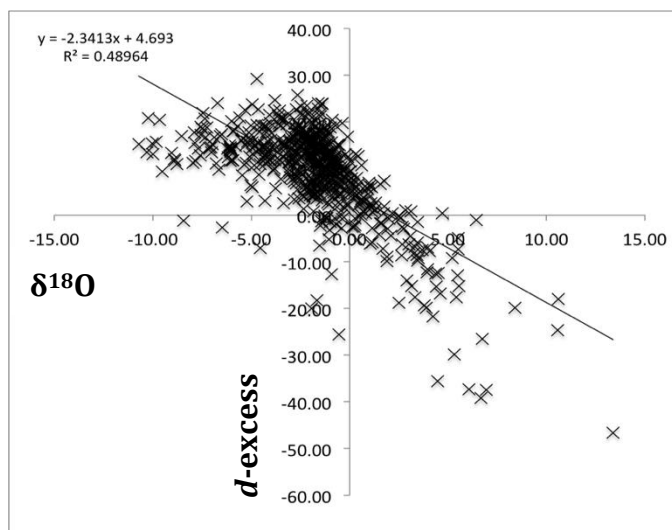


Fig. 5.22 – A bivariate plot of $\delta^{18}\text{O}$ vs. d -excess.

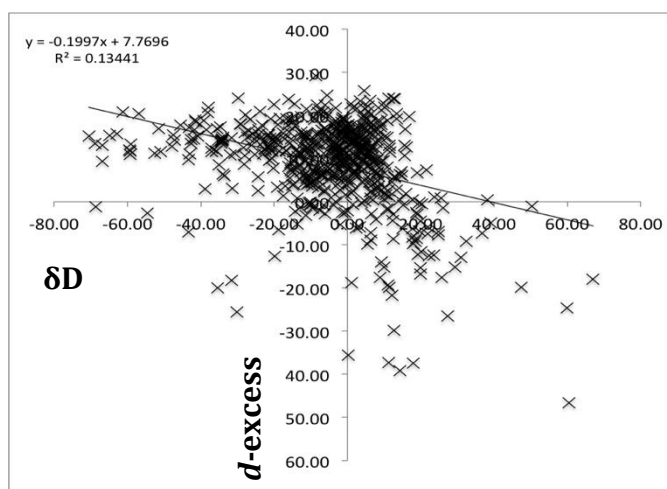


Fig. 5.23 – A bivariate plot of δD vs. d -excess.

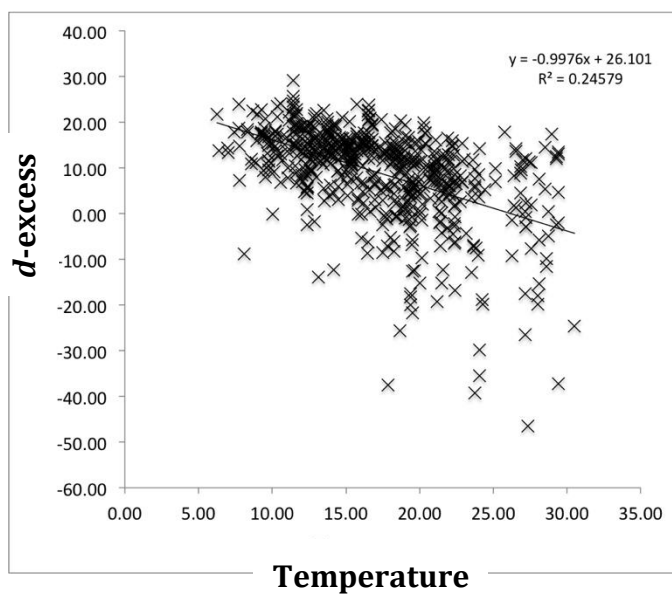


Fig. 5.24 – A bivariate plot of d -excess vs. temperature.

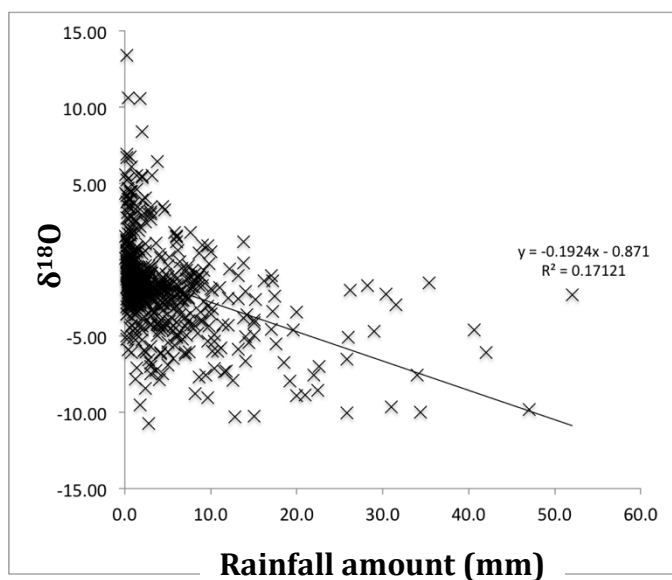


Fig. 5.25 – A bivariate plot of $\delta^{18}\text{O}$ vs. rainfall amount.

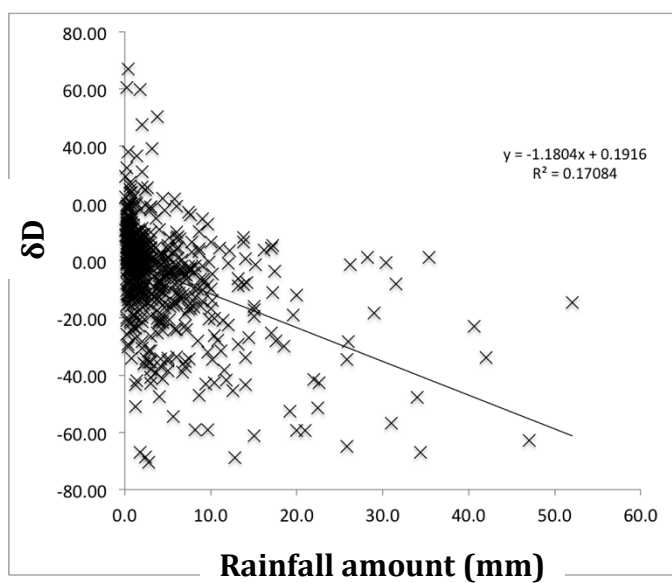


Fig. 5.26 – A bivariate plot of δD vs. rainfall amount.

The correlations between source and season, and source and rainfall amount are not statistically significant; however, the relationship between source and season is very close to being statistically significant with a p -value of 0.0556. Other studies of modern precipitation have identified significant seasonal signals in dominant moisture sources, as well as synoptic conditions, for example (Guan et al., 2013); however several studies either do not investigate, or do not state the significance of relationships, between moisture source and other parameters or isotopic signatures (Darling and Talbot, 2003; Johnson and Ingram, 2004; Baldini et al., 2010), making direct comparisons of the relationships difficult.

As a second strategy, all samples were also stratified by $\delta^{18}\text{O}$ and the most depleted and enriched 10% of rainfall events assigned moisture source classifications (**Table 5.8**). The aim was to identify the strongest relationships with extreme $\delta^{18}\text{O}$ values and the various influencing factors (**Table 5.9**). This is of particular importance in the context of the overarching aim of modern precipitation analyses within this study as it is the drivers of significant $\delta^{18}\text{O}$ variation that are of highest importance. From these analyses the relationships between source and $\delta^{18}\text{O}$, rainfall amount and season are all statistically significant; this supports previous claims that $\delta^{18}\text{O}$ is strongly influenced by moisture source and suggesting further relationships between source and rainfall amount and season that have not previously been identified. These results indicate that further investigation by this method with a larger dataset is worthwhile.

When using modern precipitation studies to interpret $\delta^{18}\text{O}$ values of the distant past that do not sit within a well-dated archive, it is not feasible to interpret high-resolution variations such as seasonal or sub-annual signals; therefore the analyses of modern precipitation that are of highest value are those that identify the key drivers of extreme $\delta^{18}\text{O}$ values. As such, a broader understanding of modern seasonal signals is sufficient and the focus should be placed on a more thorough understanding of the relationships between the most enriched and depleted $\delta^{18}\text{O}$ values and their correlations with known influences on the $\delta^{18}\text{O}$ of precipitation. In consideration of this, it was decided that the remainder of the sites should be stratified by $\delta^{18}\text{O}$ class for further analysis.

Table 5.6 – Results from the analyses of the rainfall amount stratified EUC dataset
Seasons are represented as 1- spring, 2- summer, 3- autumn, 4-winter. Sources are
represented as 1- Southern Ocean, 2- northern cloud band – Southern Ocean
interactions, 3- tropical, 4-Tasman influenced.

Date of Event	Season	Source	Rainfall Amount (mm)	$\delta^{18}\text{O}$ (VSMOW ‰)	δD (VSMOW ‰)	<i>d</i> -excess	Average Daily Temp (°C)
2/05/2014	3	1	13.8	-3.84	-8.30	22.40	16.5
5/05/2014	3	2	0.2	-1.78	-3.60	10.65	15.4
9/05/2014	3	2	14.0	-6.63	-43.27	9.78	15.4
22/05/2014	3	3	15.0	-3.97	-17.18	14.59	15.1
16/06/2014	4	2	17.6	-5.51	-28.08	15.99	9.0
25/06/2014	4	2	0.4	-1.48	5.97	17.83	7.4
28/06/2014	4	2	8.8	-3.42	-6.58	20.77	12.9
30/06/2014	4	2	0.2	-0.77	4.79	10.92	8.6
13/07/2014	4	3	0.4	-0.92	8.29	15.66	9.8
21/07/2014	4	2	0.2	0.23	-0.65	-2.46	12.4
24/07/2014	4	1	15.0	-10.25	-61.26	20.74	13.7
5/09/2014	1	2	0.4	-3.21	-12.49	13.19	9.7
24/09/2014	1	1	6.0	-2.20	-1.39	16.21	15.0
13/10/2014	1	1	0.2	1.28	11.46	1.23	17.0
20/10/2014	1	3	0.1	5.56	29.37	-15.15	20.0
21/10/2014	1	4	8.6	0.43	10.14	6.69	16.3
31/10/2014	1	3	6.6	-0.58	-2.00	2.63	22.8
15/11/2014	1	1	30.4	-2.27	-0.59	17.59	15.8
29/11/2014	1	3	8.6	-1.02	3.35	11.50	22.9
2/12/2014	2	3	7.6	1.77	16.00	1.87	27.6
14/12/2014	2	3	0.4	1.69	6.34	-7.15	21.4
8/01/2015	2	3	0.6	2.09	12.37	-4.35	23.2
13/01/2015	2	1	9.8	-4.34	-20.40	14.35	16.5
12/04/2015	3	3	0.2	6.68	14.29	-39.19	23.8
16/04/2015	3	2	12.0	-4.30	-22.40	11.97	19.7
17/04/2015	3	1	20.0	-3.43	-11.98	15.46	16.6
29/05/2015	3	2	0.2	-2.57	-1.45	19.12	12.0
31/05/2015	3	2	0.2	-3.57	-6.18	22.39	8.7
20/06/2015	4	3	0.2	-1.27	-10.39	-0.20	16.1
22/06/2015	4	2	8.8	-4.00	-15.84	16.16	15.4
1/08/2015	4	2	9.4	-7.55	-43.22	17.19	13.9
4/08/2015	4	1	0.2	-3.56	-7.86	20.65	9.6
23/08/2015	4	2	42.0	-6.10	-33.88	14.96	9.8
3/11/2015	1	1	13.2	-2.57	-8.82	11.75	18.4

5/11/2015	1	4	0.4	-0.99	1.40	9.33	12.7
18/11/2015	1	3	0.2	13.38	60.50	-46.58	27.4
26/11/2015	1	2	0.4	-0.38	6.70	9.78	18.8
23/12/2015	2	4	8.0	-1.30	-4.16	6.21	21.4
24/12/2015	2	3	7.6	-3.54	-16.58	11.70	23.6
11/01/2016	2	3	0.4	3.47	18.00	-9.75	20.2
22/01/2016	2	3	0.2	-0.21	8.03	9.69	23.8
2/02/2016	2	2	34.0	-7.58	-47.81	12.86	18.5
4/02/2016	2	2	0.6	-1.77	-2.65	11.51	21.3
21/02/2016	2	3	0.6	1.00	9.96	1.93	22.4
24/02/2016	2	3	17.2	-3.37	-11.06	15.89	22.2
15/03/2016	3	4	0.2	1.11	10.51	1.62	22.4
8/05/2016	3	2	12.6	-7.90	-45.50	17.71	18.1
16/05/2016	3	2	0.2	6.93	18.00	-37.46	17.9

Table 5.7 – Contingency tables of expected and actual values, and p-values for the Chi-square analysis of the rainfall amount stratified EUC dataset. Seasons are represented as 1- spring, 2- summer, 3- autumn, 4-winter. Sources are represented as 1- Southern Ocean, 2- northern cloud band – southern Ocean interactions, 3- tropical, 4-Tasman influenced.

Expected

Source/ $\delta^{18}\text{O}$	1	2	3	4	Actual Total
Enriched	3.75	7.92	6.67	1.67	20
Intermediate	1.31	2.77	2.33	0.58	7
Depleted	3.94	8.31	7.00	1.75	21
Actual Total	9	19	16	4	48

Source/Rain Amt	1	2	3	4	Actual Total
High	4.50	9.50	8.00	2.00	24
Low	4.50	9.50	8.00	2.00	24
Actual Total	9	19	16	4	48

Source/Season	1	2	3	4	Actual Total
1	2.25	4.75	4.00	1.00	12
2	2.25	4.75	4.00	1.00	12
3	2.25	4.75	4.00	1.00	12
4	2.25	4.75	4.00	1.00	12
Actual Total	9	19	16	4	48

Actual

Source/ $\delta^{18}\text{O}$	1	2	3	4
Enriched	1	4	12	3
Intermediate	2	3	1	1
Depleted	6	12	3	0
p value = 7.68E-03				

Source/Rain Amt	1	2	3	4
High	7	9	6	2
Low	2	10	10	2
p value = 2.80E-01				

Source/Season	1	2	3	4
1	4	2	4	2
2	1	2	8	1
3	2	7	2	1
4	2	8	2	0
p value = 5.56E-02				

Table 5.8 – Results from analyses of the $\delta^{18}\text{O}$ stratified EUC dataset. Seasons are represented as 1- spring, 2- summer, 3- autumn, 4-winter. Sources are represented as 1- Southern Ocean, 2- northern cloud band – southern Ocean interactions, 3- tropical, 4- Tasman influenced.

Date of Event	Season	Source	Rainfall Amount (mm)	$\delta^{18}\text{O}$ (VSMOW ‰)	δD (VSMOW ‰)	d -excess	Average Daily Temp (°C)
2/09/2015	1	1	3.6	-7.25	-39.10	18.84	12.9
2/08/2015	4	1	5.0	-6.90	-38.45	16.72	13.0
13/01/2015	2	1	9.8	-4.34	-20.40	14.35	16.5
24/07/2014	4	1	15.0	-10.25	-61.26	20.74	13.7
22/05/2016	3	2	0.2	4.23	12.10	-21.71	19.5
16/05/2016	3	2	0.2	6.93	18.00	-37.46	17.9
29/05/2016	3	2	0.6	4.50	23.60	-12.36	14.2
15/07/2014	4	2	0.8	-6.08	-34.11	14.52	14.0
10/07/2015	4	2	1.2	-5.28	-27.22	14.98	11.4
30/05/2014	3	2	2.0	-5.24	-30.65	11.27	15.3
23/06/2015	4	2	8.6	-7.68	-47.16	14.29	14.5
1/08/2015	4	2	9.4	-7.55	-43.22	17.19	13.9
9/05/2016	3	2	10.4	-7.13	-42.60	14.45	16.0
31/05/2014	3	2	10.8	-6.00	-27.82	20.19	15.3

8/05/2016	3	2	12.6	-7.90	-45.50	17.71	18.1
9/05/2014	3	2	14.0	-6.63	-43.27	9.78	15.4
16/06/2014	4	2	17.6	-5.51	-28.08	15.99	9.0
2/02/2016	2	2	34.0	-7.58	-47.80	12.86	18.5
23/08/2015	4	2	42.0	-6.10	-33.88	14.96	9.8
20/10/2014	1	3	0.1	5.56	29.37	-15.15	20.0
12/04/2015	3	3	0.2	6.68	14.29	-39.19	23.8
18/11/2015	1	3	0.2	13.38	60.50	-46.58	27.4
11/01/2016	2	3	0.4	3.47	18.00	-9.75	20.2
1/04/2015	3	3	0.4	3.94	19.24	-12.29	21.6
18/10/2014	1	3	0.6	3.44	26.09	-1.43	26.3
23/02/2016	2	3	0.6	3.97	20.20	-11.55	28.6
27/02/2015	2	3	0.8	6.07	11.22	-37.30	29.4
22/12/2015	2	3	1.2	2.61	20.30	-0.54	18.4
27/10/2015	1	3	1.2	3.30	19.59	-6.81	19.5
15/10/2015	1	3	1.4	5.50	36.70	-7.30	23.7
19/10/2015	1	3	2.0	8.41	47.48	-19.80	28.0
29/10/2015	1	3	4.6	3.24	17.70	-8.22	18.3

Table 5.9 – Contingency tables of expected and actual values, and p-values for the Chi-square analysis of the rainfall amount stratified EUC dataset. Seasons are represented as 1- spring, 2- summer, 3- autumn, 4-winter. Sources are represented as 1- Southern Ocean, 2- northern cloud band – southern Ocean interactions, 3- tropical, 4-Tasman influenced.

Expected

Source/ $\delta^{18}\text{O}$	1	2	3	4	Actual Total
Enriched	2.00	7.50	6.50	-	16
Depleted	2.00	7.50	6.50	-	16
Actual Total	4	15	13	0	32

Source/Rain Amt	1	2	3	4	Actual Total
High	1.63	6.09	5.28	-	13
Moderate	0.50	1.88	1.63	-	4
Low	1.88	7.03	6.09	-	15
Actual Total	4	15	13	0	32

Source/Season	1	2	3	4	Actual Total
1	1.00	3.75	3.25	-	8
2	0.63	2.34	2.03	-	5
3	1.38	5.16	4.47	-	11
4	1.00	3.75	3.25	-	8
Actual Total	4	15	13	0	32

Actual

Source/ $\delta^{18}\text{O}$	1	2	3	4
Enriched	0	3	13	0
Depleted	4	12	0	0
<i>p</i> value = 1.37E-05				

Source/Rain Amt	1	2	3	4
High	3	9	1	0
Moderate	1	1	2	0
Low	0	5	10	0
<i>p</i> value = 1.75E-02				

Source/Season	1	2	3	4
1	1	0	7	0
2	0	1	4	0
3	1	8	2	0
4	2	6	0	0
<i>p</i> value = 2.75E-03				

5.6. $\delta^{18}\text{O}$ Ranked Analyses

As determined by the exploratory analyses, further investigation was conducted only on the most extreme depleted and enriched $\delta^{18}\text{O}$ rainfall samples. These were identified in respect to the individual sites in order to allow site comparisons, and then combined to calculate correlations from the complete extreme $\delta^{18}\text{O}$ ranked dataset of 124 samples (**Table 5.10**). **Table 5.11** presents a summary of key information from the individual sites, as well as an overall site average. The justification for selecting a smaller sample size for these analyses is twofold. In the first instance, for the overarching purpose of assisting with palaeoprecipitation interpretation, it is the extreme $\delta^{18}\text{O}$ values that are of highest interest as it is these events that will be causing significant long-term variations in the palaeoclimate record.

Table 5.10 – Results from the analyses of the $\delta^{18}\text{O}$ stratified dataset from all sites. Seasons are represented as 1- spring, 2- summer, 3- autumn, 4- winter. Sources are represented as 1- Southern Ocean, 2- northern cloud band – southern Ocean interactions, 3- tropical, 4-Tasman influenced.

Picarro Code	Date of Event	Season	Source	Rain Amt (mm)	$\delta^{18}\text{O}$ (VSMO W ‰)	δD (VSMO W ‰)	d excess	Av. Daily Temp (°C)
ARU12	31/3/15	3	3	3	-1.11	4.75	13.61	16.1
ARU13	1/4/15	3	3	1	-1.01	4.27	12.33	21.6
ARU15	15/4/15	3	2	17	-1.05	4.44	12.85	15
ARU2	14/7/14	4	4	3	-7.47	-37.9	21.83	13
ARU21	23/6/15	4	2	3	-6.99	-40.77	15.16	14.5
ARU23	21/7/15	4	2	8.5	-1.16	-9.98	-0.67	17.7
ARU26	6/8/15	4	1	5	-6.05	-34.1	14.31	7
ARU27	18/8/15	4	3	9	-1.19	-10.16	-0.63	18.5
ARU28	1/9/15	1	1	7.5	-6.04	-34.28	14.02	12.4
ARU29	2/9/15	1	1	2.5	-6.04	-34.37	13.98	12.9
ARU3	22/7/14	4	2	18.5	-6.73	-29.85	23.97	7.8
ARU7	8/9/14	1	2	4	-0.91	1.71	8.98	19.2
EUC101	23/8/15	4	2	42	-6.1	-33.88	14.96	9.8
EUC107	2/9/15	1	1	3.6	-7.25	-39.1	18.84	12.9
EUC114	15/10/15	1	3	1.4	5.5	36.7	-7.3	23.7
EUC115	19/10/15	1	3	2	8.41	47.48	-19.8	28
EUC117	27/10/15	1	3	1.2	3.3	19.59	-6.81	19.5
EUC118	29/10/15	1	3	4.6	3.24	17.7	-8.22	18.3
EUC124	18/11/15	1	3	0.2	13.38	60.5	-46.58	27.4

EUC128	22/12/15	2	3	1.2	2.61	20.3	-0.54	18.4
EUC13	30/5/14	3	2	2	-5.24	-30.65	11.27	15.3
EUC132	11/1/16	2	3	0.4	3.47	18	-9.75	20.2
EUC136	2/2/16	2	2	34	-7.58	-47.8	12.86	18.5
EUC14	31/5/14	3	2	10.8	-6	-27.82	20.19	15.3
EUC140	23/2/16	2	3	0.6	3.97	20.2	-11.55	28.6
EUC15	16/6/14	4	2	17.6	-5.51	-28.08	15.99	9
EUC157	8/5/16	3	2	12.6	-7.9	-45.5	17.71	18.1
EUC158	9/5/16	3	2	10.4	-7.13	-42.6	14.45	16
EUC160	16/5/16	3	2	0.2	6.93	18	-37.46	17.9
EUC161	22/5/16	3	2	0.2	4.23	12.1	-21.71	19.5
EUC164	29/5/16	3	2	0.6	4.5	23.6	-12.36	14.2
EUC25	15/7/14	4	2	0.8	-6.08	-34.11	14.52	14
EUC27	24/7/14	4	1	15	-10.25	-61.26	20.74	13.7
EUC37	18/10/14	1	3	0.6	3.44	26.09	-1.43	26.3
EUC38	20/10/14	1	3	0.1	5.56	29.37	-15.15	20
EUC54	13/1/15	2	1	9.8	-4.34	-20.4	14.35	16.5
EUC55	27/2/15	2	3	0.8	6.07	11.22	-37.3	29.4
EUC6	9/5/14	3	2	14	-6.63	-43.27	9.78	15.4
EUC64	1/4/15	3	3	0.4	3.94	19.24	-12.29	21.6
EUC67	12/4/15	3	3	0.2	6.68	14.29	-39.19	23.8
EUC83	23/6/15	4	2	8.6	-7.68	-47.16	14.29	14.5

EUC85	10/7/15	4	2	1.2	-5.28	-27.22	14.98	11.4
EUC97	1/8/15	4	2	9.4	-7.55	-43.22	17.19	13.9
EUC98	2/8/15	4	1	5	-6.9	-38.45	16.72	13
EYR104	16/6/15	4	2	4.4	-4.62	-21.45	15.53	16.1
EYR106	22/6/15	4	2	4.2	-6.17	-36.94	12.46	15.4
EYR108	8/7/15	4	2	22	-7.57	-41.58	18.99	11.9
EYR114	21/7/15	4	2	4	-7.86	-47.45	15.44	17.7
EYR116	31/7/15	4	2	6.7	-5.22	-38.89	2.89	15.9
EYR117	1/8/15	4	2	34.4	-10	-66.89	13.11	13.9
EYR127	23/8/15	4	2	7	-6.07	-36.98	11.56	9.8
EYR13	30/5/14	3	2	14.4	-5.42	-26.98	16.37	15.3
EYR135	15/10/15	1	3	0.6	3.95	24.74	-6.89	23.7
EYR136	18/10/15	1	3	2.6	3.1	25.61	0.81	19
EYR137	27/10/15	1	3	0.5	1.98	15.14	-0.73	19.5
EYR142	7/11/15	1	3	0.7	4.4	19.9	-15.3	28.1
EYR148	25/11/15	1	2	0.2	5.2	32.4	-9.2	24
EYR155	18/12/15	2	4	0.2	3.8	11.1	-19.3	21.2
EYR158	1/2/16	2	2	26	-5.1	-28.3	12.5	29.3
EYR16	12/6/14	4	2	7.2	-4.97	-24.1	15.62	14.6
EYR162	4/3/16	3	3	3	3	17.8	-6.2	22.4
EYR176	19/4/16	3	3	1.2	2.5	1.2	-18.8	24.3
EYR180	26/4/16	3	3	2	5.4	25.7	-17.5	27.2
EYR182	30/4/16	3	2	5.8	-5.6	-23.9	20.9	16.7
EYR30	15/7/14	4	2	4.4	-7.49	-41.32	18.58	14

EYR32	23/7/14	4	2	11.6	-7.35	-38.2	20.61	16.6
EYR33	24/7/14	4	1	0.2	-5.2	-25.79	15.78	13.7
EYR47	18/10/14	1	3	0.4	3.47	18.53	-9.21	26.3
EYR48	19/10/14	1	3	0.3	3.07	19.98	-4.54	22.3
EYR49	20/10/14	1	3	2.4	2.47	19.57	-0.19	20
EYR54	19/11/14	1	3	0.4	4.71	38.13	0.45	28.8
EYR62	4/1/15	2	2	0.1	4.35	22.31	-12.49	19.7
EYR72	21/3/15	3	3	0.2	2.75	19.09	-2.88	19.4
EYR8	8/5/14	3	2	5	-5.45	-35.09	8.49	24
EYR80	11/4/15	3	3	0.4	5.32	12.77	-29.83	24.1
EYR87	1/5/15	3	2	5.6	-6.48	-54.48	-2.61	19.4
EYR9	9/5/14	3	2	21	-8.88	-59.3	11.71	15.4
EYR96	17/5/15	3	4	1	2.65	12.55	-8.68	16.5
MUN14	16/7/14	4	1	2.8	-6.56	-35.56	16.92	10.7
MUN15	21/7/14	4	2	1.6	0.69	6.35	0.86	12.4
MUN16	23/7/14	4	2	31	-9.66	-56.84	20.41	16.6
MUN18	31/8/14	4	3	0.8	0.27	1.52	-0.66	18.4
MUN2	9/5/14	3	2	8.2	-8.77	-59.21	10.94	15.4
MUN23	10/6/15	4	2	0.2	0.87	12.93	5.94	14.5
MUN27	20/6/15	4	3	1	0.42	-1.99	-5.31	16.1
MUN30	23/6/15	4	2	2.2	-5.94	-35.83	11.72	14.5
MUN37	1/8/15	4	1	22.4	-8.54	-51.41	16.92	13.9
MUN5	29/5/14	3	2	0.6	-0.3	7.21	9.62	12.3
MUN54	19/4/16	3	3	2	3.9	11.41	-19.79	24.3

MUN67	16/8/16	4	3	0.8	2.83	23.78	1.14	18.7
MUN8	11/6/14	4	2	2.4	-8.44	-68.71	-1.16	17.8
MUN9	12/6/14	4	2	11.8	-7.31	-41.82	16.67	14.6
RAW13	7/11/14	1	3	1.8	10.56	59.8	-24.66	30.5
RAW16	15/11/14	1	2	25.8	-6.5	-34.6	17.37	15.8
RAW17	18/11/14	1	3	2	5.48	31	-12.84	23.5
RAW18	19/11/14	1	3	3.2	5.51	39.2	-4.92	28.8
RAW20	21/12/14	2	3	20	-8.93	-59.4	12.05	27.2
RAW23	3/1/15	2	3	3	3.15	10	-15.14	21.5
RAW26	2/3/15	3	2	19.2	-7.97	-52.5	11.25	19.9
RAW27	3/3/15	3	2	1.2	-7.83	-51	11.66	21.2
RAW38	22/6/15	4	2	3	-6.76	-43	11.14	15.4
RAW39	23/6/15	4	2	1.8	-9.52	-66.9	9.28	14.5
RAW41	9/7/15	4	2	9.6	-9.05	-59.12	13.28	17.8
RAW47	29/7/15	4	3	1.8	3.31	8.9	-17.59	19.4
RAW48	1/8/15	4	1	25.8	-10.04	-64.92	15.4	13.9
RAW49	2/8/15	4	1	2.8	-10.72	-70.5	15.27	13
RAW55	19/10/15	1	3	0.4	10.61	67	-17.9	28

RAW61	7/11/15	1	3	4.4	3.46	21.8	-5.83	28.1
RAW62	8/11/15	1	3	1	3.69	22	-7.5	23.9
RAW71	2/2/16	2	2	7	-6.2	-35.3	14.31	18.5
RAW74	4/3/16	3	3	1.4	4.6	20	-16.76	22.4
RAW84	26/4/16	3	3	0.6	6.74	27.4	-26.5	27.2
SED10	17/11/14	1	3	3.8	6.43	50.36	-1.08	19
SED12	2/12/14	2	3	2.4	4.06	24.75	-7.73	27.6
SED14	3/1/15	2	3	6	1.5	7.83	-4.16	21.5
SED15	26/2/15	2	2	1.4	-7.07	-42	14.55	28.5
SED16	27/2/15	2	2	22.6	-7	-42.6	13.44	29.4
SED17	28/2/15	2	2	4.2	-6.07	-34.4	14.18	26.6
SED18	2/3/15	3	2	47	-9.83	-62.9	15.76	19.9
SED23	22/3/15	3	3	1.8	2.18	17.83	0.4	27.2
SED26	11/4/15	3	3	0.8	4.47	0.21	-35.55	24.1
SED4	23/7/14	4	2	15	-4.96	-16	23.74	16.6
SED5	18/9/14	1	3	3	3.43	18.84	-8.57	17.5
SED9	15/11/14	1	2	1.2	-4.82	-23.72	14.84	15.8

Therefore, by excluding the middle range of $\delta^{18}\text{O}$ values from these further analyses, there is little to no impact on the application of the modern precipitation analyses to the interpretation of the speleothem record, as they would have little impact on the large shifts and excursions evident in the speleothem $\delta^{18}\text{O}$ records. Additionally, moisture source classification is a complex and time-consuming process; therefore, investing resources into events of lesser importance that would not provide any additional support to the palaeoprecipitation interpretations was deemed unnecessary.

5.6.1. Pearson Correlation Analyses

In order to assess the relationships between $\delta^{18}\text{O}$, δD , d -excess, rainfall amount, and temperature, Pearson product moment correlation coefficients were calculated. Due to the similar locations of other modern precipitation studies (e.g. Treble et al., 2005b), similar approaches to analyses and interpretation have been undertaken here. Regarding the r values presented in this chapter, it must be noted that the relationships controlling and influencing various factors of precipitation are multi-faceted and intertwined. As a result, correlations may appear to be weaker in comparison to those produced by simple physical laws, however under these conditions may represent considerably influential relationships. The statistical significance of correlations through the individual stages of analyses are quoted accordingly.

As with the complete dataset (**Table 5.5**), the strongest correlations are, as expected, between $\delta^{18}\text{O}$ and both δD , and d -excess within the individual sites (**EUC – Table 5.12, RAW – Table 5.13, SED – Table 5.14, EYR – Table 5.15, ARU – Table 5.16, MUN – Table 5.17**) and all site averages (**Table 5.18**). The critical values required for a significance level of 0.05 for these analyses are presented in **Table 5.12**. Within the EUC dataset (**Table 5.13**), all of the correlations are statistically significant, with the strongest relationships being between temperature and $\delta^{18}\text{O}$, temperature and δD , and temperature and d -excess. All of the apparent correlations of the RAW dataset (**Table 5.14**) are statistically significant with the exception of the relationship between temperature and rainfall amount. Within this dataset the strongest correlations are between temperature and $\delta^{18}\text{O}$, δD , and d -excess. Of the SED dataset (**Table 5.15**), only the correlations between rainfall amount and $\delta^{18}\text{O}$, and rainfall amount and δD are statistically significant; this is likely, at least in part, due to the smaller sample size of this site.

Table 5.11 – Summarised information for the $\delta^{18}\text{O}$ stratified dataset (10% most enriched and 10% most depleted values, and the amount-weighted means of these extremes), by individual sites and as all sites combined.

Precipitation Event Variable		RAW			SED			EYR			ARU		
		Depleted 10%	Enriched 10%	Average	Depleted 10%	Enriched 10%	Average	Depleted 10%	Enriched 10%	Average	Depleted 10%	Enriched 10%	Average
$\delta^{18}\text{O}$ (VSMOW ‰)	Min	-10.72	3.15	-3.79	-9.83	1.50	-4.17	-10.00	1.98	-4.01	-7.47	-1.19	-4.33
	Max	-6.20	10.61	2.21	-4.82	6.43	0.81	-4.62	5.40	0.39	-6.04	-0.91	-3.48
	Average	-8.31	4.93	-1.69	-8.05	3.42	-2.32	-7.14	3.39	-1.88	-6.54	-1.09	-3.82
δD (VSMOW ‰)	Min	-70.50	8.90	-30.80	-16.00	0.21	-7.90	-66.89	1.20	-32.85	-40.77	-10.16	-25.47
	Max	-34.60	67.00	16.20	-62.90	50.36	-6.27	-21.45	38.13	8.34	-29.85	4.75	-12.55
	Average	-52.40	27.06	-12.67	-48.03	21.71	-13.16	-43.32	19.58	-11.87	-32.96	-1.77	-17.37
<i>d</i> -excess	Min	9.28	-26.50	-8.61	13.44	-35.55	-11.06	-2.61	-29.83	-16.22	13.98	-0.67	6.66
	Max	17.37	-4.92	6.23	23.74	0.40	12.07	20.90	0.81	10.86	23.97	13.61	18.79
	Average	14.09	-12.38	0.86	16.39	-5.68	5.36	13.83	-7.58	3.13	19.39	6.97	13.18
Rain Amount	Min	1.2	0.4	0.8	1.2	0.8	1.0	0.2	0.1	0.2	3.0	1.0	2.0
	Max	25.8	4.4	15.1	47.0	6.0	26.5	34.4	3.0	18.7	18.5	17.0	17.8
	Average	11.6	2.0	6.8	15.2	3.0	9.1	10.8	1.0	5.9	6.6	7.1	6.9
% SO		10	0	10	0	0	0	6	0	3	50	0	25
% CB / SO		80	0	40	83	0	41.5	94	12	53	33	50	41.5
% T		10	100	50	17	100	58.5	0	76	38	0	50	25
% TI		0	0	0	0	0	0	0	12	6	17	0	8.5
% Winter		50	10	30	16.6	0	8.3	64.7	0	32.35	66.6	33.3	49.95
% Spring		10	60	35	16.6	33.3	24.95	0	52.9	26.45	33.3	16.6	24.95
% Summer		20	10	15	50	33.3	41.65	5.8	11.7	8.75	0	0	0
% Autumn		20	20	20	16.6	33.3	24.95	29.4	35.3	32.35	0	50	25

Precipitation Event Variable		MUN			EUC			All Sites Average		
		Depleted 10%	Enriched 10%	Average	Depleted 10%	Enriched 10%	Average	Depleted 10%	Enriched 10%	Average
$\delta^{18}\text{O}$ (VSMOW ‰)	Min	-9.66	-3.00	-6.33	-10.25	2.61	-3.82	-9.66	0.84	-4.41
	Max	-5.94	3.90	-1.02	-4.34	13.38	4.52	-5.33	6.47	0.57
	Average	-8.67	1.68	-3.50	-6.90	4.64	-1.13	-7.60	2.83	-2.39
δD (VSMOW ‰)	Min	-68.71	-1.99	-35.35	-61.26	11.22	-25.02	-54.02	1.56	-26.23
	Max	-35.56	23.78	-5.89	-20.40	60.50	20.05	-34.13	40.75	3.31
	Average	-52.42	8.31	-22.06	-39.89	24.90	-7.50	-44.84	16.63	-14.10
<i>d</i> -excess	Min	-1.16	-19.79	-10.48	9.78	-46.58	-18.40	7.12	-26.49	-9.68
	Max	20.41	9.62	15.02	20.74	-0.54	10.10	21.19	3.16	12.18
	Average	16.94	-5.17	5.89	15.32	-12.30	1.51	15.99	-6.02	4.99
Rain Amount	Min	2.2	0.2	1.2	0.8	0.1	0.5	1.4	0.4	0.9
	Max	31.0	2.0	16.5	34.0	4.6	19.3	31.8	6.2	19.0
	Average	11.5	1.0	6.3	12.3	0.9	6.6	11.3	2.5	6.9
% SO		14	0	7	19	0	9.5	16.50	0.00	9.08
% CB / SO		86	43	64.5	81	19	50	76.17	20.67	48.42
% T		0	57	28.5	0	81	40.5	4.50	77.33	40.08
% TI		0	0	0	0	0	0	2.83	2.00	2.42
% Winter		85.7	71.4	78.55	50	0	25	55.60	19.12	37.36
% Spring		0	0	0	6.25	43.75	25	11.03	34.43	22.73
% Summer		0	0	0	12.5	25	18.75	14.72	13.33	14.03
% Autumn		14.3	28.6	21.45	31.25	31.25	31.25	18.59	33.08	25.83

All of the apparent correlations in the EYR dataset (**Table 5.16**) are statistically significant, with the strongest relationships being between $\delta^{18}\text{O}$ and both rainfall amount and temperature, and δD and temperature. The majority of correlations in the ARU dataset (**Table 5.17**) are statistically insignificant (largely an artefact of the smaller sample size), with only correlations between temperature and $\delta^{18}\text{O}$, δD , and d -excess being significant. In the MUN dataset (**Table 5.18**) the correlations are statistically significant except for those between temperature and $\delta^{18}\text{O}$, δD , and rainfall amount, with the strongest correlations being between rainfall amount and $\delta^{18}\text{O}$, δD and d -excess. All correlations evident in the combined site dataset (**Table 5.19**) are deemed to be statistically significant, with the strongest correlations being between $\delta^{18}\text{O}$ and temperature, d -excess and temperature, and $\delta^{18}\text{O}$ and rainfall amount.

As the isotope of interest for the purposes of palaeoclimate interpretations is $\delta^{18}\text{O}$, this will be the subject of further correlation interpretations. The relationship identified between $\delta^{18}\text{O}$ and rainfall amount from the complete dataset (**Table 5.5**), is also evident in the further analyses of the sites, both individually (except at ARU) and in the combined data correlations. The relationship between $\delta^{18}\text{O}$ and rainfall amount from the combined site $\delta^{18}\text{O}$ stratified dataset produced an r value of -0.57, compared to the r value of -0.41 from the complete dataset. Some variation in the correlation would be expected due to the difference in sample numbers in the two datasets.

Table 5.12 – The critical values required for a 0.05 significance level for each site individually and for the combined dataset of all sites.

Site	Critical r value	MUN	0.46
ARU	0.5	RAW	0.38
EUC	0.3	SED	0.5
EYR	0.28	All Sites	<0.16

Table 5.13 – Pearson correlation r values from the EUC $\delta^{18}\text{O}$ -ranked dataset.

EUC	$\delta^{18}\text{O}$	δD	d -excess	rainfall amount
δD	0.98	X	X	X
d -excess	-0.93	-0.84	X	X
rainfall amount	-0.58	-0.59	0.51	X
temperature	0.77	0.74	-0.74	-0.46

Table 5.14 – Pearson correlation r values from the RAW $\delta^{18}\text{O}$ -ranked dataset.

RAW	$\delta^{18}\text{O}$	δD	d -excess	rainfall amount
δD	0.99	X	X	X
d -excess	-0.94	-0.90	X	X
rainfall amount	-0.56	-0.53	0.61	X
temperature	0.78	0.78	-0.69	-0.33

Table 5.15 – Pearson correlation r values from the SED $\delta^{18}\text{O}$ -ranked dataset.

SED	$\delta^{18}\text{O}$	δD	d -excess	rainfall amount
δD	0.96	X	X	X
d -excess	-0.79	-0.58	X	X
rainfall amount	-0.61	-0.61	0.42	X
temperature	-0.08	-0.17	-0.11	-0.11

Table 5.16 – Pearson correlation r values from the EYR $\delta^{18}\text{O}$ -ranked dataset.

EYR	$\delta^{18}\text{O}$	δD	d -excess	rainfall amount
δD	0.97	X	X	X
d -excess	-0.86	-0.72	X	X
rainfall amount	-0.68	-0.68	0.54	X
temperature	0.68	0.64	-0.64	-0.32

Table 5.17 – Pearson correlation r values from the ARU $\delta^{18}\text{O}$ -ranked dataset.

ARU	$\delta^{18}\text{O}$	δD	d -excess	rainfall amount
δD	0.96	X	X	X
d -excess	-0.70	-0.47	X	X
rainfall amount	0.04	0.09	0.08	X
temperature	0.78	0.71	-0.62	-0.35

Table 5.18 – Pearson correlation r values from the MUN $\delta^{18}\text{O}$ -ranked dataset.

MUN	$\delta^{18}\text{O}$	δD	d -excess	rainfall amount
δD	0.97	X	X	X
d -excess	-0.74	-0.57	X	X
rainfall amount	-0.66	-0.60	0.60	X
temperature	0.37	0.21	-0.72	-0.07

Table 5.19 - Pearson correlation r values from the combined $\delta^{18}\text{O}$ -ranked dataset of all sites.

ALL SITES	$\delta^{18}\text{O}$	δD	$d\text{-excess}$	rainfall amount
δD	0.97	X	X	X
$d\text{-excess}$	-0.87	-0.74	X	X
rainfall amount	-0.57	-0.56	0.49	X
temperature	0.62	0.56	-0.62	-0.26

However, the two datasets do produce very similar values of negative correlation, and it is therefore suggested that rainfall amount does appear to have a notable influence on $\delta^{18}\text{O}$ signatures of precipitation in the region. While this relationship has been found to be insignificant or non-existent in some studies (e.g. Breitenbach et al., 2010), it has commonly found to be a key driver of $\delta^{18}\text{O}$ variability both elsewhere globally (Johnson and Ingram, 2004; Baldini et al., 2010), and elsewhere in Australia (Treble et al., 2005a; Barras and Simmonds, 2009; Liu et al., 2010).

In addition to the influence of rainfall amount, the analyses of the data presented in this thesis have also found that temperature and $\delta^{18}\text{O}$ are significantly correlated. This relationship is found in both the complete dataset ($r = 0.37$) and in the $\delta^{18}\text{O}$ -stratified data of several of the individual sites as well the combined site analyses ($r = 0.62$). This relationship has also been commonly identified in other studies of modern precipitation (Jouzel et al., 2000; Darling and Talbot, 2003; Johnson and Ingram, 2004; Liebminger et al., 2006; Barras and Simmonds, 2008); however in some cases, it has been argued that the correlation between temperature and $\delta^{18}\text{O}$ is actually a function of other seasonal variations, such as those in dominant moisture sources and/or synoptic conditions (Guan et al., 2013). In other instances, it has been argued that relationships between $\delta^{18}\text{O}$ and other factors such as rainfall amount appear more significant as they are also a function of temperature (Baldini et al., 2010), highlighting the interconnected nature of the numerous influences on $\delta^{18}\text{O}$ and emphasising the need for detailed investigations and multiply stratified analyses to identify the key influences on $\delta^{18}\text{O}$ variability at a given location.

5.6.2. Chi-squared Analyses

Chi-square tests were performed on all samples for which moisture source data was obtained. Site-specific analyses were not undertaken due to insufficient sample sizes of the majority of sites for this method. From these analyses (**Table 5.20**) it emerges that relationships between source and $\delta^{18}\text{O}$,

rainfall amount and season, are all statistically significant. As an additional test on the relationship between moisture source and $\delta^{18}\text{O}$, the amount-weighted mean $\delta^{18}\text{O}$ was calculated for each moisture source for individual sites and the combined site dataset (**Table 5.21**). From these data it is evident that there is a relationship between moisture source and $\delta^{18}\text{O}$, with tropically sourced precipitation events consistently displaying the most enriched $\delta^{18}\text{O}$ signature. Precipitation events sourced from the Southern Ocean, and Southern Ocean/NCB interactions are variable; however they are significantly more depleted than tropically sourced events. Their variability is likely a result of the broad nature of these source classifications and could be resolved in future studies if more specific moisture sources and synoptic classifications can be distinguished. There is not enough data from precipitation events sourced from the Tasman to compare to the rest of the dataset. This suggests that while numerous factors including rainfall amount and temperature have some influence on the $\delta^{18}\text{O}$ of precipitation in the region, moisture source is arguably a key driver of $\delta^{18}\text{O}$ variability, as has been found to be the case elsewhere in Australia (Barras and Simmonds, 2008; Callow et al., 2014).

The apparent seasonal signal in the dominance of the various moisture source classes corresponds with similar studies, which have also highlighted the importance of critical moisture pathways in modern precipitation (e.g. Theobald and McGowan, 2016; Theobald et al., 2016). This may have implications for applications in palaeo interpretations where seasonal dominance and variation may have been dampened or amplified. It is noted that in the classification of moisture sources, perhaps the most significant omission is that of continentally sourced precipitation. The main reason for this omission is the difficulty of isolating such events from those sourced from the tropics using the back trajectories and composite anomaly maps. Nonetheless it is an area of potential interest for further research of modern precipitation in the region if research advances allow them to be reliably isolated from tropically sourced precipitation events. Despite this omission, there is still ample information that can be obtained from the four-point classification of moisture sources applied in this study. For example, where there are greater frequencies of mid-latitude low-pressure systems (i.e. Southern Ocean sourced) interacting with tropical rainfall belts (i.e. northern cloud bands), there tends to be higher rainfall amounts. This is evidenced by the significant correlations between moisture source and rainfall amount in the $\delta^{18}\text{O}$ -stratified dataset (**Table 5.20**). This relationship is of particular importance considering the previous discussion of the influence of rainfall amount on $\delta^{18}\text{O}$ and the apparent seasonal signals evident.

5.6.3. Stratified Analyses

In consideration of the numerous potential influences on the $\delta^{18}\text{O}$ of precipitation at a given site, it is important to disentangle these signals within the $\delta^{18}\text{O}$ variation. In order to achieve this, further analyses were conducted on the complete dataset (**Table 5.22**). All r values produced are significant to the 0.05 level. Through these analyses, both potential influences of rainfall amount and season (used as a proxy for temperature) were 'controlled' in order to identify any correlations that may have been obscured in the overall analyses (**Table 5.5**) by their potentially competing influences. The results show that the correlation between rainfall amount and $\delta^{18}\text{O}$ becomes generally stronger, with the exception of in spring. This supports the contention that rainfall amount is not the only significant driver of $\delta^{18}\text{O}$ variation, and that its relationship is partly obscured by other influences such as temperature and moisture source. The correlation between temperature and $\delta^{18}\text{O}$ also appears significantly stronger when stratified by rainfall amount, suggesting that, in the overall analyses the influence of temperature on $\delta^{18}\text{O}$ is obscured by the influence of rainfall amount. However, it is important to note that when multiply stratifying the data in this way it does reduce the sample sizes used for each correlation, therefore some changes may be an artefact of this.

5.7. Site Comparisons

As previously stated, the primary purpose of the site comparison analyses is to identify if any systematic variation in precipitation exists at the six different collection sites. For these analyses, ten rainfall events were selected from the complete dataset, chosen firstly as events with precipitation samples collected from >4 sites, and secondly by the highest rainfall amount. This stage of analysis was considered in two different ways: systematic variations dependent upon distance of collection site from the coast, and systematic variations dependent upon the apparent moisture pathway of a given event across the region. It has already been established that, generally, distance inland (i.e. the continental effect) and the amount of precipitation from a given air parcel (i.e. amount effect) can considerably influence the $\delta^{18}\text{O}$ signature of a given precipitation event. By considering each of the ten selected rainfall events twofold, both of these variables are being accounted for.

Table 5.20 – Contingency tables of expected and actual values, and p-values for the Chi-square analysis of all $\delta^{18}\text{O}$ stratified data. Seasons are represented as 1- spring, 2- summer, 3- autumn, 4-winter. Sources are represented as 1- Southern Ocean, 2- northern cloud band – southern Ocean interactions, 3- tropical, 4-Tasman influenced.

Expected Values

Source/ $\delta^{18}\text{O}$	1	2	3	4	Actual Total
Enriched	5.32	26.17	22.18	1.33	55
Depleted	6.68	32.83	27.82	1.67	69
Actual Total	12	59	50	3	124

Source/Rain Amt	1	2	3	4	Actual Total
High	4.65	22.84	19.35	1.16	48
Moderate	3.39	16.65	14.11	0.85	35
Low	3.97	19.51	16.53	0.99	41
Actual Total	12	59	50	3	124

Source/Season	1	2	3	4	Actual Total
1	2.9	14.27	12.1	0.73	30
2	1.65	8.09	6.85	0.41	17
3	3.29	16.18	13.71	0.82	34
4	4.16	20.46	17.34	1.04	43
Actual Total	12	59	50	3	124

Actual Values

Source/ $\delta^{18}\text{O}$	1	2	3	4
Enriched	0	7	46	2
Depleted	12	52	4	1

p value = 1.54E-17

Source/Rain Amt	1	2	3	4
High	7	36	5	0
Moderate	4	12	18	1
Low	1	11	27	2

p value = 2.03E-06

Source/Season	1	2	3	4
1	3	4	23	0
2	1	7	8	1
3	0	19	14	1
4	8	29	5	1

p value = 1.10E-05

Table 5.21 – Amount weighted mean $\delta^{18}\text{O}$ for each moisture source at each individual site and for the combined dataset from all sites.

Site	Amount Weighted $\delta^{18}\text{O}$			
	Source 1	Source 2	Source 3	Source 4
ARU	n=3 -6.04	n=5 -3.47	n=3 -1.16	n=1 -7.47
EUC	n=4 -7.69	n=15 -6.67	n=13 4.62	n=0 -
EYR	n=1 -5.2	n=18 -7.13	n=13 3.41	n=2 2.84
MUN	n=2 -8.32	n=8 -8.44	n=4 2.32	n=0 -
RAW	n=2 -10.1	n=7 -7.37	n=11 -2.07	n=0 -
SED	n=0 -	n=6 -8.05	n=6 3.42	n=0 -
All Sites	n=12 -8.27	n=59 -6.99	n=50 0.85	n=3 -4.52

Table 5.22 – Pearson correlation r values for the stratified data analyses by rainfall amount (top) and season (bottom).

Rainfall Amount / Stratification	No. of Samples	T vs $\delta^{18}\text{O}$	T vs d -excess
Low	199	0.57	-0.62
Moderate	182	0.39	-0.52
High	187	0.37	-0.52

Season / Stratification	No. of Samples	Rainfall Amount vs $\delta^{18}\text{O}$	Rainfall Amount vs d -excess
Spring	103	-0.34	0.35
Summer	74	-0.51	0.35
Autumn	187	-0.55	0.29
Winter	204	-0.48	0.13

Initial analyses were undertaken on the complete dataset obtained from the $\delta^{18}\text{O}$ ranked analyses, as this dataset included analyses of moisture source. From analysis of the summary data (**Table 5.18**) there are no clear trends in $\delta^{18}\text{O}$ or rainfall amount across the individual sites, or any apparent systematic deviations from the average values. Amongst the correlation statistics of the individual sites (**Table 5.12** to **Table 5.17**) and combined sites (**Table 5.18** and **Table 5.20**) it is clear that moisture source, rainfall amount and temperature consistently have the strongest significant correlations with $\delta^{18}\text{O}$; however, there are no systematic changes in these relationships across the sites. Sites were also considered in respect of their proximity to the coast, with EYR, EUC and MUN being grouped as 'coastal' locations and RAW, SED and ARU grouped as 'inland' locations (**Table 5.23**). Based on this rudimentary division, the relationships between the 'source' of collection (i.e. coastal and inland) and $\delta^{18}\text{O}$ and season are not statistically significant. However, the apparent correlation between source and rainfall amount is statistically significant. This suggests that while there may be a significant difference between the rainfall amounts of precipitation events at the inland and coastal events, this does not systematically influence the $\delta^{18}\text{O}$ signature of precipitation in the region. From this it can be argued that the processes associated with rainfall amounts do not significantly drive changes in $\delta^{18}\text{O}$ of precipitation across the region.

A more in-depth analysis of potential systematic variations in precipitation was undertaken on ten specifically selected rainfall events (**Table 5.24**). None of the ten events individually revealed a systematic trend in rainfall amount or $\delta^{18}\text{O}$ based on either distance inland or on inferred moisture pathway (as interpreted from composite anomaly maps and modelled back-trajectory analyses). To further corroborate this finding, all ten events were compared to identify any potential trends that may not have resulted from these two identified potential causes. Investigations were conducted into rainfall amount (**Fig. 5.27**) and $\delta^{18}\text{O}$ (**Fig. 5.28**) variations across each site for each event. No apparent trends were identified. From this it can be argued that there is no substantial local influence on the precipitation that may affect the $\delta^{18}\text{O}$ of an individual site.

From investigations into both the complete dataset and the specifically selected individual events, it can be concluded that any given site is likely representative of the region as a whole, and thus the $\delta^{18}\text{O}$ record preserved within a speleothem would also be generally representative of the precipitation of the Nullarbor region.

5.8. Summary of Modern Precipitation Analyses

Within the analyses discussed there are several notable trends in the relationships between $\delta^{18}\text{O}$ and its influencing factors. These trends are evident in the individual site analyses as well as in the combined site analyses. From the Pearson correlations, the strongest relationships are consistently between $\delta^{18}\text{O}$ and either temperature or rainfall amount (**Table 5.25**).

However, the strength and significance of these relationships is variable across the sites. Comparisons revealed no significant trends across the sites, so it is most likely that these differences result from the variability of collected rainfall observations at each site. The Chi-squared analyses of the combined site dataset revealed significant relationships between source and $\delta^{18}\text{O}$, and rainfall amount and season (used as a proxy for temperature), indicating that all of these factors are influenced to some extent by moisture source. This has important implications for the application of these analyses to a palaeoprecipitation context; if there is a difference in dominant moisture source, as predicted, this will influence all of these factors, and ultimately $\delta^{18}\text{O}$. The strongest relationship identified in the Chi-squared analyses is between moisture source and $\delta^{18}\text{O}$. The strength of this is supported by the individual site analyses of the amount-weighted mean $\delta^{18}\text{O}$ for each moisture source, whereby tropically sourced precipitation events consistently have the most enriched $\delta^{18}\text{O}$ signature, and the $\delta^{18}\text{O}$ signal from the Southern Ocean and Southern Ocean / NCB moisture sources are consistently more depleted. As previously stated, this has important implications for palaeoprecipitation analyses in this region; since moisture source has a substantial influence on $\delta^{18}\text{O}$, any significant shifts will influence the preserved $\delta^{18}\text{O}$ signal.

5.9. Analyses for Palaeoprecipitation

The primary purpose for modern precipitation analyses in this study is to assist in the interpretations of the palaeoprecipitation signals preserved within Nullarbor speleothems. For this stage of analysis, no precipitation events with rainfall amounts lower than 12.5 mm were used, as these are the rainfall events likely to be reflected in the speleothem $\delta^{18}\text{O}$ rather than evaporated at the surface prior to percolating into the cave. Pearson correlations were conducted on the complete dataset ($n=50$) (**Table 5.26**) and Chi-squared analyses on all data that included moisture source information ($n=41$) (**Table 5.27**).

Table 5.23 – Contingency tables of expected and actual values, and p-values for the Chi-square analysis of inland and coastal sites. Seasons are represented as 1- spring, 2- summer, 3- autumn, 4-winter.

Expected Values

Source $\delta^{18}\text{O}$	Inland	Coastal	Actual Total
Enriched	57.38	136.62	194
Intermediate	54.72	130.28	185
Depleted	55.9	133.1	189
Actual Total	168	400	568

Source Rain Amt	Inland	Coastal	Actual Total
High	55.61	132.39	188
Moderate	55.61	132.39	188
Low	56.79	135.21	192
Actual Total	168	400	568

Source Season	Inland	Coastal	Actual Total
1	30.46	72.54	103
2	21.89	52.11	74
3	55.31	131.69	187
4	60.34	143.66	204
Actual Total	168	400	568

Actual Values

Source $\delta^{18}\text{O}$	Inland	Coastal
Enriched	52	142
Intermediate	51	134
Depleted	65	124
<i>p</i> value =		0.20412557

Source Season	Inland	Coastal
1	35	68
2	25	49
3	51	136
4	57	147
<i>p</i> value =		0.507482279

Source Rain Amt	Inland	Coastal
High	63	125
Moderate	70	118
Low	35	157
<i>p</i> value =		9.33E-05

Table 5.24 – Data used for the comparison of single precipitation events across multiple sites. Sources are represented as 1- Southern Ocean, 2- northern cloud band – southern Ocean interactions, 3- tropical, 4-Tasman influenced.

Picarro Code	Event Number	Date of Event	Rainfall Amount (mm)	Moisture Source	$\delta^{18}\text{O}$ (VSMOW ‰)	δD (VSMOW ‰)	<i>d-excess</i>
ARU4	1	23/07/2014	1.0	2	-5.12	-23.20	17.74
RAW5		23/07/2014	10.4	2	-5.33	-20.10	22.60
EYR32		23/07/2014	11.6	2	-7.35	-38.20	20.61
SED4		23/07/2014	15.0	2	-4.96	-16.00	23.74
MUN16		23/07/2014	31.0	2	-9.66	-56.80	20.41
EUC34	2	23/09/2014	2.2	2	-2.50	-5.07	14.93
MUN19		23/09/2014	3.4	2	-2.79	-5.60	16.74
RAW11		23/09/2014	9.0	2	-3.98	-14.20	17.64
EYR44		23/09/2014	31.5	2	-2.96	-8.20	15.50
EUC43	3	14/11/2014	4.0	2	0.37	10.91	7.98
RAW15		14/11/2014	4.6	2	-4.47	-16.50	19.20
SED8		14/11/2014	12.0	2	-2.54	-0.90	19.39
MUN20		14/11/2014	17.2	2	-1.38	5.20	16.25
EYR52		14/11/2014	26.2	2	-2.01	-1.40	14.73
SED9	4	15/11/2014	1.2	2	-4.82	-23.72	14.84
EYR53		15/11/2014	6.8	2	-2.20	-3.90	13.73
RAW16		15/11/2014	25.8	2	-6.50	-34.60	17.37
EUC44		15/11/2014	30.4	2	-2.27	-0.59	17.59
EUC55	5	27/02/2015	0.8	3	6.07	11.22	-37.30
ARU11		27/02/2015	8.0	3	-1.80	-9.80	4.58
EYR68		27/02/2015	9.2	3	-0.69	-7.50	-2.03
RAW24		27/02/2015	10.4	3	-4.91	-26.20	13.07
SED16		27/02/2015	22.6	3	-7.00	-42.60	13.44
EYR70	6	2/03/2015	1.0	2	-2.46	-12.70	6.97
EUC56		2/03/2015	3.2	2	-0.86	1.04	7.93
RAW26		2/03/2015	19.2	2	-7.97	-52.50	11.25
SED18		2/03/2015	47.0	2	-9.83	-62.90	15.76
ARU16	7	16/04/2015	1.5	2	-1.74	-9.50	4.42
EYR82		16/04/2015	4.8	2	-1.95	0.10	15.65
EUC68		16/04/2015	12.0	2	-4.30	-22.40	11.97
RAW34		16/04/2015	15.0	2	-4.14	-19.50	13.66
SED28		16/04/2015	17.0	2	-4.55	-25.40	11.00
EUC97	8	1/08/2015	9.4	2	-7.55	-43.22	17.19
MUN37		1/08/2015	22.4	2	-8.54	-51.40	16.92
RAW48		1/08/2015	25.8	2	-10.04	-64.92	15.40
EYR117		1/08/2015	34.4	2	-10.00	-66.89	13.11
ARU25		1/08/2015	52.0	2	-2.32	-14.58	3.98
MUN44	9	23/08/2015	1.6	2	-3.00	-13.60	10.39
RAW52		23/08/2015	2.0	2	-3.86	-21.30	9.61
EYR127		23/08/2015	7.0	2	-6.07	-36.98	11.56
EUC101		23/08/2015	42.0	2	-6.10	-33.88	14.96
RAW59	10	3/11/2015	4.6	2	-4.15	-14.70	18.50
EUC121		3/11/2015	13.2	2	-2.57	-8.80	11.75
ARU33		3/11/2015	14.0	2	-5.03	-33.90	6.38
EYR140		3/11/2015	40.6	2	-4.60	-22.90	13.90

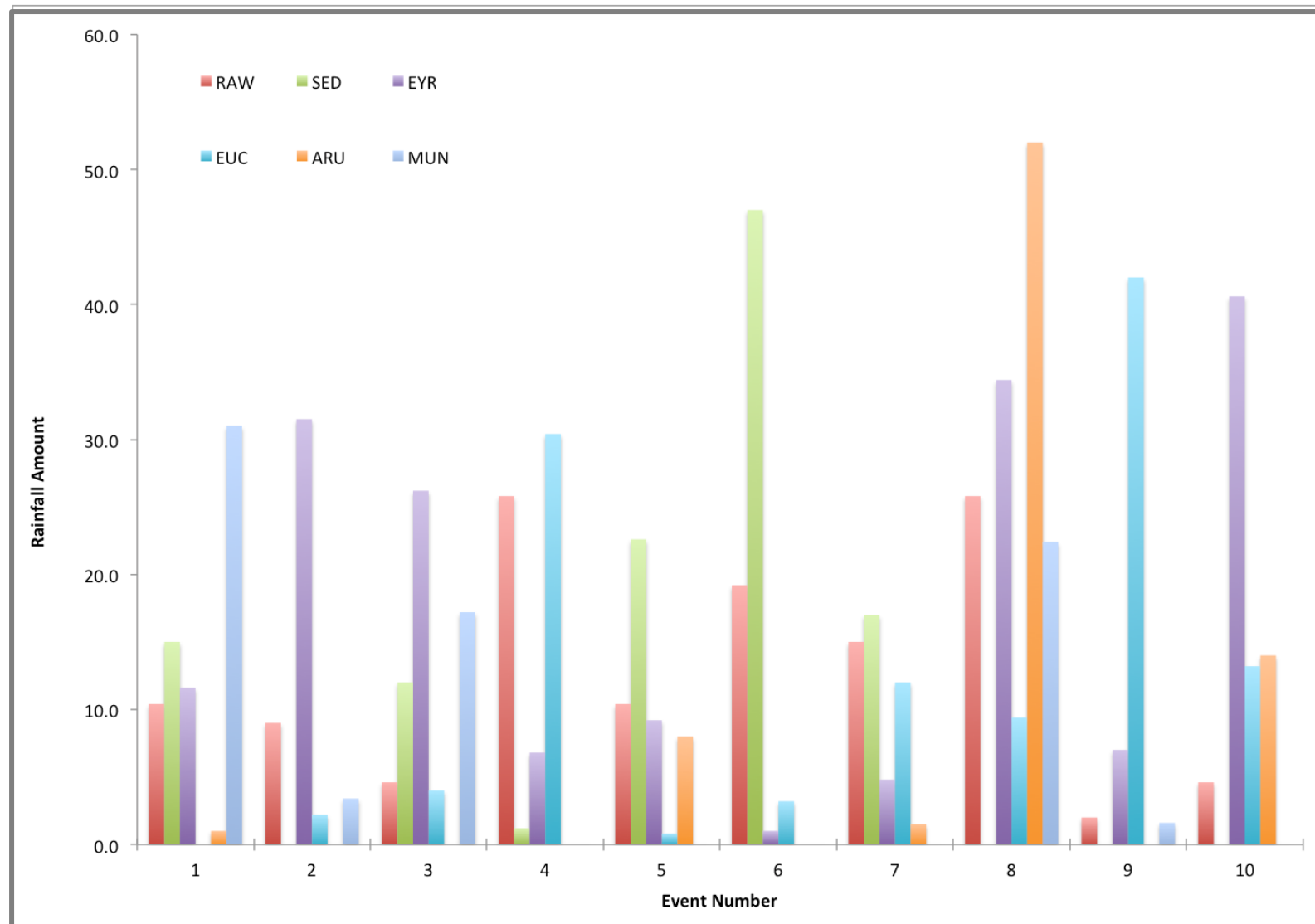


Fig. 5.27 – The variability of rainfall amount shown by site comparisons for the ten individual precipitation events identified in Table 5.24.

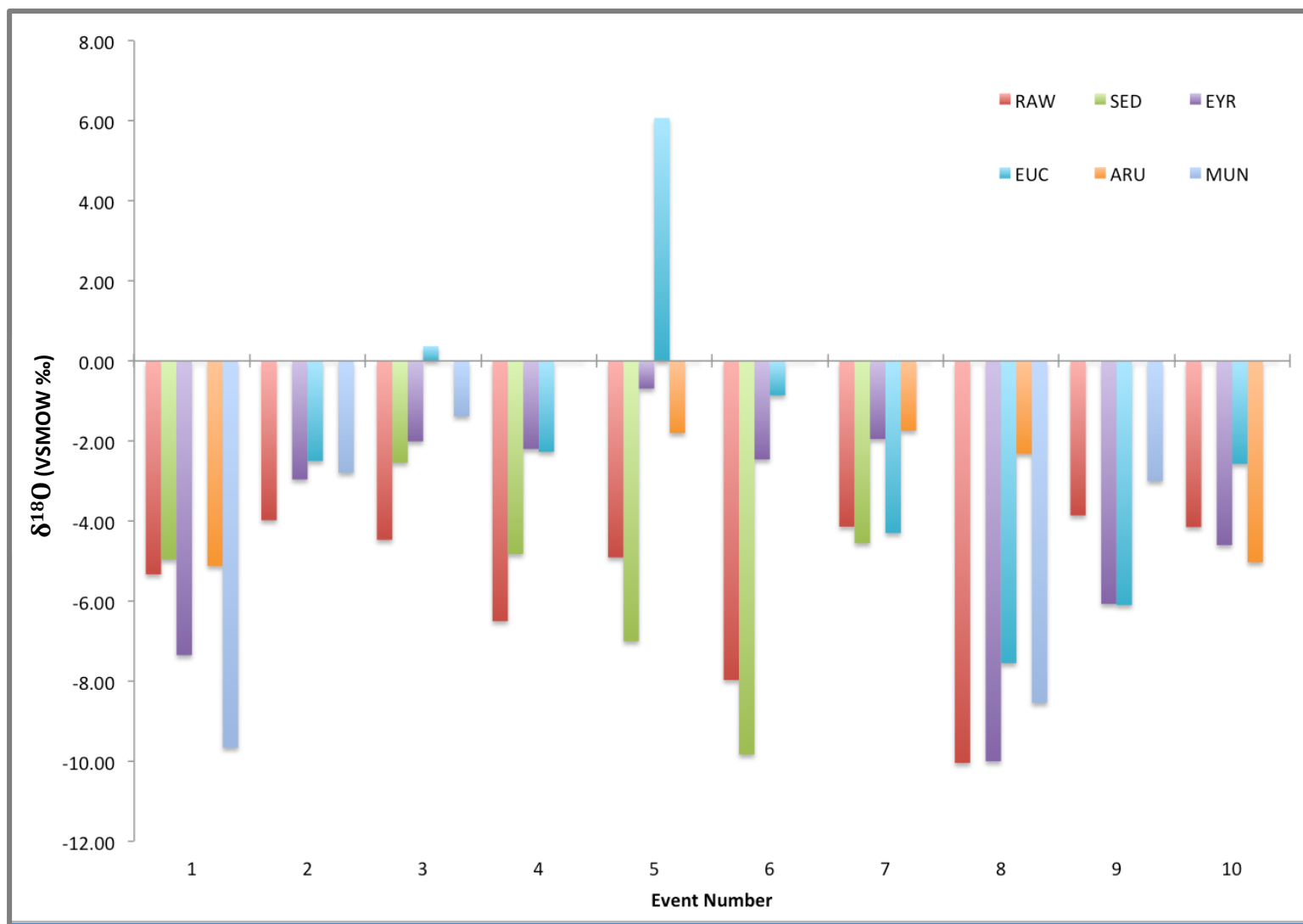


Fig. 5.28 – The variability of $\delta^{18}\text{O}$ shown by site comparisons for the ten individual precipitation events identified in Table 5.24.

Table 5.25 – A summary of the strongest Pearson correlations with $\delta^{18}\text{O}$ at each site, and for the analyses of the combined site dataset, as determined by the highest r value, and therefore most powerful influence on $\delta^{18}\text{O}$ variation, at each site.

Site	Strongest Correlation with $\delta^{18}\text{O}$
EUC	temperature
RAW	rainfall amount
SED	rainfall amount / temperature
EYR	temperature
ARU	rainfall amount
MUN	temperature
All sites	rainfall amount / temperature

Several of the Pearson correlations produced statistically insignificant r values (with a critical $r > 0.23$ required for significance at the 0.05 level); the strongest significant correlations are between temperature and both $\delta^{18}\text{O}$ and d -excess. The Chi-squared analyses suggest that the relationship between $\delta^{18}\text{O}$ and moisture source is not statistically significant, while the relationship between moisture source and season is significant. This contrasts the results of the Chi-squared analyses of the complete $\delta^{18}\text{O}$ -stratified dataset, in which the apparent correlation between moisture source and $\delta^{18}\text{O}$ is statistically significant. The statistics from this reduced dataset do show some similarities to the previously discussed datasets, however there are also notable differences. While the general trends in correlations remain the same as the averaged $\delta^{18}\text{O}$ stratified data (henceforth the 'maximum dataset'), there are notable differences in the strength of these correlations. The correlation between $\delta^{18}\text{O}$ and moisture source is substantially less than in the maximum dataset and is not statistically significant.

Table 5.26 – Pearson correlation r values from the palaeotemperature stratified data.

	$\delta^{18}\text{O}$	δD	d -excess	rainfall amount
δD	0.98	X	X	X
d -excess	-0.42	-0.25	X	X
rainfall amount	-0.19	-0.21	-0.04	X
temperature	0.41	0.33	-0.53	-0.18

Table 5.27 – Contingency tables and p-values for the Chi-squared analysis of the palaeotemperature stratified data. Seasons are represented as 1- spring, 2- summer, 3- autumn, 4-winter. Sources are represented as 1- Southern Ocean, 2- northern cloud band – Southern Ocean interactions, 3- tropical, 4-Tasman influenced.

Expected

Source/d ¹⁸ O	1	2	3	4	Actual Total
Enriched	0.17	0.73	0.1	-	1
Intermediate	0.85	3.66	0.49	-	5
Depleted	5.98	25.61	3.41	-	35
Actual Total	7	30	4	0	41

Source/Season	1	2	3	4	Actual Total
1	1.54	6.59	0.88	-	9
2	1.02	4.39	0.59	-	6
3	2.05	8.78	1.17	-	12
4	2.39	10.24	1.37	-	14
Actual Total	7	30	4	0	41

Actual

Source/d ¹⁸ O	1	2	3	4
Enriched	0	1	0	0
Intermediate	1	4	0	0
Depleted	6	25	4	0

p value = 9.06E-01

Source/Season	1	2	3	4
1	2	7	0	0
2	0	3	3	0
3	2	9	1	0
4	3	11	0	0

p value = 2.88E-02

However, it is suggested that this is likely the result of the relationship being obscured by the limited dataset, as the majority (59.2%) of low and intermediate rainfall amounts are attributed to tropically sourced precipitation events (as calculated from all of the data containing moisture source classifications). These events account for 74.6% of the enriched $\delta^{18}\text{O}$ values; therefore by excluding all low and moderate rainfall amounts, the influence of source on $\delta^{18}\text{O}$ is significantly reduced. From this it can be argued that while moisture source is in

fact an important control on $\delta^{18}\text{O}$ overall, it may not be represented in speleothem $\delta^{18}\text{O}$ in cases where the majority of precipitation was from high rainfall amount events, as opposed to the mixing of multiple low rainfall amount events. However, if there are indications that during the Pliocene the Nullarbor experienced a significantly increased frequency of precipitation events, the lower rainfall amounts excluded from this section of analysis may have more significance due to mixing effects in the soil and bedrock. This will be considered, along with other interpretations of this dataset, in **Chapter 8**, following the multi-proxy analyses of the speleothems. Despite these differences in the minimum and maximum datasets, it can still be argued that, overall, the key influences on $\delta^{18}\text{O}$ in this palaeotemperature analyses dataset are temperature and moisture source.

5.10 Conclusions

While there are limitations to the level of detail that can be achieved in these interpretations due to the short timescale of collection data obtained for this study, the data presented here have provided an invaluable insight into the influences on modern precipitation $\delta^{18}\text{O}$ in the Nullarbor region. Ideally, with the continued collection of precipitation samples in the region, further details of influences on precipitation in the region will become available. For example, such longer studies by (Hope, 2006; Hope et al., 2006) and (Smith et al., 2000a) have found important relationships between shifts in the sub-tropical jet stream, SSTs and MSLP. (Hope et al., 2006) found significant weakening of the sub-tropical jet stream and meridional temperature gradient and suggest that this has resulted in a decline in the baroclinicity required for surface cyclones in this region. This suggests that there has also been a progression towards fewer cyclone systems reaching the Nullarbor region in the past several decades. While this may potentially be evident in the isotopic values of the precipitation data obtained in this study, it is not possible to reliably say that there is evidence of a prolonged deterioration such as this due to the short time period (two years) for sample collection in this study. To this end, the modern precipitation collection will continue in the Nullarbor region beyond this study to research these longer timescale changes in modern precipitation systems and drivers. Such relationships would be of extreme interest and it is suggested that they are considered in future research of the modern precipitation of the region once a longer collection period has been obtained.

However, there are still several useful relationships that have been identified from this dataset. The various stages of interrogation can be

considered together to provide robust conclusions, which are summarised as follows:

- **$\delta^{18}\text{O}$ variation is largely driven by moisture source.**
 - Consistently (across several individual sites), the most dominant influence on $\delta^{18}\text{O}$ variation in precipitation in the Nullarbor region is moisture source. Precipitation sourced from the Southern Ocean or NCB/ Southern Ocean interactions display generally depleted $\delta^{18}\text{O}$ values in comparison to the generally enriched $\delta^{18}\text{O}$ values from tropical and Tasman influenced moisture sources.
- **The relationship between $\delta^{18}\text{O}$ and rainfall amount, is in fact also a function of moisture source.**
 - This is suggested by the strong correlation between rainfall amount and moisture source.
 - In the context of speleothem research this is of greatest importance as it suggests that it is similarly sourced palaeoprecipitation that is most likely to have infiltrated into the cave and be preserved in growing speleothems, due to the larger rainfall amounts. Alternatively, the frequency of individual events from other sources would have to increase significantly for those $\delta^{18}\text{O}$ signals to be preserved in the speleothem.
 - Higher $\delta^{18}\text{O}$ values preserved within the speleothem record, are likely to represent low-rainfall periods dominated by tropical spring to autumn rainfall that would be affected by longer residence times in the overlying soils and bedrock.
 - Periods of lower $\delta^{18}\text{O}$ values would suggest shorter residence times.

These points will be further explored following the multi-proxy analyses of the speleothems obtained from this study (see Chapter 8).

- **In general terms, higher $\delta^{18}\text{O}$ values are associated with lower rainfall amounts sourced from the tropics during spring and autumn.**
- **In general terms, lower $\delta^{18}\text{O}$ values are associated with higher rainfall amounts during winter months and sourced from Southern Ocean / NCB interactions.**

→ **There are no noticeable local effects on precipitation across the region covered by the six collection sites.**

- The site data from the six rainfall collection sites, which lie in close proximity to the caves used in this study show relatively minor variations in $\delta^{18}\text{O}$. Due to the relatively consistent topography, vegetation and climate across the region, it is unlikely that significant differences would have been found given a larger number of sampling stations around the caves. As such it can be concluded that any cave site within the area covered by the rainfall data will broadly represent the overall signal of precipitation across the southern sector of the Nullarbor region.
- This is of particular importance in consideration of the final aim of the modern precipitation analyses in this study, i.e. to aid interpretations of palaeoprecipitation signals preserved in speleothems.

6. Palaeotemperatures

6.1. Fluid-inclusion Methods

6.1.1. Preliminary Sample Preparation

Fluid-inclusion analyses were undertaken during four separate visits to the laboratories of the Quaternary Research Group at The University of Innsbruck, Austria. Two of these visits were for exploratory analyses, to assess the locations and quantities of inclusions within the various stalagmites. Subsequent visits focused on obtaining multiple samples from different layers of the speleothems from which preliminary measurements had produced successful results. For preliminary analyses, only speleothems BT (**Fig. 6.1**) and M2 (**Fig. 6.2**) were used. Sample preparation was undertaken at The University of Melbourne using a handheld dental air drill with an 800- μm diameter dental burr. Aliquots of approximately 1-1.5 g were obtained for each sample position, obtained as two solid masses from either side of the growth axis (as marked in red in **Fig. 6.1** and **Fig. 6.2**), with enough material being obtained from each layer to allow for at least one replicate analysis.

6.1.2. Subsequent Sample Preparation

Several outliers were identified from the preliminary results, for which the replicate analyses across a sample layer were not within error of each other. This issue was in retrospect assumed to result from a subsampling bias. As a result, a new strategy for subsampling was developed for all further analyses. For the preliminary samples, subsampling was achieved by drilling samples across distinct layers, and then dividing each layer somewhat randomly into smaller aliquots for analysis (**Fig. 6.3, 1**). Therefore it is likely that each

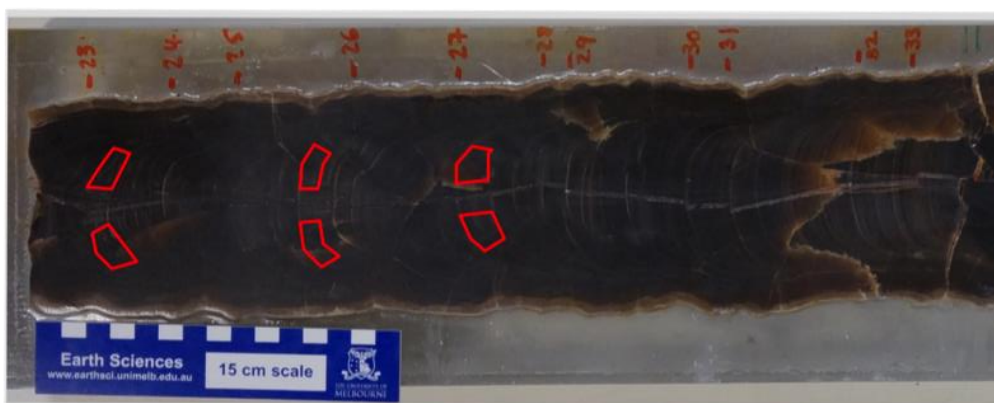


Fig. 6.1 – Investigative fluid-inclusion sampling locations from the tip of speleothem BT.

subsample disproportionately reflected the growth layers within the sample by containing higher quantities of some layers than others, unevenly across all



subsamples. For all future analyses, subsampling was conducted via drilling during the initial extraction of samples from the stalagmite to ensure that each subsample was composed of a more proportionate weight from each growth layer (**Fig. 6.3, 2**). Subsequent sampling focused on reducing the sampling spacing intervals in M2, and on obtaining results from a variety of smaller speleothems (**Fig. 6.4**). The use of additional speleothems in this aspect of the study was necessary due to the unsuitability of primary sample BT for fluid-inclusion analyses due to its insufficient water quantities. As such it was essential to use alternative samples to compare to the primary sample M2 to verify the reliability of the results obtained. While it is suggested to analyse replicate samples for all speleothem studies to increase the level of confidence in the results, it is particularly necessary when applying novel techniques such as fluid-inclusions where there are known limitations (i.e. the heterogeneous nature of fluid-inclusions), and limited ability to statistically account for potential errors in the absence of multiple analyses research and/or understanding of the complex processes at work.

Fig. 6.2 – All fluid-inclusion sampling locations in speleothem M2. For all layers, samples have been taken from either side of the growth axis to allow for adjacent traditional stable isotope analyses. For later analyses conducted after samples for conventional stable isotopes had been obtained, the fluid-inclusion sampling locations are pictured to cover the entire central section of the speleothem.

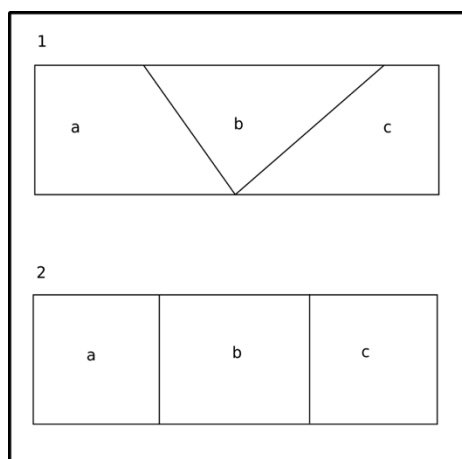


Fig. 6.3 - Fluid-inclusion sampling strategies - 1 represents the original sampling strategy used for preliminary analyses for which subsamples were randomly broken resulting in growth layers to be disproportionately represented, 2 represents the strategy used for all subsequent sampling aimed at rectifying this problem.

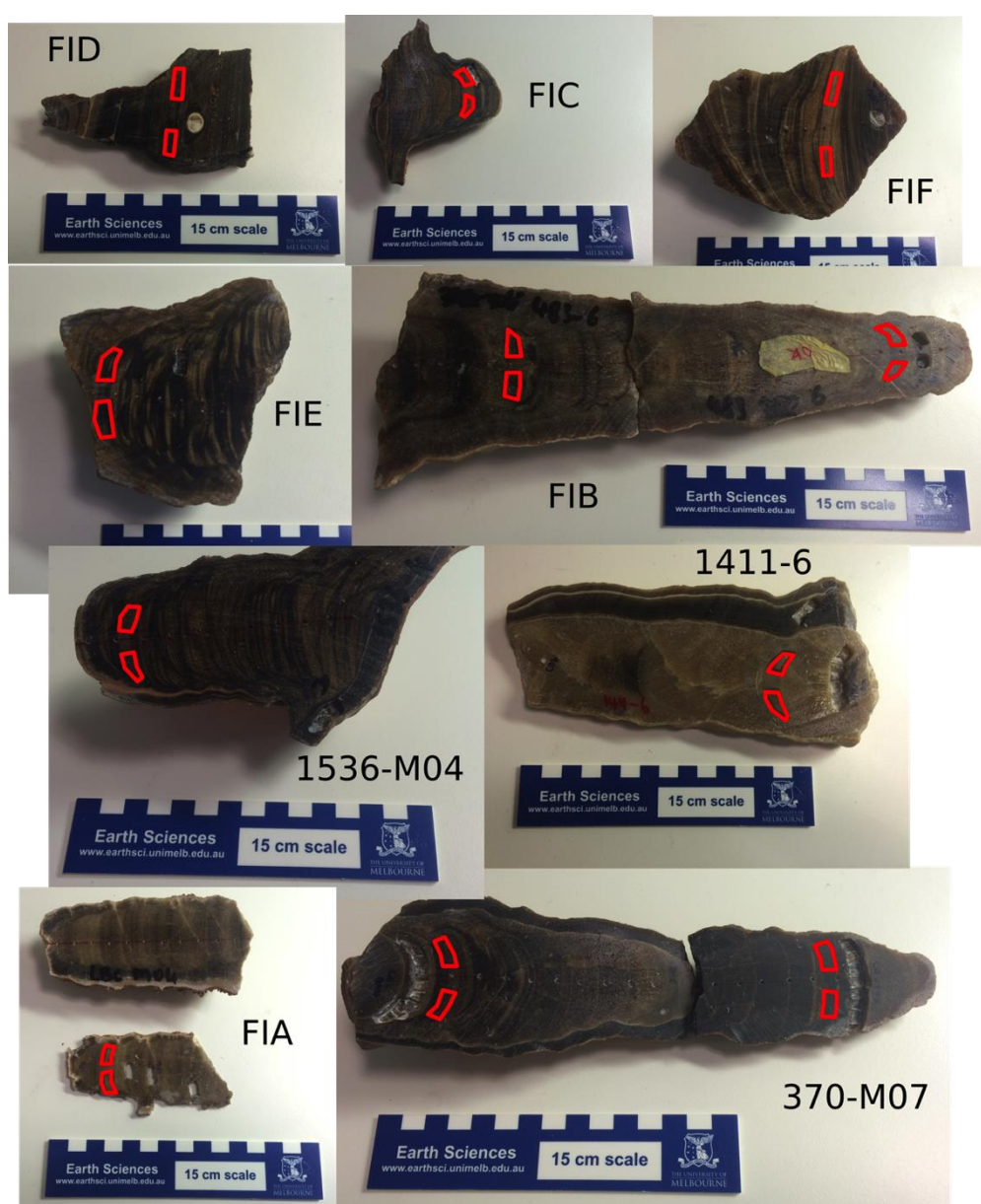


Fig. 6.4 - All additional samples used in this study, which have all been dated within the MPWP. Investigative fluid-inclusion sampling locations in red. Subsequent sampling focused on larger areas from which successful results were obtained.

6.1.3. Analysis Protocol

Fluid-inclusion analyses were conducted at The University of Innsbruck using the equipment (**Fig. 6.5**) and procedures described in Dublyansky and Spötl (2009). The only significant modification to this method was the installation of an alternative valve that is pre-fitted with a filter to prevent calcite powders being carried through the system by the helium carrier gas.

The Innsbruck method uses two in-house standards ('Haus1', and 'Tap') of known isotopic value, which were run daily at varying volumes (0.2, 0.35, and 0.5 ml) to normalise sample results to the V-SMOW scale and to allow for calibration of the results based on variable water yield. Prior to each sample being run, conditioning water of a known $\delta^2\text{H}$ value similar to that expected from the sample was injected through the crusher. In the case of Nullarbor samples, the most appropriate conditioning sample was the in-house standard 'W26' with a $\delta^2\text{H}$ composition of -60‰. The purpose of running such a standard is twofold: to reduce the potential for adsorption at various stages of the method, and to reduce the potential for memory effects in the glassy carbon tube on the measurements of the sample. To access and measure the fluid-inclusions within the speleothem, the solid aliquot(s) of sample were weighed then placed inside the online crusher, which is set on a basal plate heated to 110 °C; the entire sample transfer line is heated to this temperature from this point. Once the crusher was reconnected to the system, time was allowed for the mass spectrometer background ion-beam levels (variable daily between ~45-65 mV) to be reached.

The time necessary was variable each time the crusher was reconnected, but generally took between 30 to 60 minutes. The sample was then crushed by manual rotation of the crusher device, thus releasing the fluid-inclusions held within the sample. This liquid is vaporised in the heated chamber and carried through the heated capillary line, then trapped cryogenically in the cryo-focusing cell using liquid nitrogen to reduce the chambers temperature to -150 °C. A period of three minutes is allowed for the sample to collect in the trap, which is then flash heated at a rate of ~3,000 °C/min to a temperature of 250 °C, allowing transfer of the sample, in vapour form, into the TC/EA reactor. The reactor is set to a temperature of 1400 °C; this ensures complete pyrolysis of the sample water molecule into carbon monoxide and hydrogen. The reaction that takes place with the glassy carbon results in the evolution of molecular carbon monoxide from the oxygen. These gas molecules are separated in a chromatographic column, before being transferred to the Delta V mass spectrometer where hydrogen is first analysed, followed by carbon monoxide from which oxygen values are then

derived. The data obtained from the mass spectrometer was then reduced using an in-house programme formatted in Microsoft Excel. The data reduction involves a linearity correction to the raw data based on a regression line produced from the daily measurements of the injected standards to account for amount-dependent variability. The instrument data is also converted onto the V-SMOW scale during this process using linear regression equations developed from the relationships between instrument ratios and the known values of the standards.

6.1.4. Statistical Analyses

Once the data had been reduced it was necessary to apply further statistical analyses to allow the identification of outliers among the results. Values for the error-weighted mean, standard deviation of the error-weighted mean, and probability of fit for each of the replicated samples were then derived. Due to the variable nature of fluid-inclusion incorporation into speleothems (see **section 2.4.3**), and the uncertainties surrounding their preservation in particularly old samples, such as those used in this study, such analyses are vital for accurate and reliable interpretations.

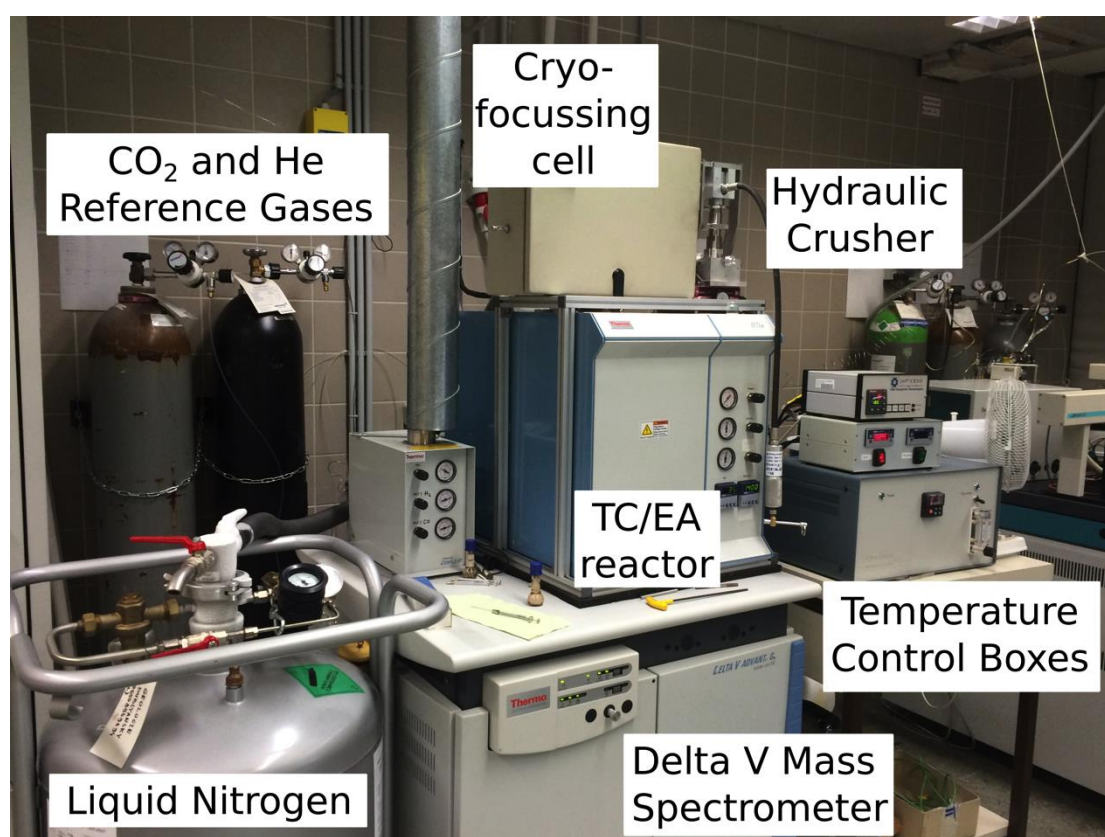


Fig. 6.5 – Annotated photograph of the fluid-inclusion line at The University of Innsbruck.

6.1.5. Stable Isotope Analysis of Fluid-Hosting Calcite

Stable isotope analyses were also conducted on the crushed calcite generated from fluid-inclusion analyses that produced successful results. The crushed calcite was collected and stored for both conventional stable isotope and clumped-isotope analyses. Each sample was individually prepared under the same procedure. To ensure complete homogenisation, the sample remnants were ground in a ball mill set to vibrate at 25 oscillations per second for 30 minutes. The contents were then passed through a 500 μm sieve, and <500 μm and >500 μm particles separated into different vials. The <500 μm fraction was used for all further analyses. The stable isotopes of these samples were run following the same conventional stable isotope analyses method discussed in **section 7.1.2** at The University of Melbourne.

As an additional test, short sections along the central growth axis adjacent to fluid-inclusion sampling were drilled for stable isotope analyses (e.g. **Fig. 6.6**). This was implemented for all samples for which a complete stable isotope profile was not obtained, and at all locations from which successful fluid-inclusion analyses were obtained. Averages were then calculated for each of these short profiles in order to assess the relationship between the calcite from the central growth access and that of the fluid-inclusion sample. This can be used to test the homogeneity of the fluid-inclusion samples and their appropriateness as a reasonable representation of the calcite isotopic composition of each sample.

6.2. Clumped-isotope Methods

6.2.1. Sample Preparation

The samples used for all clumped-isotope analyses were obtained from the homogenised powders recovered following the fluid-inclusion analyses (see **section 6.1.5**). These powders were used in lieu of drilling additional samples directly from the speleothems, as the use of the same powders allows for more

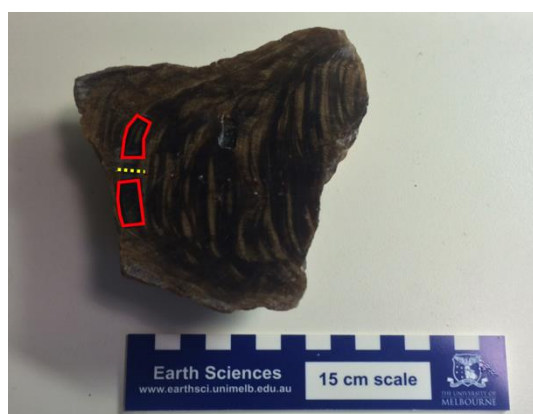


Fig. 6.6 - An example of how stable isotope profiles (yellow dashed line) were obtained parallel to fluid-inclusion locations (red boxes) in the additional speleothems.

reliable interpretations of relationships between fluid-inclusion stable isotopes, calcite conventional calcite stable isotopes, and calcite clumped-isotope palaeothermometry. Clumped-isotope analyses were conducted in three different laboratories to allow for preliminary inter-laboratory comparisons: at the CNRS-LSCE, Gif-sur-Yvette, France, at the School of Earth and Environmental Science, University of Wollongong, Australia, and at the School of Geography, University of Melbourne.

6.2.2. Sample Analyses: LSCE-CNRS Gif-sur-Yvette Laboratory

At the LSCE laboratory, subsamples of approximately 0.3 – 0.4 mg were measured out into individual foil caps. The carbonate clumped-isotope measurement system has been set up as an automated ‘online’ system using a common acid bath digestion technique (**Fig. 6.7**). Once the samples are loaded into the sample carousel, they are individually dropped into the acid bath, which is maintained at 90 °C. The gas evolved from the acid digestion is carried through the preparation system under vacuum by ultra-high purity helium carrier gas. The cryogenic removal of water is achieved as the sample gas is passed through a series of LN₂ and CO₂/EtOH slurry mix traps. These trap all condensable gases, with non-condensable gases able to be pumped away under vacuum. Volatile species that interfere with mass 47 were removed by passing the sample CO₂ through a Porapak trap. The purified CO₂ is then collected by cryogenic trapping, and transferred to the mass spectrometer for measurement via gas expansion. An Isoprime 100 dual-inlet mass spectrometer, fitted with six Faraday cups, was used. Each sample was analysed for approximately 3 hours, before the line was automatically pumped out prior to the next sample being run. A combination of calcite (ETH-1 and ETH-2) and high-temperature gas standards (Daëron et al., 2016), all prepared in the same laboratory, were also analysed throughout the sample runs for temperature calibration and to allow for monitoring of background variations and calculations of any potential drift. Further details of the methodological procedure are presented in Daëron et al. (2016). Samples and standards were prepared personally in the lab, then run at a later date by Dr Mathieu Daëron and Dr Dominique Blamart.

6.2.3. Sample Analyses: The University of Wollongong

In contrast to the LSCE laboratory, an offline preparation system is used at the University of Wollongong (**Fig. 6.8, Fig. 6.9**), which involves extracting the gas from the calcite in individual reaction vessels and flame-sealing it in Pyrex glass tubes prior to measurement on the mass spectrometer. Identical processes were used for the measurement of samples and standards. Four standards of

known isotopic composition were used: AR1 and AR2 (in house analytical reagent carbonates), and CM1 and CM2 (derived from Carrara marble). Sample sizes of approximately 7.5 – 8.0 mg of each sample (or standard), were used and weighed into individual side arm reaction vessels. 2 ml of 103% phosphoric acid was injected into the vessel before it was attached to the extraction line to be evacuated to remove atmospheric gases. The vacuum system is a version similar to those described by (Epstein et al., 1953) and (Ghosh et al., 2006a). Following the evacuation of atmospheric gases samples were equilibrated in a 25 °C water bath (controlled by a Julabo immersion heater with ± 0.1 °C precision) for 4 hours before being momentarily and individually removed for acidification. Once all reactions had been initiated, the samples remained in the water bath for 12 hours to ensure the complete reaction of the calcite powders.

To extract the gas, the reaction vessels were reattached to the extraction line through the side-arm vessel connection ports. The extraction line was then evacuated again for a minimum of 30 minutes until the target vacuum was reached. Following this, samples were then collected individually by being passed through a series of LN₂ and CO₂/EtOH slurry mix traps. Introduction of the CO₂/EtOH slurry mix allows water vapour to remain trapped while allowing the CO₂ to pass through. This “dries” the CO₂, and prepares it for the volatile

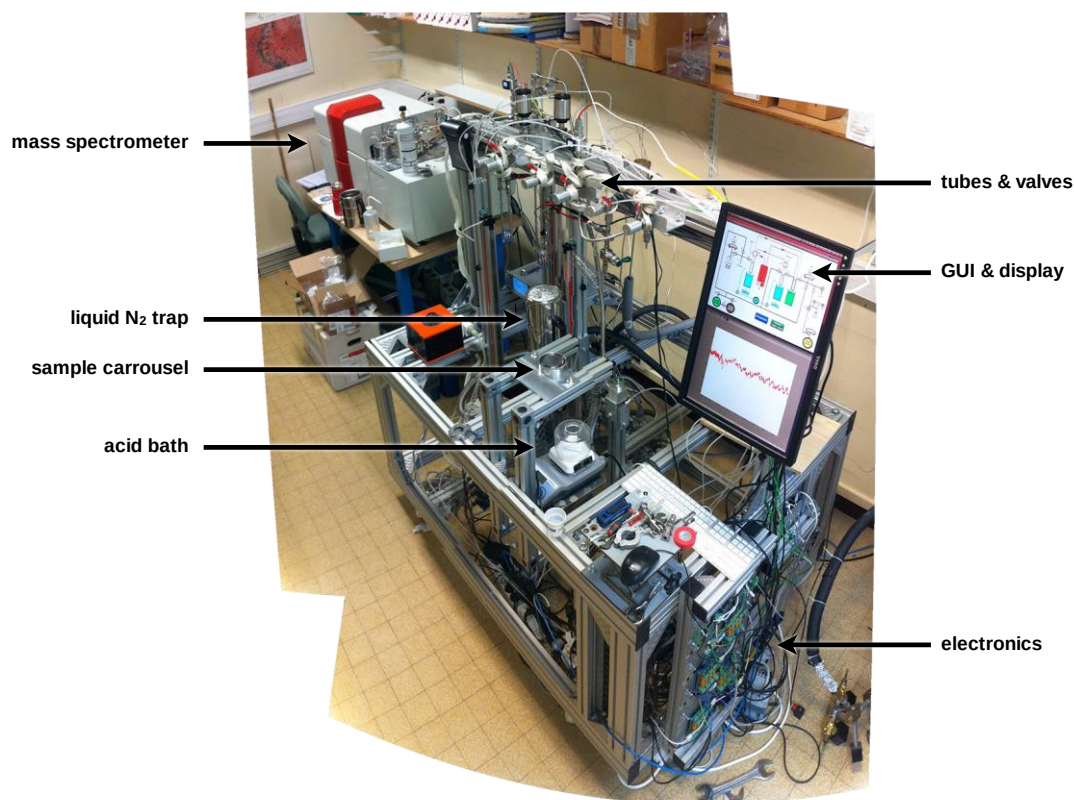


Fig. 6.7 – Photograph of the extraction line for clumped-isotope analysis preparation at LSCE-CNRS Gif-sur-Yvette Laboratory. Provided by Dr. Mathieu Daëron.

purification step. The dried CO₂ gas is then measured by freezing it using LN₂, into the area of the extraction line past the second atmosphere vent. Gas yield is then measured with a mercury filled manometer. This step is necessary for monitoring the transfer of the gases as well as for later calibration. The measured CO₂ gas is then trapped into a Pyrex glass break seal for transfer to the gas chromatograph for further purification and sealed using a propane gas torch.

Samples were then purified by using Helium to carry the CO₂ through the fused silica capillary, where it was held at -20°C for 40 minutes, prior to the CO₂ being collected in a valved stainless steel U-trap using LN₂ for collection, or to a flame ionisation detector for alternative analyses. The purpose of this stage is to remove any further gases that may remain in the sample gas after extraction. The purified sample gas was then collected in the U-trap using LN₂ and extracted using needle valves. Samples were then either transferred directly to the mass spectrometer, or reconnected to the extraction line to be resealed in glass break seals. While this stage may not always be necessary, it is used consistently as a precautionary measure due to the highly sensitive nature of the measurements

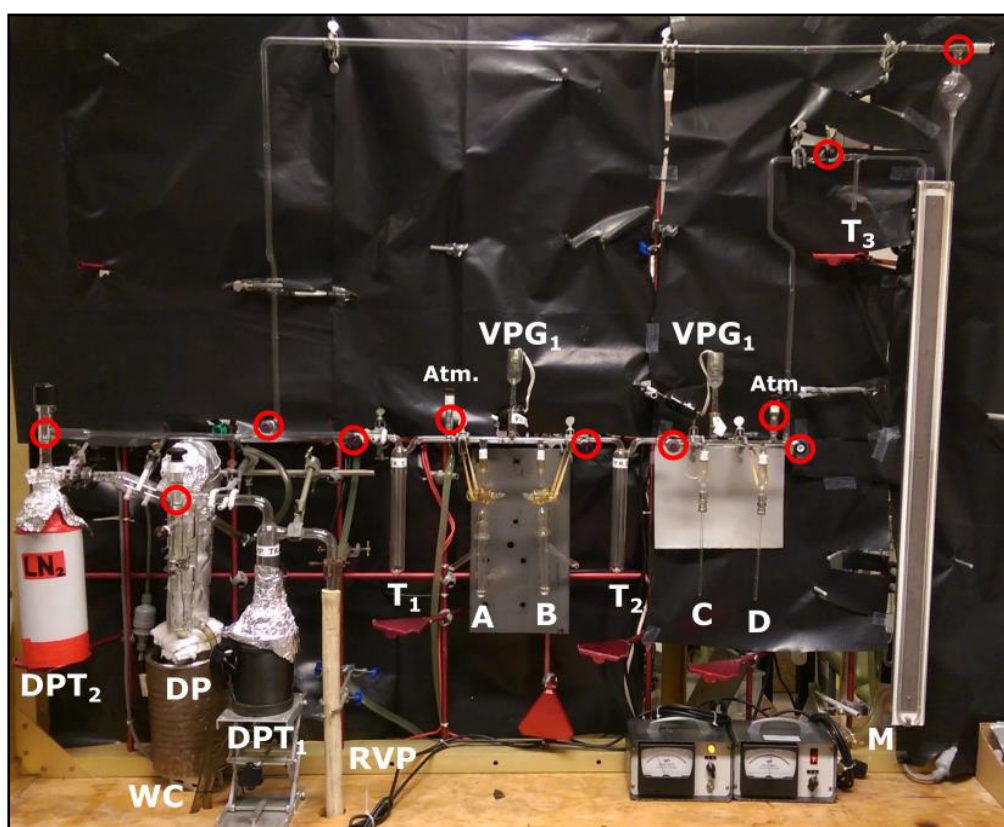


Fig. 6.8 – Photograph of the extraction line for clumped-isotope analysis preparation at The University of Wollongong, provided by Dr Florian Dux. A and B mark the side-arm vessel connection ports, C and D mark the break-seal tube connection ports, DP marks the mercury diffusion pump, T₁, T₂, and T₃ mark the removable dewar flasks.

required for clumped-isotope analyses that stem from the extremely low natural abundance of the relevant isotopes.

Gases were subsequently analysed on a Thermo Finnigan MAT 253 dual-inlet mass spectrometer fitted with eight Faraday cups. The vacuum system of the mass spectrometer was utilised along with a further liquid nitrogen trap in order to ensure the complete removal of any helium carrier gas residue from the purification process. The run time per sample was approximately four hours. Heated and equilibrated CO₂ samples were used to bring the final clumped-isotope results into the absolute reference frame. Gas extractions of samples and standards were undertaken personally, and purification and analyses at a later date by Prof. Allan Chivas and Dr Florian Dux.

6.2.4. Sample Analyses: The University of Melbourne

Analyses were also conducted at The University of Melbourne (**Fig. 6.10**) using a Nu Instruments Perspective-IS stable isotope ratio mass spectrometer, coupled to a NuCarb carbonate sample preparation system and an automated cold trap/purification system. The mass spectrometer is fitted with 10 faraday cups, allowing for the analysis of clumped-isotope ratios. Subsamples of approximately 0.4 – 0.6 mg were required for each replicate analysis. Each sample was individually injected with 120 µL of H₃PO₄, and reacted for 10 minutes at 70 °C. The evolved gas is then held in a water trap for 5 minutes at -95 °C before being passed through a PoraPak trap for 25 minutes at -34 °C, and then trapped in a LN₂ cold finger. A pressure transducer is used to estimate the sample yield before the sample is held in a second cold finger. Sample and reference gases are analysed alternately over a period of 20 minutes for each aliquot. Between each sample analysis, the absorption trap is cleaned through vacuum pumping at 150 °C to remove any potential contaminants. Alongside the sample runs, five carbonate standards (ETH-1, 2, 3, and 4, and an in-house Carrara Marble standard – NCM) were run, and used to correct the results onto the absolute reference frame. Samples were prepared and run by Dr Florian Dux and laboratory assistants at The University of Melbourne.

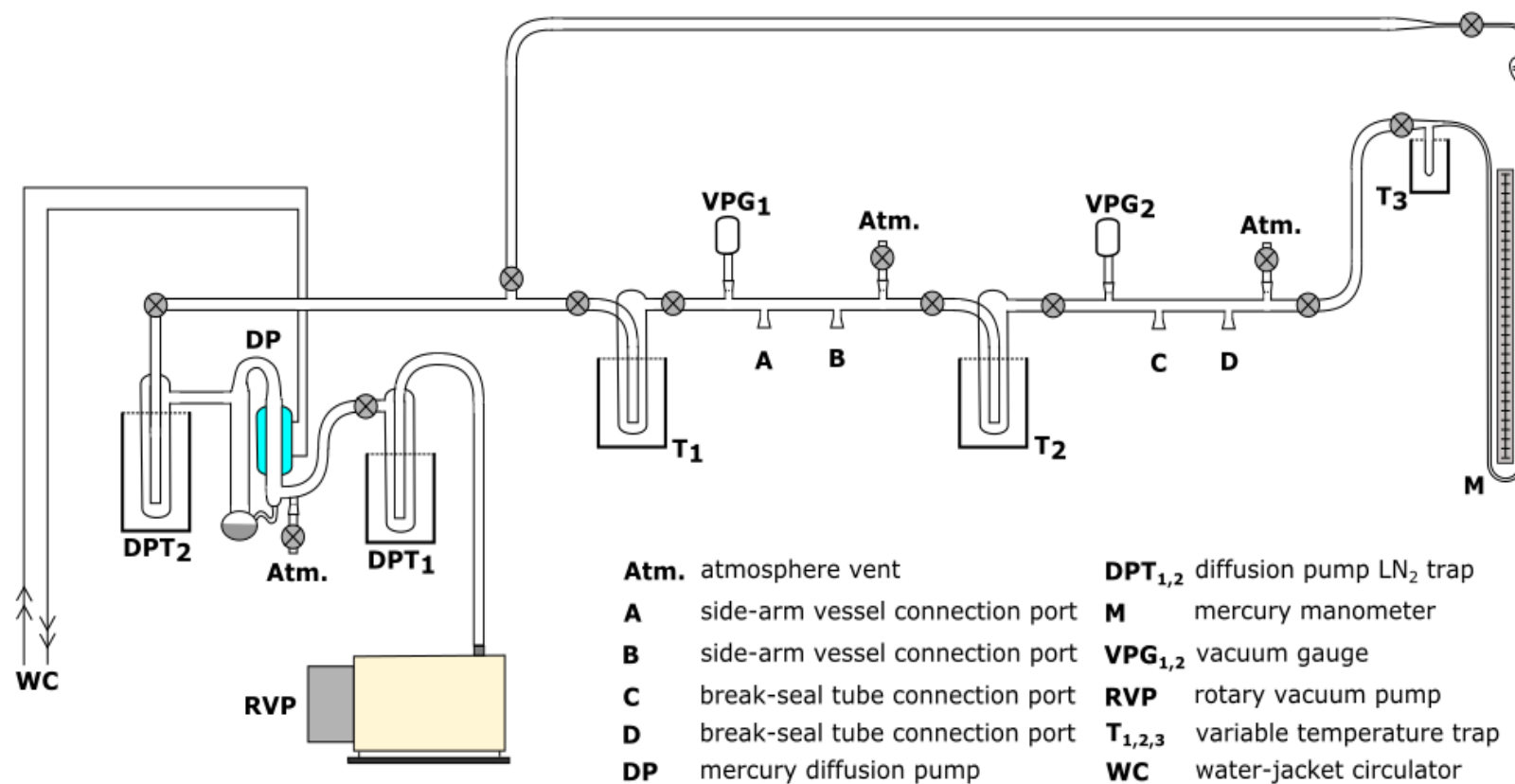


Fig. 6.9 – Schematic of the extraction line for clumped-isotope analysis preparation at The University of Wollongong, provided by Dr Florian Dux. Removable dewar flasks are represented by T₁, T₂, and T₃. A dual edged 100cm ruler is used for measurements at the monometer.

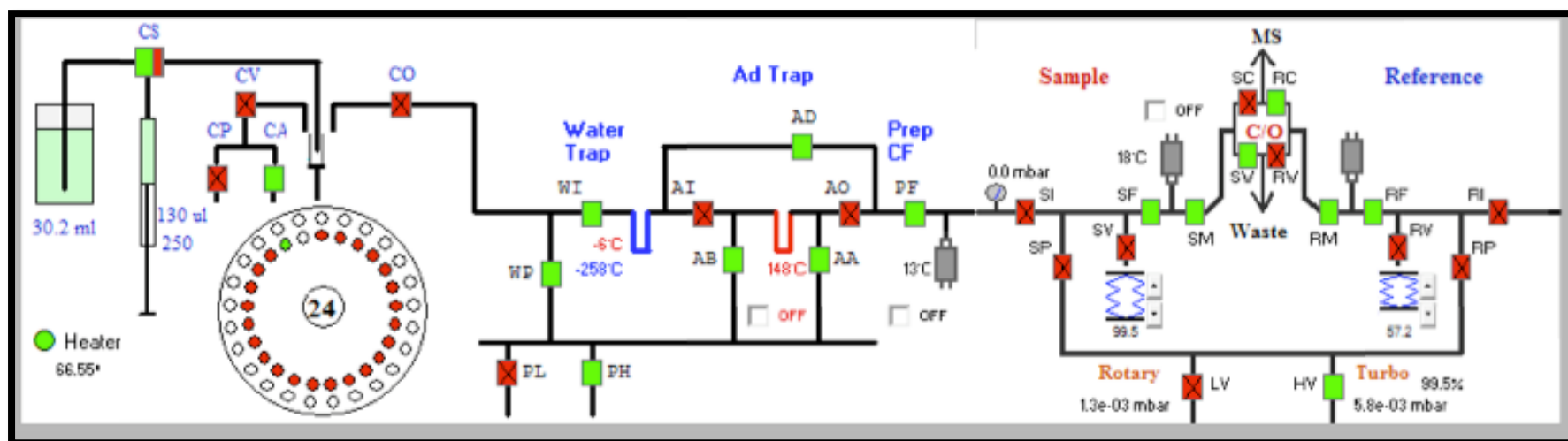


Fig. 6.10 – Schematic of the extraction line for clumped-isotope analysis preparation at The University of Melbourne. Provided by Dr. Florian Dux.

6.3. Fluid-inclusion Results and Discussion

6.3.1. Initial Treatment of Results

In total, samples were obtained from 3 layers of speleothem BT (**Fig. 6.1**), 45 layers of speleothem M2 (**Fig. 6.2**), and 50 layers from six additional speleothems (**Fig. 6.3**). This totalled 221 individual runs, including repeats (**Appendix 3**). Of these, 108 runs contained adequate water content ($>0.2 \mu\text{L/g}$) to produce measurable isotopic ratios. This is the required volume of water to produce significantly large peak areas for precise analyses (Dublyansky and Spötl, 2009). The results of all successful runs were arranged by speleothem and the layer from which they were obtained, then subjected to an elimination process in order to identify the reliable results to be used for further analyses and interpretations. Initially, all layers from which only one successful measurement was obtained were omitted, as there was no way to check the reliability of the single data points. Where multiple replicates were obtained for an individual layer, significant outliers were identified and omitted. For these samples, it was assumed that the anomalies were consistent across both $\delta^2\text{H}$ and $\delta^{18}\text{O}$.

For the remaining samples, the amount-weighted average of the measurements across each layer, and their standard deviation, was calculated; amount-weighted mean (y) has been calculated using the following equation:

$$y = \frac{(\frac{S_1}{W_1} + \frac{S_2}{W_2} + \frac{S_3}{W_3})}{(\frac{1}{W_1} + \frac{1}{W_2} + \frac{1}{W_3})}$$

where ‘ S ’ represents the subsample number and ‘ W ’ represents the water amount measured within the sample during the crushing process (S_3 and W_3 are only used for the sample which had 3 successful repetitions), any samples with a standard deviation $>\pm 5 \text{ ‰}$ for $\delta^2\text{H}$, or $>\pm 1 \text{ ‰}$ for $\delta^{18}\text{O}$ were omitted.

The final accepted results were from 29 samples, across 13 layers, of 4 different speleothems (**Table 6.1**). From these accepted results, the individual measurements ranged from -62.48 to -35.62 ‰ for $\delta^2\text{H}$, and -7.11 to -1.83 ‰ for $\delta^{18}\text{O}$. Due to the nature of fluid-inclusions and their incorporation into speleothems, water contents are not uniform across individual growth layers or along the length of a given speleothem. For this reason, amount-weighted mean values are used where applicable in analyses.

Table 6.1 – Final accepted fluid-inclusion results for all speleothems, including replicates for each layer.

Speleo- them	Layer	Sample	$\delta^2\text{H}$ (VSMOW ‰)								$\delta^{18}\text{O}$ (VSMOW ‰)							
			Rep 1	Wtr Amt	Rep 2	Wtr Amt	Rep 3	Wtr Amt	Amt Wtd Mean	SD	Rep 1	Wtr Amt	Rep 2	Wtr Amt	Rep 3	Wtr Amt	Amt Wtd Mean	SD
M2	19	FIM 13	-57.21	0.34	-51.62	0.44			-54.77	4.0	-6.57	0.34	-6.80	0.44			-6.67	0.2
	25	FIM 17	-61.13	0.31	-59.49	0.41			-60.42	1.2	-5.89	0.31	-5.48	0.41			-5.72	0.3
	26	FIM 18	-51.21	0.45	-50.13	0.51			-50.70	0.8	-6.43	0.45	-6.20	0.51			-6.32	0.2
	5	M2F 2R	-40.45	1.05	-39.32	0.51			-39.69	0.8	-6.57	1.05	-5.96	0.51			-6.16	0.4
	10	M2F 3	-36.09	1.13	-39.22	0.55			-38.20	2.2	-7.11	1.13	-6.35	0.55			-6.60	0.5
	11	M2F 3R	-37.34	0.50	-36.46	0.88			-37.02	0.6	-6.59	0.50	-5.95	0.88			-6.36	0.5
	9	M2F 6	-39.38	0.42	-40.20	0.49			-39.76	0.6	-5.99	0.42	-4.71	0.49			-5.40	0.9
	12	M2F 7	-43.81	0.48	-49.46	0.38			-46.97	4.0	-6.00	0.48	-5.29	0.38			-5.60	0.5
FIF	1	1411-11	-36.77	0.74	-35.62	1.00	-40.04	0.81	-37.58	2.3	-4.66	0.74	-6.40	1.00	-6.03	0.81	-5.62	0.9
FIA	1	2200-4	-39.57	0.53	-44.06	0.41			-42.10	3.2	-2.64	0.53	-1.83	0.41			-2.19	0.6
	2	FIA 2	-62.48	0.30	-57.83	0.29			-60.12	3.3	-3.12	0.30	-2.87	0.29			-2.99	0.2
FID	1	FID 6	-61.72	0.40	-55.26	0.57			-59.06	4.6	-3.60	0.40	-3.16	0.57			-3.41	0.3
	2	FID 7	-55.37	0.48	-53.57	0.51			-54.50	1.3	-3.91	0.48	-4.33	0.51			-4.11	0.3

6.3.2. Reduction of Data

For further analyses, results were grouped according to the speleothem and layer from which they were obtained (**Table 6.1**). From these, amount-weighted means have been calculated. There is little difference between the two values for each sample, with an average standard deviation of 0.2, and maximum of 0.9. The amount-weighted mean values are more representative of the true value across a given layer as they account for the variations in volume, and thus better represent the isotopic composition, of the whole calcite layer. Consequently, these values will be used herein.

6.3.3. Comparing Water and Calcite Stable Isotopes

Assessments of consistency between the stable isotopes of remnants of individual crushes and their adjacent transect powders were made, as well as between these powders and the stable isotopes of the inclusions themselves (**Table 6.2**). The absolute differences in the values from these analyses were low showing good correspondence between the crushed samples and the adjacent transects. The absolute differences of the homogenised remnants of each crush and the averaged adjacent transect measurements is also low, averaging at 0.12 ppm.

Table 6.2 – A comparison of $\delta^{18}\text{O}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{calcite}}$ from both fluid-inclusion sample crushes and adjacent stable isotope transects. δD calculated $\delta^{18}\text{O}$ values have been calculated using the modern GMWL. “Absolute difference (calcite)” compares the crush calcite $\delta^{18}\text{O}$ and transect calcite $\delta^{18}\text{O}$ for the purpose of assessing how representative the crush calcite is of the adjacent stable isotope transects from which they were obtained. Amount weighted values are used where applicable.

Sample	Crush Water $\delta^{18}\text{O}$ (VSMOW ‰)	δD Calculated $\delta^{18}\text{O}$ (VSMOW ‰)	Crush Calcite $\delta^{18}\text{O}$ (VPDB ‰)	Transect Calcite $\delta^{18}\text{O}$ (VPDB ‰)	Absolute difference (Calcite)
FIM 13	-6.65	-8.14	-5.14	-5.11	0.03
FIM 17	-5.74	-8.82	-5.06	-4.75	0.31
FIM 18	-6.33	-7.59	-4.80	-4.77	0.03
M2 2R	-6.08	-6.20	-4.97	-4.91	0.06
M2 3	-6.49	-6.08	-4.97	-4.95	0.02
M2 3R	-6.44	-5.89	-4.61	-5.05	0.44
M2 6	-5.45	-6.22	-5.00	-4.87	0.13
M2 7	-5.56	-7.16	-4.93	-5.02	0.09
1411-11	-5.54	-5.96	-4.56	-4.47	0.09
2200-4	-2.14	-6.55	-3.18	-3.22	0.04
FIA 2	-2.99	-8.76	-3.17	-3.41	0.24
FID 6	-3.45	-8.70	-4.45	-4.28	0.17
FID 7	-4.11	-8.07	-4.50	-4.51	0.01

This is significant as it demonstrates the level of consistency across the layers of the speleothem as well as the degree to which the samples obtained for crushes are representative of the section of speleothem from which they were obtained. The range of $\delta^{18}\text{O}$ values in the transect calcite and crush calcite measurements is very similar (1.89 and 1.97 respectively), again indicating that the crush samples are adequately representative of the layer of speleothem from which they were obtained. This strengthens confidence in the reliability of the results and supports their use in subsequent interpretations.

As discussed previously, there is a general consensus that $\delta^{18}\text{O}$ values calculated from $\delta^2\text{H}$ measurements have a greater level of reproducibility than $\delta^{18}\text{O}$ measured directly (Dennis et al., 2000; Affolter et al., 2019). Within this thesis, this theory is somewhat supported by the considerably larger range of values of the crush water amount-weighted mean $\delta^{18}\text{O}$ of -4.51, in comparison to -2.93 from the δD measurements. It is also potentially supported by the more similar values of the measured fluid-inclusion $\delta^{18}\text{O}$ to the calcite $\delta^{18}\text{O}$, as it suggests possible long-term exchange between the inclusion water and calcite (Schwarcz et al., 1976; Fleitmann et al., 2017), although this may be coincidental. Despite these possible agreements, for speleothems as ancient as those in this study, there are significant difficulties in reliably calculating $\delta^{18}\text{O}$ from δD . These largely stem from uncertainties in the appropriate MWL to apply in these calculations. As such, it is essential to assess in more detail whether the measured $\delta^{18}\text{O}$, or the $\delta^{18}\text{O}$ calculated from the δD measurements, are likely a truer representation of the original dripwater given the uncertainties associated with both. This is addressed in the following section.

6.3.4. Deriving Palaeotemperatures

As discussed in **Chapter 2**, it is theoretically possible to produce palaeotemperatures from the stable isotope analyses of fluid-inclusions and the host calcite. Initially, assessments were made between the measured $\delta^{18}\text{O}$ and the $\delta^{18}\text{O}$ derived from $\delta^2\text{H}$ measurements and using both the GMWL and the LMWL to ascertain the most reliable results. These analyses were undertaken because, while $\delta^2\text{H}$ is commonly used to calculate $\delta^{18}\text{O}$ values for use in subsequent palaeotemperature analyses (Schwarcz et al., 1976; Matthews et al., 2000; McGarry et al., 2004; Johnston et al., 2018), it has not been attempted with speleothems of the same antiquity as those in this study. As such, investigation into the most appropriate $\delta^{18}\text{O}$ values to use in these specific samples is essential.

Table 6.3 – Comparisons of the measured $\delta^{18}\text{O}$ amount-weighted mean against the amount-weighted mean $\delta^{18}\text{O}$ as calculated from the measured $\delta^2\text{H}$ and GMWL.

Sample	GMWL Calc. $\delta^{18}\text{O}$ (VSMOW ‰) Amt Wtd Mean	Measured $\delta^{18}\text{O}$ (VSMOW ‰) Amt Wtd Mean	Absolute Difference
FIM 13	-8.14	-6.65	1.49
FIM 17	-8.82	-5.74	3.08
FIM 18	-7.59	-6.33	1.26
M2 2R	-6.20	-6.08	0.12
M2 3	-6.08	-6.49	0.41
M2 3R	-5.89	-6.44	0.55
M2 6	-6.22	-5.45	0.77
M2 7	-7.16	-5.56	1.60
1411-11	-5.96	-5.54	0.42
2200-4	-6.55	-2.14	4.41
FIA 2	-8.76	-2.99	5.77
FID 6	-8.70	-3.45	5.25
FID 7	-8.07	-4.11	3.96

Table 6.4 – A comparison of the measured and calculated $\delta^{18}\text{O}$ values through their application in preliminary palaeotemperature analyses.

Sample	$\delta^{18}\text{O}$ calcite	Measured $\delta^{18}\text{O}$ Derived Temp (°C) Kim and O'Neil (1997)	Calculated $\delta^{18}\text{O}$ Derived Temp (°C) Kim and O'Neil (1997)	Measured $\delta^{18}\text{O}$ Derived Temp (°C) Craig (1965)	Calculated $\delta^{18}\text{O}$ Derived Temp (°C) Craig (1965)	Measured $\delta^{18}\text{O}$ Derived Temp (°C) O'Neil et al. (1969)	Calculated $\delta^{18}\text{O}$ Derived Temp (°C) O'Neil et al. (1969)
FIM 13	-5.14	7.1	0.8	10.9	5.5	10.5	4.7
FIM 17	-5.06	10.7	-2.3	14.1	2.9	14.0	1.8
FIM 18	-4.80	7.0	1.6	10.8	6.2	10.4	5.5
M2 2R	-4.97	8.8	8.3	12.4	11.9	12.2	11.7
M2 3	-4.97	7.0	8.8	10.8	12.4	10.4	12.2
M2 3R	-4.61	5.7	8.1	9.6	11.7	9.2	11.4
M2 6	-5.00	11.8	8.3	15.0	12.0	14.9	11.7
M2 7	-4.93	10.9	4.0	14.3	8.2	14.2	7.6
1411-11	-4.56	9.4	7.5	12.9	11.3	12.7	11.0
2200-4	-3.18	18.6	-0.7	21.4	4.2	21.6	3.3
FIA 2	-3.17	14.6	-9.3	17.7	-2.5	17.7	-4.5
FID 6	-4.45	18.5	-4.2	21.2	1.4	21.4	0.1
FID 7	-4.50	15.6	-1.5	18.6	3.6	18.6	2.5

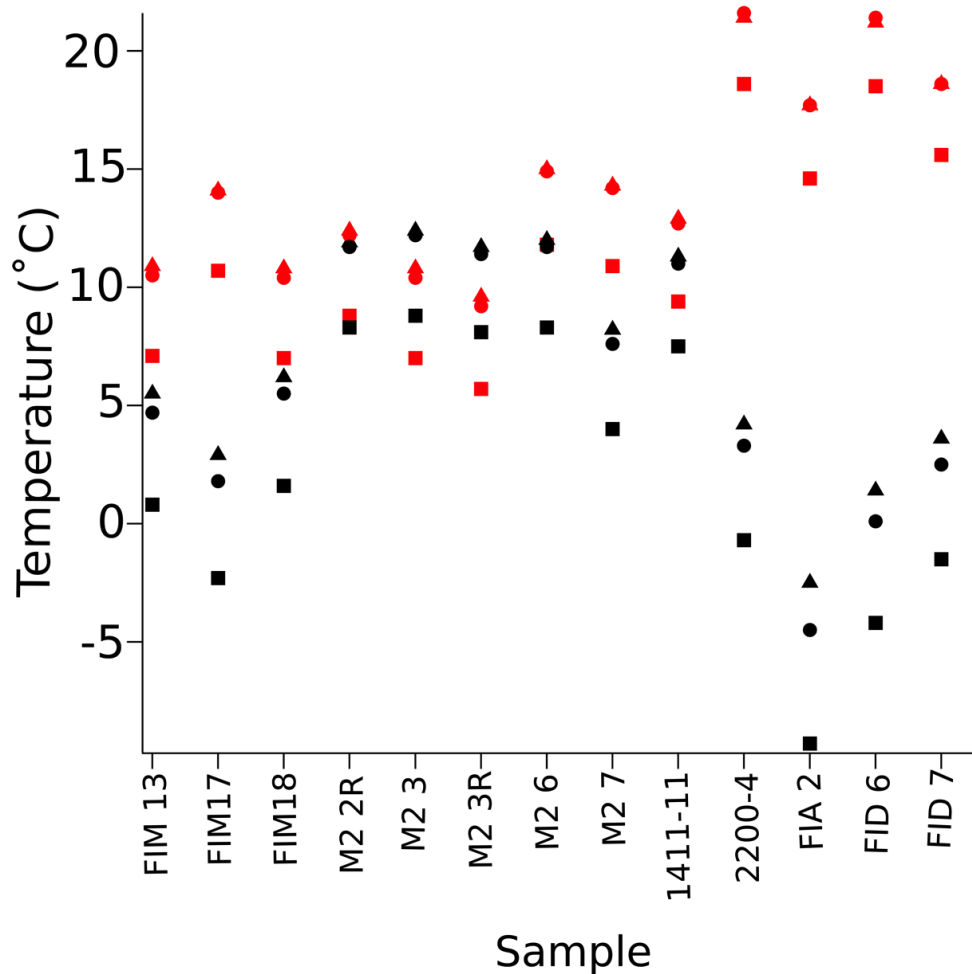


Fig. 6.11 - A plot of the temperatures obtained from the preliminary palaeotemperature analyses of measured (red) and calculated (black) $\delta^{18}\text{O}$ values of the fluid-inclusions. The markers represent the following equations: square – Kim and O’Neil (1997); triangle – Craig (1965); and circle – O’Neil et al. (1969).

Significant differences were found between the measured and calculated $\delta^{18}\text{O}$ values (**Table 6.3**), with the absolute difference between the two sets of values ranging from 0.12 to 5.77, and an average of 2.09. Preliminary attempts to derive palaeotemperatures from the two datasets highlight the significance of the differences evident (**Table 6.4, Fig. 6.11**). For these analyses the three most commonly applied equations of Kim and O’Neil (1997), Craig (1965), and O’Neil et al. (1965) were used. The extent of the variation evident is suggested to result partially from the previously discussed issues with the reliability of measured $\delta^{18}\text{O}$ values, and partially due to the expected differences between the MWL values used and the actual MWL at the time of speleothem deposition (with the

true MWL likely lying somewhere between the two), which may exacerbate the difference between the two sets of values. The temperatures derived from the calculated $\delta^{18}\text{O}$ values are consistently lower for all three equations (Craig, 1965; O'Neil et al., 1969; Kim and O'Neil, 1997), yielding in several cases negative temperature values, an impossibility due to the requirement for persistent positive centigrade temperatures for speleothem deposition. This suggests that the measured $\delta^{18}\text{O}$ values are more reliable than the calculated $\delta^{18}\text{O}$ values, and should therefore be used for further analyses. As this study is attempting to estimate palaeotemperatures of a more distant past (with an unknown MWL) than those commonly reported in speleothem studies, the most common approach of using calculated rather than measured $\delta^{18}\text{O}$ values, is arguably less applicable. This is supported by the significant uncertainties of MWLs at the time of speleothem deposition, by which the reliability of a framework from which to calculate $\delta^{18}\text{O}$ values is greatly restricted. Additionally, among the main reasons for the use of calculated $\delta^{18}\text{O}$ rather than measured $\delta^{18}\text{O}$ values, is the increased likelihood of $\delta^{18}\text{O}$ to exchange with the surrounding calcite in comparison to $\delta^2\text{H}$ (Dennis et al., 2000), whereas δD is generally unaffected by these processes (Demény et al., 2016). As the concordant isochrons produced for U-Pb dating (see **Chapter 4**) are indicative of a lack of diagenetic alteration in the speleothems used in this study (including M2), it can be suggested that this particular issue is of less relevance in this instance. As such, the measured $\delta^{18}\text{O}$ values are assumed to be the most reliable values and are used henceforth. The use of the measured $\delta^{18}\text{O}$ values in this case is further supported by the low standard deviations evident between repeated measurements from individual layers in multiple speleothems.

There are several equations (as displayed in **Chapter 2**), which have been developed for obtaining palaeotemperatures from fluid-inclusions, each producing slightly different results (**Appendix 4, Appendix 5**). It must be noted however, that none of these equations account for any potential disequilibria effects or for exchange between the $\delta^{18}\text{O}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{calcite}}$ over time. To account for this, a better understanding of palaeo-LMWs would be required to allow $\delta^{18}\text{O}$ to be calculated from the more stable $\delta^2\text{H}$. In the absence of this knowledge, the measured $\delta^{18}\text{O}$ values are used, and the subsequent temperatures produced treated with caution.

The procedure for calculating temperatures from the fluid-inclusion analyses is based upon that used by (Johnston et al., 2018), with two significant differences. Firstly, amount-weighted averages have been used in this study, and secondly, measured $\delta^{18}\text{O}$ values have been used rather than $\delta^{18}\text{O}$ values

calculated from $\delta^2\text{H}$ and a MWL. The reasoning behind both of these variations on the Johnston et al. (2018) method have been outlined previously. Temperature errors have been calculated on an individual sample basis. Amount-weighted mean values were used for each layer to calculate the $\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$ value, and the standard deviation of the replicate analyses for each sample used to calculate minimum and maximum $\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$ values (**Table 6.5**). These data were then input into the various temperature equations for each sample to derive the +/- temperature error for each equation for comparison. Calculations focused the three most commonly applied equations of Craig (1965):

$$T = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2$$

O'Neil et al. (1969):

$$1000 \ln \alpha = 2.78(10^3 T^{-1}) - 3.39$$

and Kim and O'Neil (1997):

$$1000 \ln \alpha = 18.03(10^3 T^{-1}) - 32.42$$

and a selection of more modern equations; the revised version of the Kim and O'Neil (1997) equation as developed by Kim et al. (2007):

$$1000 \ln \alpha = 3.59(10^3 T^{-1}) - 1.79$$

the equation of Tremaine et al. (2011):

$$1000 \ln \alpha = 16.1(10^3 T^{-1}) - 24.6$$

and that of Daëron et al. (2019):

$$1000 \ln \alpha = 17.57(10^3 T^{-1}) - 29.13$$

While it was considered pertinent to calculate the temperatures from numerous equations for comparison, the suitability of the applied equations was first considered. Firstly, the Craig (1965) equation is not deemed to be suitable, as it is a non-linear polynomial equation. The equation of O'Neil et al. (1969) was developed using largely high-temperature carbonates formed under

hydrothermal-like conditions, it is therefore argued to be less applicable to speleothems than alternative equations.

Table 6.5 – The standard deviation of $\delta^{18}\text{O}$ water subsamples and replicate analyses for each layer (see Table 7.1), and the $\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$ data used for the temperature error calculations. Minimum and maximum $\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$ values are calculated using the standard deviation of the replicate analyses.

Sample	$\delta^{18}\text{O}_{\text{calcite}}$	$\delta^{18}\text{O}_{\text{water}}$	Std Dev of $\delta^{18}\text{O}$ Water subsamples	$\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$	Minimum $\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$	Maximum $\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$
FIM 13	-5.14	-6.65	0.16	1.51	1.35	1.67
FIM 17	-5.06	-5.74	0.29	0.68	0.39	0.97
FIM 18	-4.80	-6.33	0.16	1.53	1.37	1.69
M2 2R	-4.97	-6.08	0.43	1.11	0.68	1.54
M2 3	-4.97	-6.49	0.54	1.53	0.98	2.07
M2 3R	-4.61	-6.44	0.45	1.83	1.38	2.28
M2 6	-5.00	-5.45	0.90	0.45	-0.45	1.35
M2 7	-4.93	-5.56	0.50	0.63	0.13	1.13
1411-11	-4.56	-5.54	0.91	0.98	0.07	1.89
2200-4	-3.18	-2.14	0.57	-1.04	-1.61	-0.47
FIA 2	-3.17	-2.99	0.17	-0.18	-0.35	-0.01
FID 6	-4.45	-3.45	0.31	-1.00	-1.31	-0.69
FID 7	-4.50	-4.11	0.30	-0.39	-0.69	-0.09

Table 6.6 – The temperatures and errors produced by the palaeotemperature equation of Tremain et al. (2011).

Sample	$\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$	T (°C)	+/- T (°C)
FIM 13	1.51	11.4	0.9
FIM 17	0.68	15.7	1.5
FIM 18	1.53	11.4	0.8
M2 2R	1.11	13.5	2.2
M2 3	1.53	11.4	2.8
M2 3R	1.83	9.8	2.3
M2 6	0.45	16.9	4.8
M2 7	0.63	16.0	2.7
1411-11	0.98	14.2	4.8
2200-4	-1.04	25.0	3.2
FIA 2	-0.18	20.3	0.9
FID 6	-1.00	24.7	1.7
FID 7	-0.39	21.4	1.6

For this reason, the use of this equation has also been deemed inappropriate. The Kim and O'Neil (1996) equation is also considered inappropriate, as it has been shown to produce consistently lower than expected (and in many cases lower than possible) temperatures (Coplen, 2007; Zhang et al., 2008). The updated equation (Kim et al., 2007) appears to produce temperatures only marginally higher than the Kim et al. (2007) equation; considering the 8 °C offset noted using the original equation (Coplen, 2007), it is still considered to be unrealistically low. Both the equations of Tremaine et al. (2011) and Daëron et al. (2019) have the advantage of having been developed from in-situ cave studies, as opposed to laboratory-based experiments as is the case for the previously discussed equations. While this is associated with some uncertainty to the application of speleothems in other locations due to the site-specific parameters used for developing the equations, it makes them arguably more appropriate to use for deriving palaeotemperatures from ancient speleothems where site-specific modern cave monitoring is not possible. The Daëron et al. (2019) equation is used in place of the Coplen (2007) equation, as their data from slow growing sub-aqueous calcite was found to be in agreement with the predicted line from Coplen (2007), thus validating the original equation but refined with additional data. Both equations produced significantly higher temperatures than that of Kim et al. (2007), which is argued to result from the significantly different states of equilibrium under which the laboratory and cave calcites formed (Tremaine et al., 2011; Daëron et al., 2019). For this study the equation of Tremaine et al. (2011) will be used as the Daëron et al. (2019) equation is based upon very slow growing sub-aqueous calcite deposits, which were arguably formed under conditions much closer to equilibrium than is common amongst speleothems (Daëron et al., 2019), thus making it less applicable to this study.

Therefore, the results of the Tremaine et al. (2011) equation (**Table 6.6**) were used for further analyses of sample M2 in order to assess the apparent temperature variation across the growth period of the speleothem (**Fig. 6.12**). These results suggest fluctuations in temperature throughout the growth of the sample, with a minimum temperature of 9.8 °C, a maximum temperature of 16.9 °C, (or inclusive of errors a minimum temperature of 7.5 °C, and maximum temperature of 21.7 °C) and an average temperature of 13.3 °C, considerably lower than the modern day average temperature of the Nullarbor of 18 °C. While these temperatures are theoretically possible for speleothem growth, they are not in keeping with current understanding of global temperatures during this time period, by which temperature 2-4 °C warmer than present would be

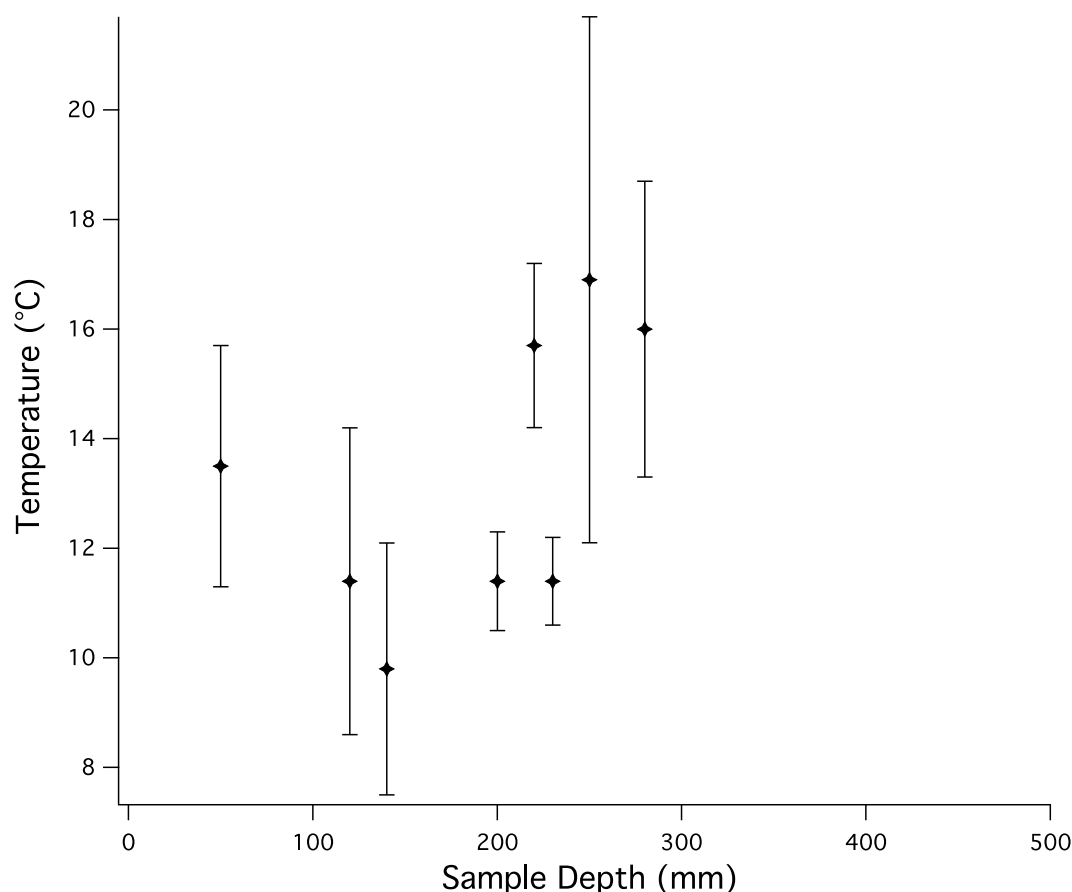


Fig. 6.12 – Final accepted palaeotemperatures from speleothem M2, displayed in reference to their approximate sample depth (precise locations not used due to the large sample sizes encompassing several mm down the growth axis).

expected, based on the modelled global average of 3-4 °C warmer (Crowley, 1996; Haywood et al., 2009), and the modelled increase for the Nullarbor of 2-3 °C warmer than present (Salzmann et al., 2011). It is possible that parts of speleothem M2 and the additional speleothems may represent cooler periods within the Pliocene; however, it is highly unlikely that these cooler stadials encompass their entire growth periods. Therefore, the consistently cooler temperatures produced are unlikely to be representative of the absolute temperatures at the time of speleothem deposition.

It can be argued that the key problem in resolving accurate palaeotemperatures here is in the equation itself, as there is no certainty in the fractionation factors applied, as highlighted by the notable difference between average temperatures and ranges of values produced by different equations (**Appendix 4**). Ideally the fractionation factor used should be site specific to account for local and cave conditions. As such, without a detailed understanding of local conditions at the time of deposition, which is not possible in this study

due to the age of the speleothems, and the lack of modern speleothem growth in the Nullarbor region, there will always be uncertainties in the fluid-inclusion derived palaeotemperatures. While knowledge of cave topology provides some constraints, for example sample locations in relation to known entrances, it is not possible to account for significant changes in important factors such as cave ventilation, therefore such constraints must be applied with caution. Nevertheless, as the issue is suggested to relate to the fractionation factor applied in the palaeotemperature equation, any error should be systematic across all samples, although it is possible that there is some variation in the fractionation factor across the growth period of the speleothems. However, it is argued that this variation would not be sufficient to explain the level of variability evident in this data, and it can therefore be reasonably argued that while the precise temperatures may not be accurate, the fact that this level of variation exists within the speleothem profile represents significant temperature variations during its period of growth. This is in agreement with previous research on the Pliocene, which has identified variations in both temperature and precipitation, likely on a time scale of several thousand years (Leroy and Dupont, 1994; Lawrence et al., 2006). Speleothem M2 does not appear to display a trend of gradual cooling that we know to have occurred throughout the Pliocene (Haywood et al., 2009), however it may be that this gradual decrease in temperature is concealed with the errors of the calculated temperatures. Alternatively, it is possible that the speleothem growth occurred over too few years to display this long-term trend over the low-frequency (long timescale) variations. If accepting the lowest calculated temperature at 9.8 °C, this is comparable to the temperature of Australia during the Last Glacial Maximum, which has been calculated to have been at least 9 °C cooler than today (Miller et al., 1997; Hesse et al., 2004). While we argue that some level of temperature variation was present during the MPWP, based on other studies of the period (De Schepper et al., 2014) it is improbable that temperatures would have dropped this low for long enough periods to have been preserved in the speleothem signal. The highest temperature calculated from speleothem M2 is 16.9 °C, approximately 1 °C cooler than present, further suggest that the calculated temperatures are too low. While it is possible that speleothem M2 represents a cooler period within the MPWP, it is more likely that the true temperature lies in the upper end of the margin of error associated with these calculations, with the higher temperatures from the complete dataset representing particularly warm periods. As such, it was deemed necessary to apply the use of an alternative

method (i.e. clumped-isotope analyses) to attempt to refine Pliocene palaeotemperature estimates from the Nullarbor speleothems.

6.3.5. Developing a Palaeo- LMWL

The results from the individual fluid-inclusion measurements were compiled and used to construct a LMWL (**Fig. 6.13**), and are shown in comparison to the modern LMWL and GMWL in **Fig. 6.14**. There is no correlation between δD and $\delta^{18}O$, and the line of best fit has a negative slope, which is an impossibility. Although the apparent lack of a positive slope is likely a function of the relatively small spread of the fluid-inclusion dataset (compared to the large range of values typically observed for developing LMWLs from modern precipitation), it may also be a consequence of the considerable random scatter evident in the fluid-inclusion data. Theoretically, this may result from errors in the measurement of the fluid-inclusion $\delta^{18}O$, or as a function of them being uniformly affected by diagenesis. The former can be ruled out in most cases due to the good reproducibility of replicate analyses. The latter is also unlikely given the ability for U-Pb ages to be produced from the speleothems, and the reliance of this method on a lack of diagenetic alteration. It is therefore argued to either result from the smaller dataset than typically used for developing LMWLs, or due to the true relationship being obscured within the accepted errors of the individual measurements.

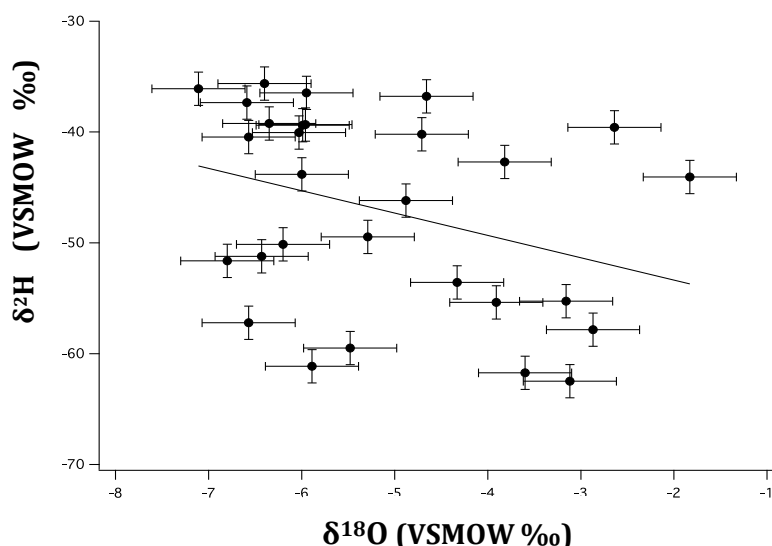


Fig. 6.13 – LMWL derived from all accepted fluid-inclusion results, accounting for errors in both $\delta^{18}O$ and δ^2H .

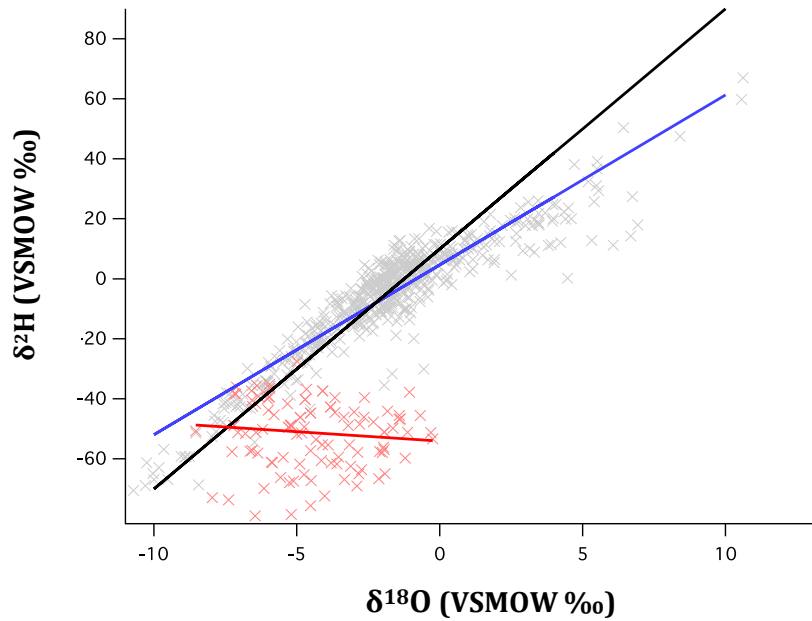


Fig. 6.14 – A comparison of meteoric water lines –GMWL in black, LMWL for the Nullarbor as calculated from modern precipitation isotope data in blue. The raw modern precipitation isotope data is shown in light grey, and the raw fluid-inclusion data in light red. As the palaeo LMWL for the Nullarbor derived from fluid-inclusion isotope data has been shown to be impossible, the red line shows the line of best fit through the fluid-inclusion data.

6.3.6. *Palaeoprecipitation*

In addition to the use of the fluid-inclusion data for deriving palaeotemperatures, it is also possible to use them to make interpretations about palaeoprecipitation (Griffiths et al., 2010; Fleitmann et al., 2017). As fluid-inclusions are theoretically representative of the drip waters from which the speleothems formed, which in itself is representative of the precipitation above the cave, it is possible to use them to make interpretations about influences on precipitation $\delta^{18}\text{O}$ such as moisture source. Such interpretations can be greatly improved through the application of modern precipitation studies and analyses, such as those presented in **Chapter 5**. As this chapter is focused on the ability to obtain palaeotemperatures from ancient speleothems, the potential for palaeoprecipitation analyses from fluid-inclusions will be discussed as part of the multi-proxy analyses in **Chapter 7**.

6.3.7. *Further Research Required*

As a consequence of the methodological issues associated with fluid-inclusion analyses, advances in the application of the method are required to better constrain past meteoric water lines. It is argued that obtaining larger datasets would not help to better constrain past meteoric water lines. This is

evident from the inability to derive a LMWL from the relatively large fluid-inclusion dataset produced in this study. However, when using modern data for deriving MWLs, significantly larger datasets are commonly used; therefore it is possible that more extensive fluid-inclusion studies may obtain the degree of scatter required for the development of a LMWL. However, the number of samples generally used for the development of LMWLs are not readily achievable in fluid inclusion analyses (due to the large sample sizes required and limited appropriate speleothems available), therefore, attempts must be made to reduce the sample sizes required for measurement, and to improve the precision of the measurements. Advances in these two areas will improve the reliability of any MWLs developed, and are also vital for the accurate estimation of palaeotemperatures using fluid-inclusions alone. Developments in this field will significantly advance the potential of speleothems, providing them with the capacity to provide reliable insight into palaeoprecipitation and to produce precise, independent estimates of and palaeotemperatures.

There is also a need for further research into the potential application of multi-proxy approaches using fluid-inclusions. This includes exploring the potential of noble gas abundances within fluid-inclusions and further investigation of the use of carbonate clumped-isotope palaeothermometry alongside fluid-inclusions to solve the palaeotemperature equation more reliably.

6.4. Clumped-isotope Results and Discussion

6.4.1. Initial Treatment of Results

In total, samples from four layers of speleothem M2, and one layer from each of the four the smaller speleothems were obtained. Each layer was represented by two or more subsamples for which reliable fluid-inclusion measurements were obtained. Of these samples, two layers were analysed at the LSCE, seven layers were analysed at The University of Wollongong, and three layers at The University of Melbourne (**Table 6.7**). At the LSCE and The University of Wollongong laboratories, three replicates were measured for each subsample; at The University of Melbourne, a minimum of four replicate were measured for each subsample; only successful measurements are presented here. Subsamples for which only one measurement was obtained were still used in calculating averages across complete layers, as there were always still multiple samples from within the same layer, which could be averaged and analysed. However, there were four subsamples from The University of Wollongong for which the temperatures (using the Zaarur et al., (2013)

calibration) produced were very low or negative, which is an impossibility due to the nature of speleothem growth. These anomalous results are suggested to result from contamination during sample preparation, however it is not possible to determine at which stage such contamination may have occurred. There are several opportunities for contamination during the sealing of the break seals, or for cracks to develop in the vials at a later time (a cause of the loss of several samples prior to measurement). Accordingly, these samples were omitted from further consideration. There were no layers for which only a single clumped-isotope result was obtained, and as such all layers for which samples have been analysed are presented here.

To allow direct comparisons of Δ_{47} measurements across different laboratories, raw measurements must be converted onto an absolute reference frame. This is achieved through a number of steps. Firstly, samples must be corrected for any non-linearity effects resulting from the mass spectrometric analysis (i.e. isotopic scrambling – Huntington et al., 2009); this is rectified through standard sample measurements to create a linear trend from which the difference between the equilibrated and working gases can be calculated. At this stage, the raw values must then be converted into the absolute reference frame to allow for inter-laboratory comparisons. The precise empirical transfer functions applied for this conversion vary between laboratories and have evolved over time as a result of variations in instrument set-up and methods, and as an increasing number of standards are run.

Once converted onto the absolute reference frame, sample measurements are then used to determine palaeotemperatures. Due to the differences in methods, different calibration processes are also required for the calculation of temperature from the absolute Δ_{47} measurements. Numerous Δ_{47} - T calibration equations have been developed using natural biogenic and abiogenic carbonates, and synthetic carbonate precipitation experiments. As with the palaeotemperature equations, each of these calibration curves produces different temperatures, as shown in **Fig. 2.11**. While it is not entirely appropriate to directly compare calibrations made with different standards (i.e. gas or calcite) in this way, this figure exemplifies the degree of variation evident from the different calibrations.

The calibration curve applied to a given sample is dependent on both the type of carbonate being analysed, and the preferences of a laboratory (related to the details of the methods used). For the samples run at The University of Wollongong, the following calibration was used:

$$\Delta_{47} = (0.0555 \pm 0.0027) \times 10^6 \times T^2 - (0.0780 \pm 0.0298)$$

(Zaarur et al., 2013)

The application of this equation to the samples is justified by the similarities in the methodological approaches used in the development of the equation and in the measurement of the samples including the acid-digestion temperature, purification technique, and range of formation temperatures assessed. For the samples run at LSCE and The University of Melbourne, the following calibration was used:

$$\Delta_{47} = \frac{40761}{T^2} - 0.4897 + \Delta_{47-ETH3}$$

(Daëron, 2016, pers. comm.)

where $\Delta_{47-ETH3}$ is the average in-house measured value of the ETH-3 standard. This equation has been developed at the LSCE laboratory using the measurement of synthetic calibration samples. It has also been applied to The University of Melbourne data for consistency and ease of comparison between the two online systems for clumped-isotope analyses.

Table 6.7 – A summary of the clumped-isotope data obtained from The University of Wollongong (highlighted in grey), LSCE (highlighted in red), The University of Melbourne (blue). Δ_{47} (‰) values are presented alongside their calculated temperature and 2 SD errors. Temperatures from The University of Wollongong are calculated using the Zaarur et al. (2013) calibration, and from The University of Melbourne and LSCE using the Daëron (2016, pers. comm.) calibration.

Laboratory	Speleo- them	Sample Layer	Sub- sample	Replicate	Δ_{47} (‰)	T (°C)	± (°C)
LSCE	M2	2R	1	a	0.604	33.8	4.5
				b	0.615	29.9	4.5
				c	0.585	40.7	4.5
			2	a	0.598	35.9	4.5
				b	0.609	32.0	4.5
				c	0.598	35.9	4.5
			3	a	0.585	40.7	4.5
				b	0.626	26.3	4.5
				c	0.577	43.8	4.5
	M2	3R	1	a	0.623	27.2	4.5
				b	0.604	33.8	4.5
				c	0.600	35.2	4.5
			2	a	0.619	28.6	4.5

				b	0.595	37.0	4.5
				c	0.625	26.6	4.5
The University of Wollongong	FIE	8	a	1	0.717	21.6	7.1
				2	0.710	23.2	6.0
			b	1	0.726	19.5	8.2
				2	0.736	17.3	4.8
	FIA	2	a	1	0.668	33.6	6.6
				2	0.684	29.5	6.4
			b	1	0.719	21.1	6.9
				2	0.720	20.9	6.4
	FIM	17	a	1	0.664	34.6	5.9
				2	0.659	35.9	2.9
			b	1	0.726	19.5	4.8
				2	0.733	17.9	5.8
				3	0.749	14.4	6.6
	FID	7	a	1	0.738	16.8	4.6
			d	1	0.718	21.3	5.9
				2	0.709	23.4	3.1
	1411	11	a	1	0.705	24.4	3.4
			e	1	0.753	13.6	4.4
	M2	3R	2	1	0.680	30.5	7.4
				2	0.675	31.8	2.9
				3	0.666	34.1	5.1
	M2	6	1	1	0.740	16.4	5.7
				2	0.722	20.4	2.7
			2	1	0.717	21.6	7.2
				2	0.718	21.3	7.8
The University of Melbourne	M2	2R	1	1	0.664	23.8	8.2
				2	0.690	15.8	9.5
				3	0.644	30.1	10.1
				4	0.696	13.8	8.1
				5	0.724	6.2	7.5
			2	1	0.694	14.5	8.1
				2	0.684	17.4	7.1
				3	0.630	35.2	12.2
				4	0.680	18.7	7.1
				5	0.678	19.1	9.1
		3R	1	1	0.676	20.0	7.8
				2	0.633	34.3	11.3
				3	0.685	17.2	7.0
				4	0.682	18.1	10.4
			2	1	0.656	26.1	6.3
				2	0.656	26.2	9.0
				3	0.683	17.6	7.7
				4	0.670	21.7	8.6

				1	0.690	15.6	8.2
				2	0.659	25.2	9.0
		6	2	3	0.641	31.4	10.3
				4	0.672	21.1	10.7
				5	0.685	17.2	9.7

6.4.2. Comparisons of Carbon and Oxygen Stable Isotope Measurements

During the process of clumped-isotope analyses, measurements are also obtained for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. As such, these have been compared to the measurements obtained from the traditional stable isotope analyses of both the fluid-inclusion remnant powders. While the accuracy of $\delta^{18}\text{O}$ measurements are reduced due to the tuning parameters required to optimise Δ_{47} measurements (Daëron, 2017, pers. comm.), if significant contamination had occurred during the extraction and preparation of the CO_2 gas for clumped-isotope analyses (for example exchange with water in the line or dirty samples), one would expect this to be reflected in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results as well as in the Δ_{47} measurements. The comparison of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values derived from both clumped-isotope analyses and traditional stable isotope analyses from the crush remnants is presented in **Table 6.8**. The most significant deviation, or offset, between the two sets of measurements is in the $\delta^{18}\text{O}$ obtained from the clumped-isotope analyses at the LSCE laboratory. The degree and consistency of the offset could be indicative of the previously discussed sample splashback and resulting memory effect issues, or it may simply be an effect of the greater number of replicate analyses run for each sample, which tends to result in increased accuracy and higher precision. However, as the clumped-isotope measurements of $\delta^{18}\text{O}$ from The University of Wollongong are in much stronger agreement with the traditional stable isotope measurements, it can be assumed that the aforementioned deviation relates to the clumped-isotope analyses undertaken at LSCE. Excluding these data, the remaining dataset seems to be in reasonable agreement. While not always within standard deviation of each other, the differences can be explained by the large sample sizes from which the individual analyses were run. Due to these large sample sizes, the degree of differences apparent can be explained by incomplete homogenisation of the samples. Despite efforts to homogenise the crush remnants from fluid-inclusion analyses, it is possible that in subsampling these remnants, slight differences in the isotopic signatures would be captured. This is not deemed to reflect the reliability of the clumped-isotope data or palaeotemperatures produced, due to the well-understood limitations to the precision of conventional isotope data during clumped-isotope measurements.

Table 6.8 – A comparison of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values obtained from clumped-isotope analyses and traditional stable isotope analyses of the fluid-inclusion crush remnants. Shading indicates the laboratory at which clumped-isotope analyses were undertaken – The University of Wollongong (highlighted in grey), LSCE (highlighted in red), The University of Melbourne (highlighted in blue).

Sample	Clumped-isotope Analyses				Stable Isotope Analyses				Within SD (Y/N)	
	$\delta^{13}\text{C}$ (VPDB ‰)	SD	$\delta^{18}\text{O}$ (VPDB ‰)	SD	$\delta^{13}\text{C}$ (VPDB ‰)	SD	$\delta^{18}\text{O}$ (VPDB ‰)	SD	$\delta^{13}\text{C}$ (VPDB ‰)	$\delta^{18}\text{O}$ (VPDB ‰)
FIE 8 a	-9.27	0.01	-5.07	0.05	-9.21	0.08	-5.05	0.06	Y	Y
FIE 8 b	-9.69	0.71	-4.99	0.17	-9.02	0.06	-5.04	0.05	Y	Y
FIA 2 a	-6.73	0.01	-3.83	0.01	-6.58	0.12	-3.09	0.04	N	N
FIA 2 b	-6.63	0.00	-3.01	0.04	-6.53	0.07	-3.25	0.15	N	N
FIM 17 a	-10.12	0.13	-5.26	0.37	-9.85	0.08	-4.96	0.16	N	Y
FIM 17 b	-10.08	0.62	-5.39	0.48	-10.19	0.02	-5.16	0.09	Y	Y
FID 7 a	-11.51	0.01	-4.33	0.01	-11.34	0.04	-4.41	0.03	N	N
FID 7 c	-11.57	0.00	-4.43	0.05	-11.40	0.04	-4.62	0.01	N	N
FID 7 d	-11.56	0.02	-4.27	0.09	-11.42	0.05	-4.55	0.12	N	N
1411.11 a	-9.47	0.01	-4.56	0.02	-9.36	0.04	-4.51	0.08	N	Y
1411.11 e	-9.38	0.01	-4.60	0.02	-9.25	0.05	-4.55	0.11	N	Y
M2 3R 1	-9.22	0.01	-4.43	0.02	-9.10	0.04	-4.62	0.03	N	N
M2 3R 2	-9.43	0.01	-4.95	0.04	-8.96	0.03	-4.59	0.04	N	N
M2 6.1	-9.95	0.01	-4.74	0.24	-9.90	0.03	-4.95	0.10	N	Y
M2 6.2	-10.21	0.27	-4.89	0.03	-10.00	0.08	-5.05	0.01	Y	N
CIC	-10.46	0.05	-8.33	0.04	-10.59	0.04	-5.20	0.04	N	N
CIT	-10.62	0.01	-8.33	0.07	-10.63	0.03	-5.25	0.07	Y	N
M2 2R 1	-9.40	0.00	-8.07	0.04	-9.40	0.06	-4.99	0.10	Y	N
M2 2R 2	-9.10	0.01	-8.03	0.08	-9.09	0.02	-4.95	0.04	Y	N
M2 2R 3	-9.07	0.00	-8.09	0.05	-9.07	0.03	-4.95	0.09	Y	N
M2 3R 1	-9.10	0.02	-7.69	0.04	-9.10	0.04	-4.62	0.03	Y	N
M2 3R 2	-8.96	0.03	-7.65	0.03	-8.96	0.03	-4.59	0.04	Y	N
M2 2R 1	-9.38	0.01	-4.89	0.04	-9.40	0.06	-4.99	0.10	Y	Y
M2 2R 2	-9.10	0.00	-4.80	0.02	-9.09	0.02	-4.95	0.04	Y	N
M2 3R 1	-8.99	0.01	-4.51	0.03	-9.10	0.04	-4.62	0.03	Y	N
M2 3R 2	-9.03	0.01	-4.39	0.01	-8.96	0.03	-4.59	0.04	N	N
M2 6.2	-9.84	0.01	-4.89	0.04	-10.00	0.08	-5.05	0.01	N	N

6.4.3. Deriving Initial Palaeotemperature Estimates

Error-weighted mean temperatures and error-weighted 95% uncertainties were calculated (Reiners et al., 2017) for both sub-samples (i.e. from the same calcite powders) and for the sample layers (i.e. layers of speleothem growth) for analyses from LSCE, The University of Wollongong, and The University of Melbourne (**Table 6.9**) using the following equation:

$$t_{ewm} = \frac{\sum w_i t_i}{\sum w_i}$$

where the weights are given as:

$$w_i = \frac{1}{\sigma_i^2}$$

and uncertainties calculated as:

$$\sigma_{t_{ewm}} = \frac{1}{\sqrt{\sum w_i}}$$

Mean Square Weighted Deviation (MSWD, also referred to as the reduced chi-square statistic) was also calculated to test for synchrony within the single populations using the following equation:

$$\chi_{red}^2 = MSWD = \frac{1}{n-1} \sum_{i=1}^n \frac{(x_i - \bar{x})^2}{\sigma_i^2}$$

This statistic assesses the reproducibility of the replicate analyses from the individual sample layers. From these analyses, probability of fits <5% are likely a result of analytical scatter alone rather than as a result of being from the same population, and are therefore excluded. There are several sub-samples and sample layers for which the probability of fit is <0.05, including all analyses from the LSCE laboratory. This suggests either analytical scatter or heterogeneity in the abundance of Δ_{47} across the single layers of speleothem in these samples. If the former were the cause, more intensive analyses of the sub-samples and sample layers with a greater number of replicate analyses would resolve this. If it is a result of the latter, it implies that more detailed investigations into possible fractionation within speleothem samples is required for reliable temperature estimates from clumped-isotope analyses. Within the scope of this study it is not possible to undertake further investigation into the true cause of this scatter, therefore these data are therefore omitted from further analyses.

Table 6.9 – All error-weighted mean (EWM) temperatures and their associated 95% error-weighted uncertainties for each sub-sample and sample layer (in bold) alongside the mean square weighted deviation (MSWD) and the probability of fit (PoW). EWMs with PoF's <5% are highlighted in red.

Laboratory	Speleo- them	Sample Layer	Sub- sample	EWM T (°C)	± (°C)	MSWD	PoF
LSCE	M2	2R	1	34.8	13.6	5.91	0.00
			2	34.6	2.6	1.00	0.37
			3	40.7	26.3	17.22	0.00
			EWM	35.8	6.5	7.61	0.00
		3R	1	32.1	10.6	3.61	0.03
			2	30.7	13.7	6.02	0.00
			EWM	31.4	4.7	3.95	0.00
The University of Wollongong	FIE	8	a	22.5	4.6	0.12	0.73
			b	17.9	4.1	0.21	0.64
			EWM	20.0	3.1	0.87	0.45
	FIA	2	a	31.5	4.6	0.79	0.37
			b	21.0	4.7	0.00	0.97
			EWM	26.4	10.0	3.67	0.01
	FIM	17	a	35.6	2.6	0.16	0.69
			b	17.8	3.2	0.78	0.48
			EWM	28.6	12.3	19.00	0.00
	FID	7	a	-	-	-	-
			d	22.9	2.7	0.40	0.53
			EWM	21.3	2.4	2.83	0.06
	1411	11		-	-	-	-
				-	-	-	-
			EWM	20.4	66.4	15.10	0.00
	M2	3R	EWM	32.2	2.4	0.42	0.66
		6	1	19.7	2.4	1.60	0.20
			2	21.5	5.3	0.00	0.95
			EWM	20.0	2.1	0.66	0.57
		6	EWM	21.5	4.2	1.81	0.12
The University of Melbourne	M2	2R	1	20.3	11.5	2.66	0.05
			2	17.4	3.9	0.26	0.85
			EWM	18.7	2.9	1.39	0.20
		3R	1	20.7	4.3	2.36	0.07
			2	23.1	3.8	1.18	0.32
			EWM	22.1	2.9	1.62	0.13
		6	EWM	21.5	4.2	1.81	0.12

6.4.4. Inter-Laboratory Comparisons

As previously discussed, due to the novel nature of clumped-isotope analyses, particularly in application to speleothems, inter-laboratory comparisons are of great importance. Due to the different methods used at each of the laboratories it is not reasonable to statistically analyse the differences between them. However, the difference in the minimum temperatures (26.3 °C from LSCE data, 16.4 °C from The University of Wollongong data, 14.5 °C from The University of Melbourne data) and maximum temperatures (43.8 °C from LSCE data, 35.9 °C from The University of Wollongong data, 34.3 °C from The University of Melbourne data) derived from individual replicates is of interest and points to a systematic difference between the three laboratories. There are several potential reasons for these apparent differences between the laboratories.

One such reason is the different acid-reaction protocols used. As the LSCE lab uses a common acid bath, there are several possible influences of this on the sample results. Firstly, there is the potential issue of memory effect. While efforts are made to reduce this possibility through flushing the prep line with carrier gas between each digestion, and frequently replacing the acid bath, it cannot be completely ruled out as a potential issue. If memory effects were present, it may help explain the lower temperature range evident.

A second potential methodological issue, which may have resulted in the smaller temperature range at LSCE, are the possibilities of sample splash back or incomplete sample reaction due to the automated dropping of the sample into the acid bath from significant height. Alternatively, with sample splash back there is also the opportunity of previous samples contaminating later samples as batches of several samples are run successively without removal and cleaning of the acid bath unit. This means that it is possible for powder remnants to remain on the walls of the acid bath, and incorporated into later sample analyses. As the acid bath is only removed and the acid replaced once daily, there is significant potential for sample contamination in this stage of the method. Since the running of these samples, alterations to the methodology used at the LSCE laboratory have been implemented in order to significantly reduce the potential for any sample splash back or incomplete sample reactions.

A third possible cause for the variability between the three laboratories is the differing data processing methodologies. There is not yet a single universally agreed upon method for the processing of Δ_{47} data, and different methods can provide slight temperature differences for a single dataset; therefore the use of different methods across the three laboratories may have accentuated the

differences between the temperatures produced. As advances in the applications of Δ_{47} data to speleothems continue, a primary goal should be to refine the processing of raw Δ_{47} values to enable a more universal approach and reduce the potential for these effects in multi-laboratory analyses in the future.

For attempts at more robust inter-laboratory comparisons, replicates of one sample, M2 3R, were analysed at LSCE, The University of Wollongong, and The University of Melbourne to allow for a direct comparison of reproducibility, Δ_{47} results, and associated palaeotemperatures (**Table 6.10**). As with all other samples, each subsample was replicated to ensure reproducibility of results and to allow the omission of apparent anomalous results. Unfortunately, several subsamples and replicate analyses did not yield accepted results; therefore there were too few measurements for robust comparison. Additionally, by excluding the data detailed in **section 6.4.3** with probability of fits <5%, there are no remaining data from LSCE for comparison with the other laboratories.

With the accepted data from The University of Wollongong and The University of Melbourne, three replicate analyses two from The University of Wollongong (**Fig. 6.15** – in blue) and one from The University of Melbourne (**Fig. 6.15** – in red), produce significantly higher temperatures than average, and are therefore omitted from further analyses. This leaves only one replicate from The University of Wollongong, supporting earlier suggestions that there may be a systematic difference between the three laboratories. Despite this possibility, all replicate analyses from both The University of Wollongong and The University of Melbourne for sample layer M2 3R that were not deemed as outliers are used as a single dataset for further analyses, as supported by the error-weighted mean statistic.

A second sample, M2 6, was run at two of the three laboratories – The University of Wollongong and The University of Melbourne (**Table 6.11**). The analyses of **section 6.4.3** did not identify the need to exclude any of the data from this sample at either laboratory. **Fig. 6.16** shows that all of the replicate analyses at both laboratories were all within error of one another, and relate well to the error-weighted mean statistic.

A third sample, M2 2R, was run at both The University of Melbourne and LSCE, however it was determined in **section 6.4.3** that the data from LSCE did not produce reliable data for sub-samples from within this sample layer. Therefore, no comparisons can be made, and solely the data from The University of Melbourne is used for calculating an error-weighted mean.

Table 6.10 – Results of the inter-laboratory comparison of an individual sample layer within speleothem M2 – ‘M2 3R’. Temperatures from The University of Wollongong were calculated using the calibration of Zaarur et al. (2013), those from The University of Melbourne and LSCE were calculated using the calibration of Daëron (2016 – pers. comm.). Error-weighted mean (EWM) temperatures and their associated 95% error-weighted uncertainties shown for each sub-sample and sample layer (in bold) alongside the mean square weighted deviation (MSWD) and the probability of fit (PoF). EWMs with PoF’s <5% are highlighted in red.

Laboratory	Sub-sample	Replicate	$\Delta 47$ (‰)	T (°C)	± (°C)	MSWD	PoF
LSCE	1	a	0.623	27.2	4.5	-	-
		b	0.604	33.8	4.5	-	-
		c	0.6	35.2	4.5	-	-
	EWM			32.1	10.6	3.61	0.03
	2	a	0.619	28.6	4.5	-	-
		b	0.595	37	4.5	-	-
		c	0.625	26.6	4.5	-	-
	EWM			30.7	13.7	6.02	0
	EWM			31.4	4.7	3.95	0
The University of Wollongong	2	1	0.68	30.5	7.4	-	-
		2	0.675	31.8	2.9	-	-
		3	0.666	34.1	5.1	-	-
EWM			32.2	2.4	0.42	0.66	
The University of Melbourne	1	1	0.676	20	7.8	-	-
		2	0.633	34.3	11.3	-	-
		3	0.685	17.2	7	-	-
		4	0.682	18.1	10.4	-	-
		EWM		20.7	4.3	2.36	0.07
	2	1	0.656	26.1	6.3	-	-
		2	0.656	26.2	9	-	-
		3	0.683	17.6	7.7	-	-
		4	0.67	21.7	8.6	-	-
		EWM		23.1	3.8	1.18	0.32
EWM			22.1	2.9	1.62	0.13	

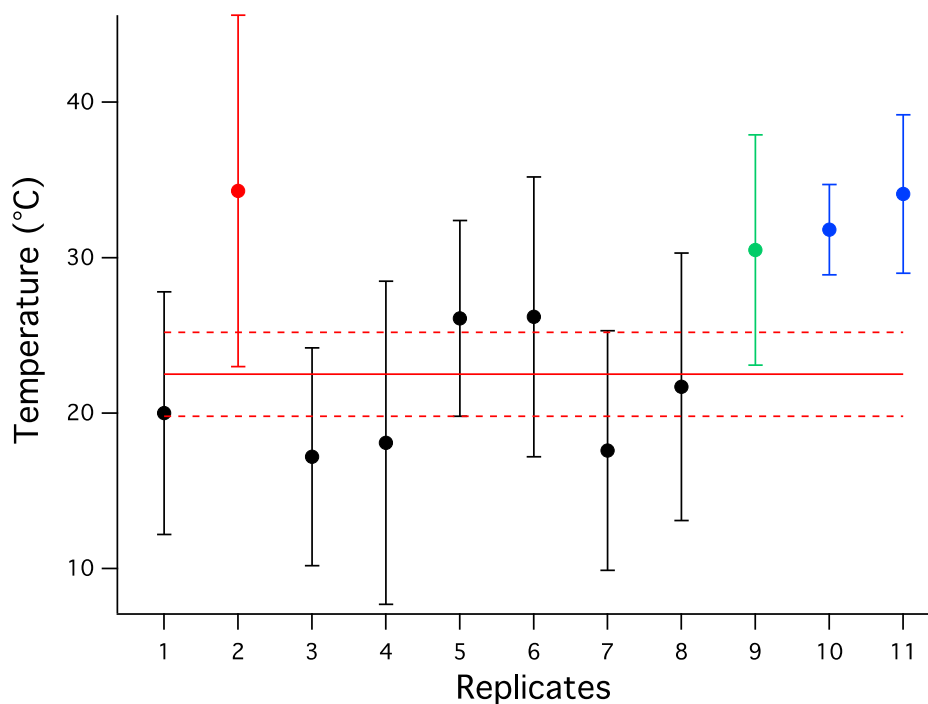


Fig. 6.15 – All replicate measurements from The University of Wollongong (green) and The University of Melbourne (black) for sample layer M2 3R, and their associated 2σ errors. Solid red line indicates the EWM, dashed red lines indicate the upper and lower bounds of the 95% EWU. Replicates identified as outliers from The University of Wollongong in blue and from The University of Melbourne in red.

Table 6.11 – Results of the inter-laboratory comparison of an individual sample layer within speleothem M2 – ‘M2 6’. Temperatures from The University of Wollongong were calculated using the calibration of Zaarur et al. (2013), those from The University of Melbourne using the calibration of Daëron (2016 – pers. comm.). Error-weighted mean (EWM) temperatures and their associated 95% error-weighted uncertainties shown for each sub-sample and sample layer (in bold) alongside the mean square weighted deviation (MSWD) and the probability of fit (PoW).

Laboratory	Sub-sample	Replicate	$\Delta 47$ (‰)	T (°C)	$\pm$ (°C)	MSWD	PoF
The University of Wollongong	1	1	0.74	16.4	5.7	-	-
		2	0.722	20.4	2.7	-	-
	EWM			19.7	2.4	1.6	0.2
	2	1	0.717	21.6	7.2	-	-
		2	0.718	21.3	7.8	-	-
	EWM			21.5	5.3	0	0.95
EWM				20	2.1	0.66	0.57
The University of Melbourne	2	1	0.69	15.6	8.2	-	-
		2	0.659	25.2	9	-	-
		3	0.641	31.4	10.3	-	-
		4	0.672	21.1	10.7	-	-
		5	0.685	17.2	9.7	-	-
EWM				21.5	4.2	1.81	0.12

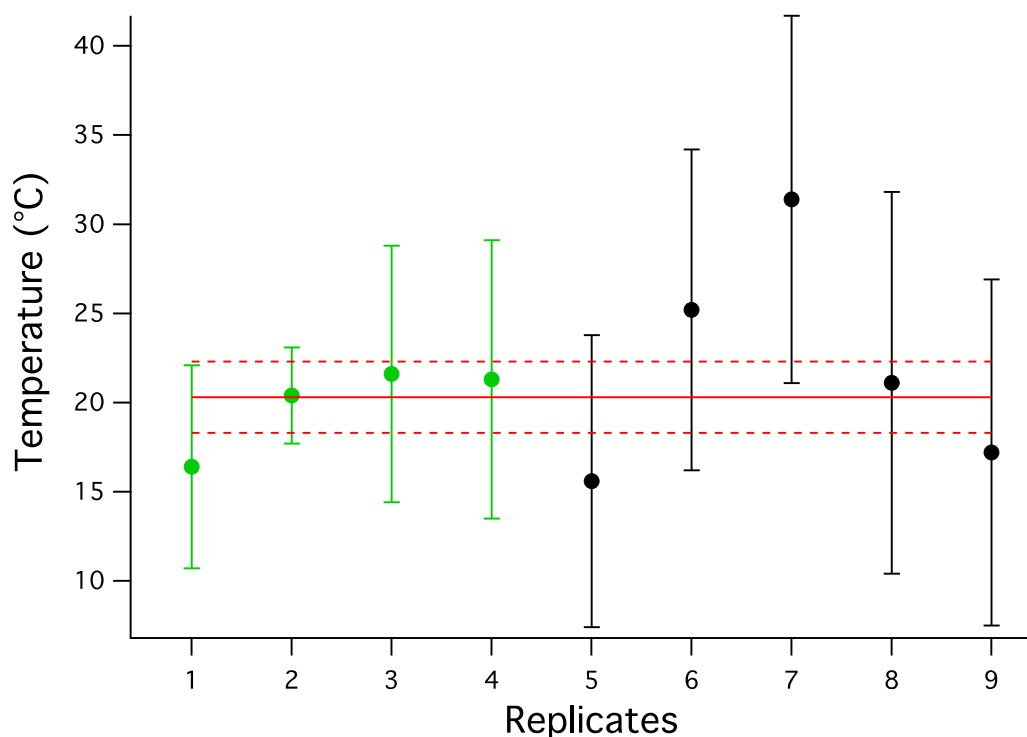


Fig. 6.16 – All replicate measurements from M2 6, and their associated 2 SE errors. Measurements undertaken at The University of Melbourne (black), at The University of Wollongong (green). Solid red line indicates the EWM, dashed red lines indicate the upper and lower bounds of the 95% EWU.

6.4.5. Deriving Final Palaeotemperature Estimates

In order to derive final palaeotemperature estimates, each sample layer was assessed for outliers. This was achieved by plotting individual replicates and their associated 2 SD errors with the error-weighted means and associated 95% error-weighted uncertainty. The analyses of the University of Wollongong data highlighted that replicate analyses from samples 1411-11 and FIM 17 could not be resolved. In addition, for sample FIA 2 there is one outlier to be omitted (**Fig. 6.17**). Despite the discouraging initial analyses of the LSCE data, they were also included in these analyses to assess whether outliers could be identified and omitted for the recalculation of error-weighted means (**Fig. 6.18**). Neither sample produced error-weighted means with probability of fits >5% despite the omission of one outlier in sample M2 3R. Within the University of Melbourne dataset only two outliers were identified, both in sample M2 2R (**Fig. 6.19**). For sample layers M2 3R and M2 6 where replicates were run at both The University of Wollongong and The University of Melbourne, the collated analyses presented in **Fig. 6.15** and **Fig. 6.16** were favoured. Excluding the outliers identified in these analyses, these data were used to derive final error-weighted means and error-weighted uncertainties for each sample layer (**Table 6.12**).

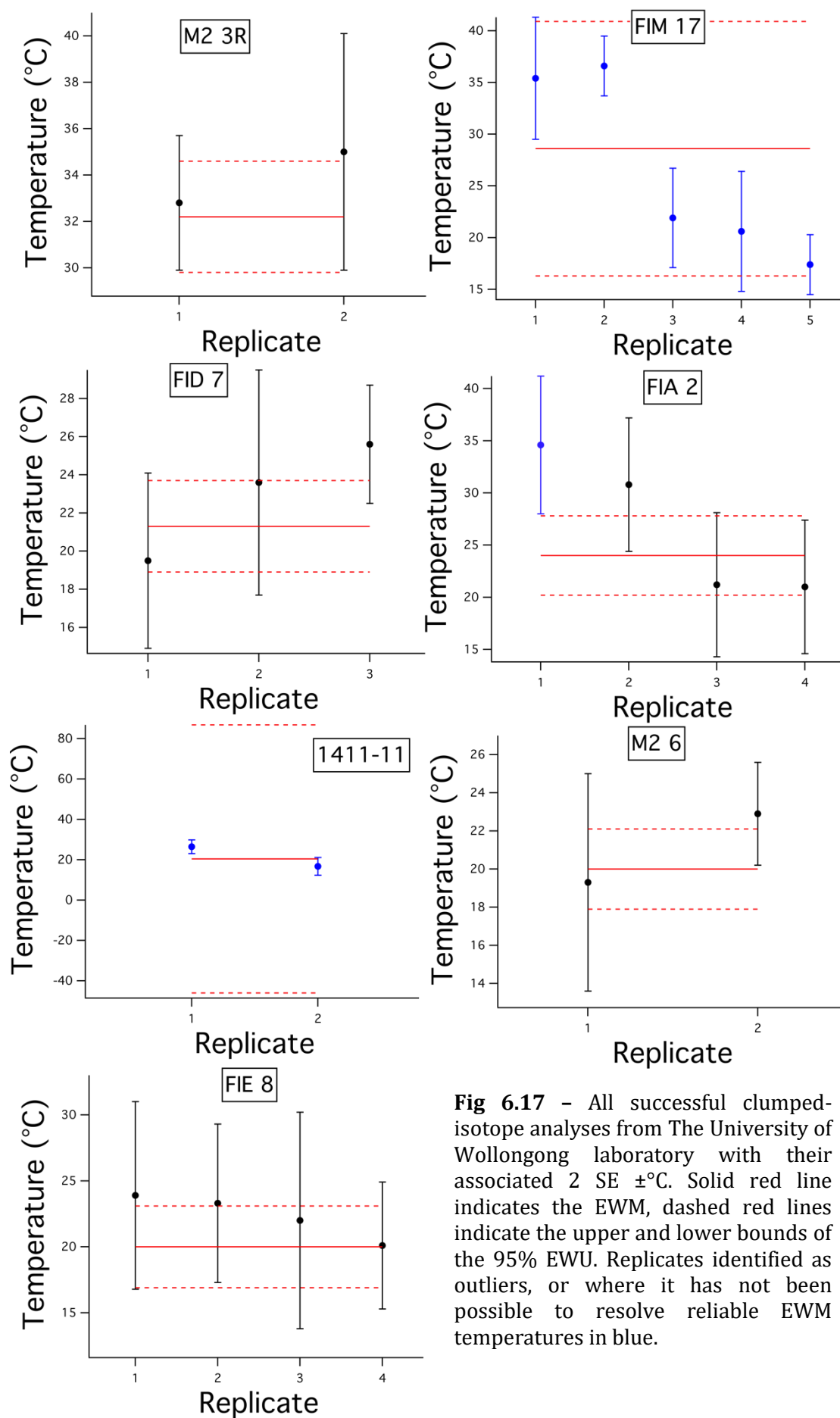


Fig 6.17 - All successful clumped-isotope analyses from The University of Wollongong laboratory with their associated $2 \text{ SE } \pm^\circ\text{C}$. Solid red line indicates the EWM, dashed red lines indicate the upper and lower bounds of the 95% EWU. Replicates identified as outliers, or where it has not been possible to resolve reliable EWM temperatures in blue.

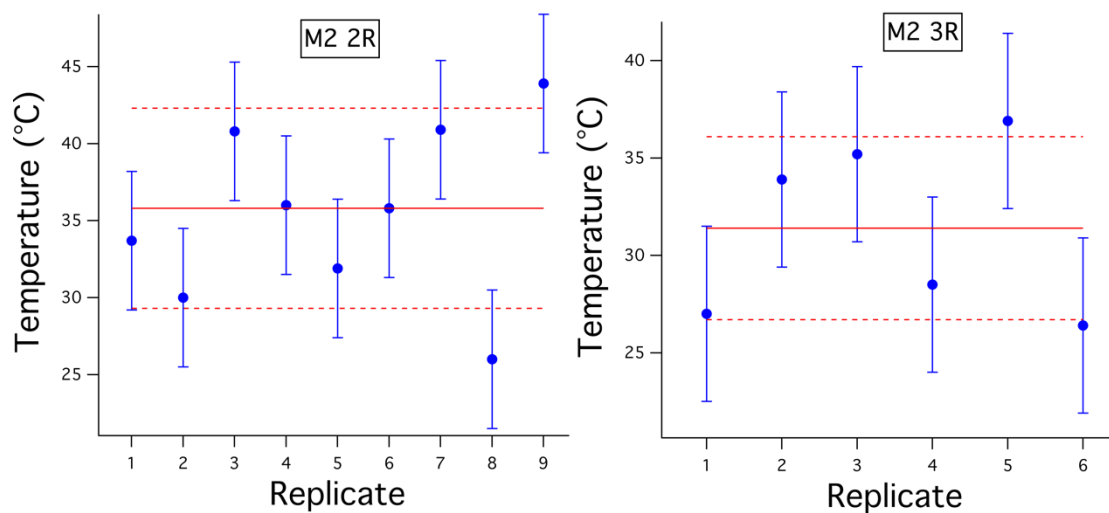


Fig 6.18 – All successful clumped-isotope analyses from the LSCE laboratory with their associated 2 SE $\pm$ °C. Solid red line indicates the EWM, dashed red lines indicate the upper and lower bounds of the 95% EWU. Replicates identified as outliers, or where it has not been possible to resolve reliable EWM temperatures in blue.

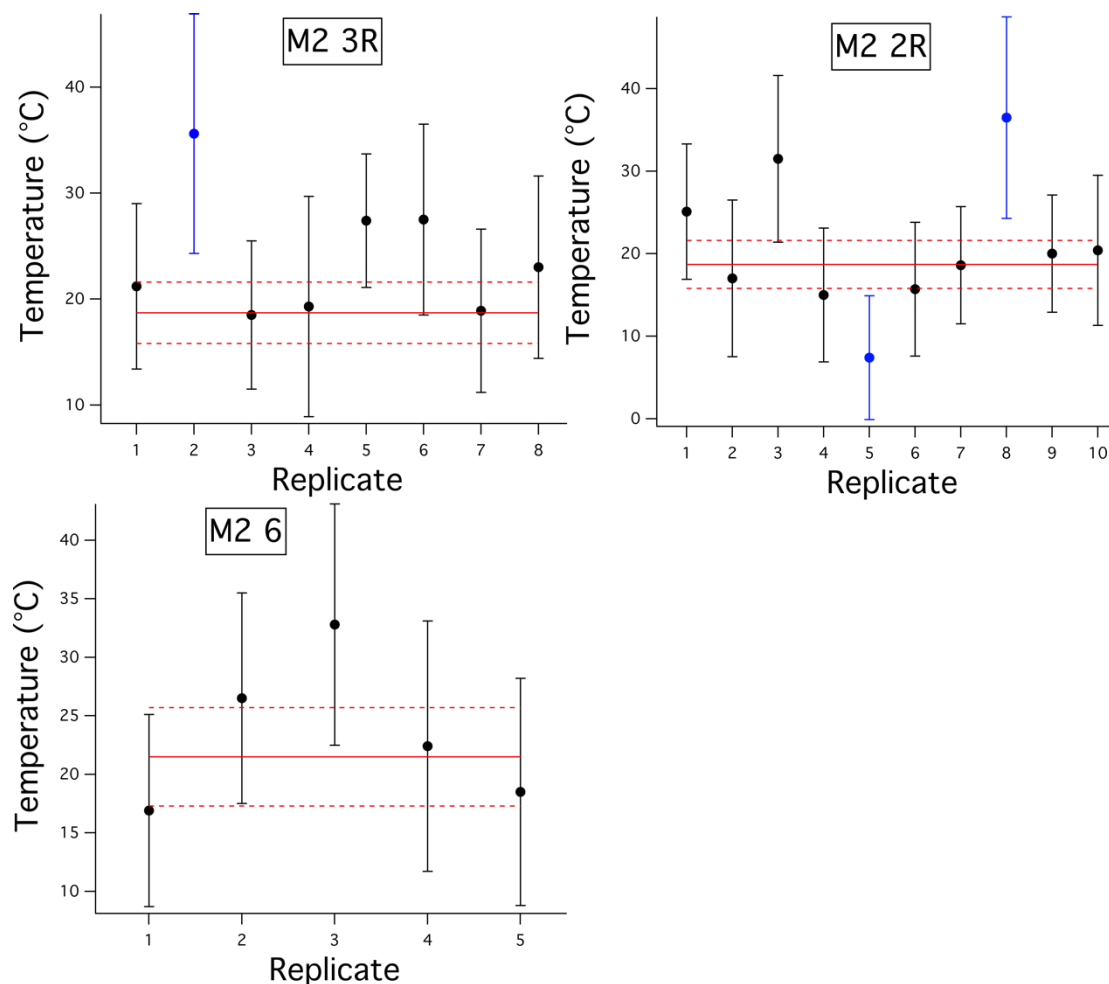


Fig 6.19 – All successful clumped-isotope analyses from The University of Melbourne laboratory with their associated 2 SE $\pm$ °C. Solid red line indicates the EWM, dashed red lines indicate the upper and lower bounds of the 95% EWU. Replicates identified as outliers, or where it has not been possible to resolve reliable EWM temperatures in blue.

Table 6.12 – Error-weighted mean (EWM) temperatures and their associated 95% error-weighted uncertainties for all sample layers from which replicate analyses have overlapping errors. Outliers identified from **Fig. 6.15**, **Fig. 6.16**, **Fig. 6.17**, **Fig. 6.18**, and **Fig. 6.19** have been excluded for these calculations. EWMs with a probability of fit <5% are highlighted in red.

Laboratory	Sample	EWM T (°C)	± EWU (°C)	MSWD	PoF
LSCE	M2 3R	31.4	4.7	3.95	0.00
The University of Wollongong	FIE 8	20	3.1	0.87	0.45
	FIA 2	24	3.8	2.3	0.1
	M2 3R	32.2	2.4	0.42	0.66
	M2 6	20	2.1	0.66	0.57
	FID 7	21.3	2.4	2.83	0.06
The University of Melbourne	M2 2R	18.7	2.9	1.39	0.2
	M2 3R	22.1	2.9	1.62	0.13
	M2 6	20.3	2	1.21	0.29
Multi-lab averages	M2 3R	22.5	2.7	1.68	0.11
	M2 6	20.3	2	1.21	0.29

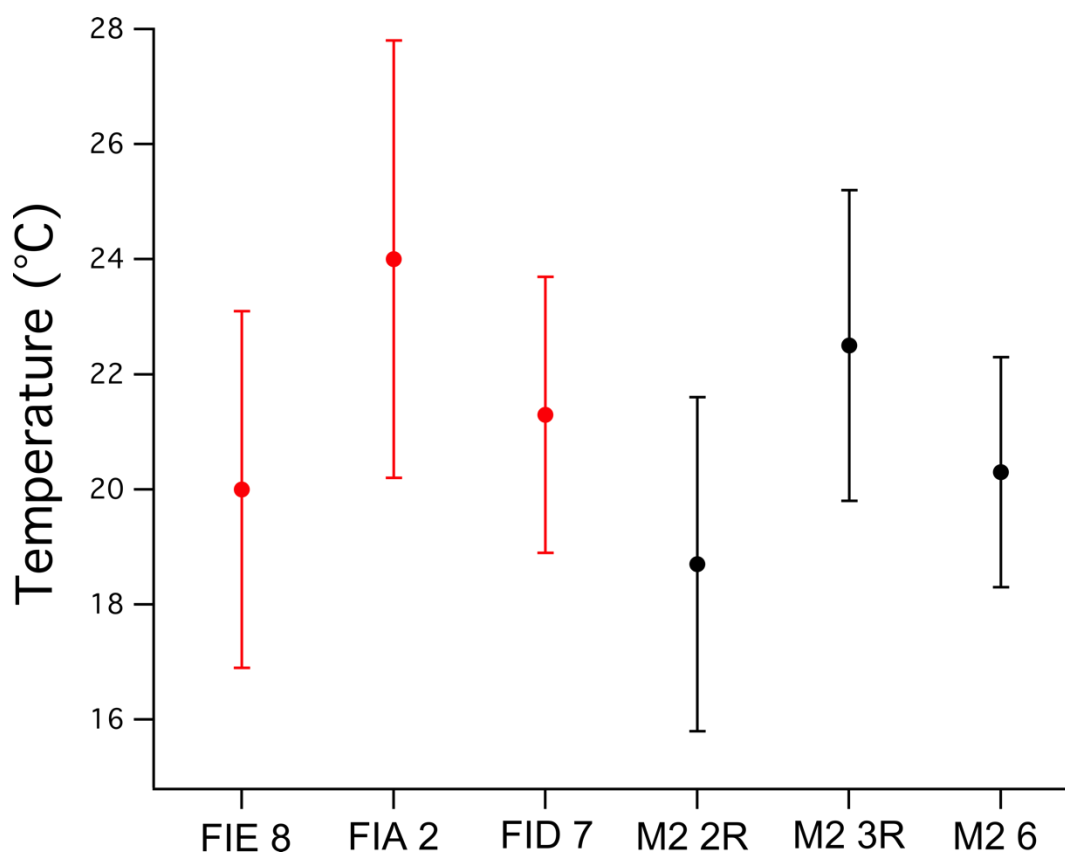


Fig 6.20 – Final accepted palaeotemperatures obtained from all clumped-isotope analyses and their associated 95% error-weighted uncertainties. Samples from speleothem M2 in black, samples from all additional speleothems in red.

Table 6.13 – All final accepted error-weighted mean (EWM) palaeotemperatures obtained from all clumped-isotope analyses and their associated 95% error-weighted uncertainties.

Sample	EWM T (°C)	± EWU (°C)
FIE 8	20.0	3.1
FIA 2	24.0	3.8
FID 7	21.3	2.4
M2 2R	18.7	2.9
M2 3R	22.5	2.7
M2 6	20.3	2.0

Excluding sample layers for which probability of fits were <5%, a total of 6 accepted palaeotemperature estimates were derived from these analyses (**Fig. 6.20, Table 6.13**). These data suggest an approximate range in temperatures of 5.3 °C, with a minimum temperature of 18.7 °C ±2.9 °C and a maximum temperature of 24.0 °C ±3.8 °C. It is suggested that while the temperature variation may not have been as extreme as suggested by these temperature estimates, the apparent variation is potentially reflective of the cool minima and warm maxima of climate cycles during the MPWP. In order to fully assess the potential of the speleothems for this purpose, it would be necessary to significantly reduce the errors of the temperatures through additional replicates, and to successfully calculate temperatures from several more layers. In this regard, it would be beneficial for the application of clumped isotope analyses to speleothems if future research focused on the more rigorous testing of individual samples with substantially more replicates than undertaken in this study. This would serve to assess the possibility of reducing the potential analytical scatter apparent in this study, and to further reduce the errors associated with the estimates.

Through future methodological advances, it may be possible to use the clumped-isotope method alone to extract reliable palaeotemperatures from speleothems, however at this stage this thesis concludes that this is not yet the possible. As such, while the combination of the palaeotemperatures presented here and the current understanding of the offset between measured and actual temperatures in laboratory based studies can be used to provide an estimate of the temperature range of the Nullarbor region in the Pliocene, it is not deemed reliable to ultimately define a palaeotemperature estimate. It is for this purpose that the following combined analyses of fluid-inclusion and clumped-isotope analyses was undertaken.

6.5. Combined Analyses Results and Discussion

6.5.1. Deriving Palaeotemperature Estimates

Results from five sample layers from three speleothems have been deemed reliable from *both* the fluid-inclusion and the clumped-isotope analyses (**Table 6.14**). These data show that generally speaking, the accepted fluid-inclusion temperatures are lower than the accepted clumped-isotope temperatures, although three of the five samples are within error of each other. This is in keeping with the current understanding of problems associated with the two methods. Clumped-isotopes are known to produce higher than expected temperatures (Daëron et al., 2011) due to issues of disequilibrium speleothem precipitation. While the temperatures produced by fluid-inclusion analyses in the literature are significantly more varied (Matthews et al., 2000; Zhang et al., 2008; Labuhn et al., 2015; Fleitmann et al., 2017), it is known that certain palaeotemperature equations, particularly that of Kim and O'Neil (1997), are associated with consistently lower than expected temperatures (Coplen, 2007; Zhang et al., 2008). This may be transferred to other palaeotemperature equations where the applied fractionation factors deviate from the actual fractionation factor that would be required to obtain accurate palaeotemperatures.

The accepted fluid-inclusion and clumped-isotope data were compared (**Fig. 6.21**). From this is it evident that the temperatures derived from the two analyses for samples M2 2R and M2 3R do not appear to be statistically related. This is supported by the error-weighted means and error-weighted uncertainties calculated (**Table 6.15**), in which both of these samples have probabilities of fit <5% are therefore omitted. The final accepted data are presented in **Fig. 6.22**.

Table 6.14 – Palaeotemperature estimates derived from individual fluid-inclusion analyses and clumped-isotope analyses and their associated 95% EWU / 2 SE $\pm$ temperature.

Sample	Clumped-isotope EWM T (°C)	$\pm$ EWU (°C)	Fluid-inclusion AWM T (°C)	2 SE $\pm$ (°C)
FIA 2	24.0	3.8	20.3	0.9
FID 7	21.3	2.4	21.4	1.6
M2 2R	18.7	2.9	13.5	2.2
M2 3R	22.5	2.7	9.8	2.3
M2 6	20.3	2.0	16.9	4.8

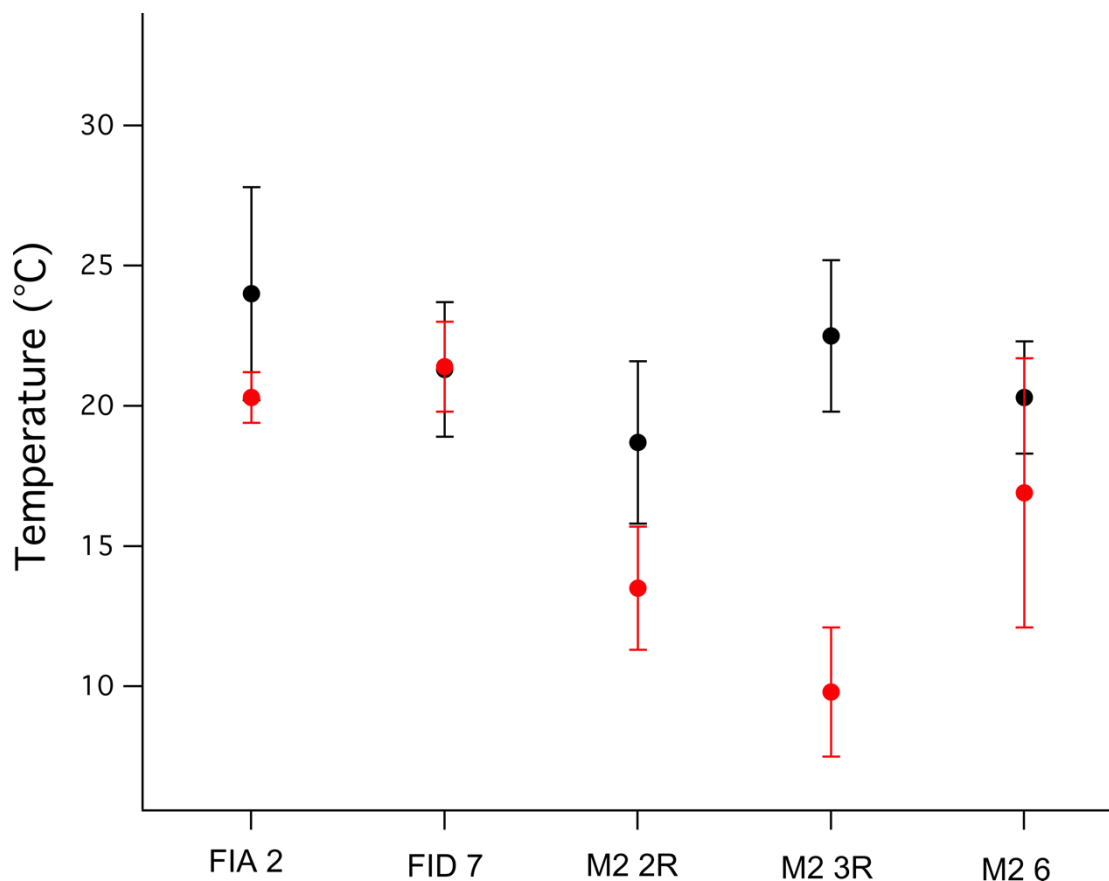


Fig. 6.21 – All sample layers for which both fluid-inclusion derived temperatures (red), and clumped-isotope derived temperatures (black) were obtained, with their associated 95% error-weighted uncertainty / 2 SE $\pm^{\circ}\text{C}$.

Table 6.15 – The final accepted temperature estimates derived from the error-weighted mean calculated from both methods, and their associated 95% error weighted uncertainty. Samples for which probability of fits <5% were derived are highlighted in red.

Sample	EWM T (°C)	$\pm$ EWU (°C)	MSWD	PoF
FIA 2	20.5	0.9	3.59	0.06
FID 7	21.4	1.3	0.005	0.94
M2 2R	15.4	31.8	8.16	0.00
M2 3R	15.1	80.0	51.28	0.00
M2 6	18.8	1.8	1.71	0.19

As these analyses resulted in temperatures and errors with satisfactory probability of fits, these are all deemed to be reasonable estimates of the temperature of the Nullarbor Plain during the MPWP. The final accepted temperatures range from a minimum of $18.8^{\circ}\text{C} \pm 1.8^{\circ}\text{C}$ to a maximum of $21.4^{\circ}\text{C} \pm 1.3^{\circ}\text{C}$. Based on our overall understanding of global temperatures during the

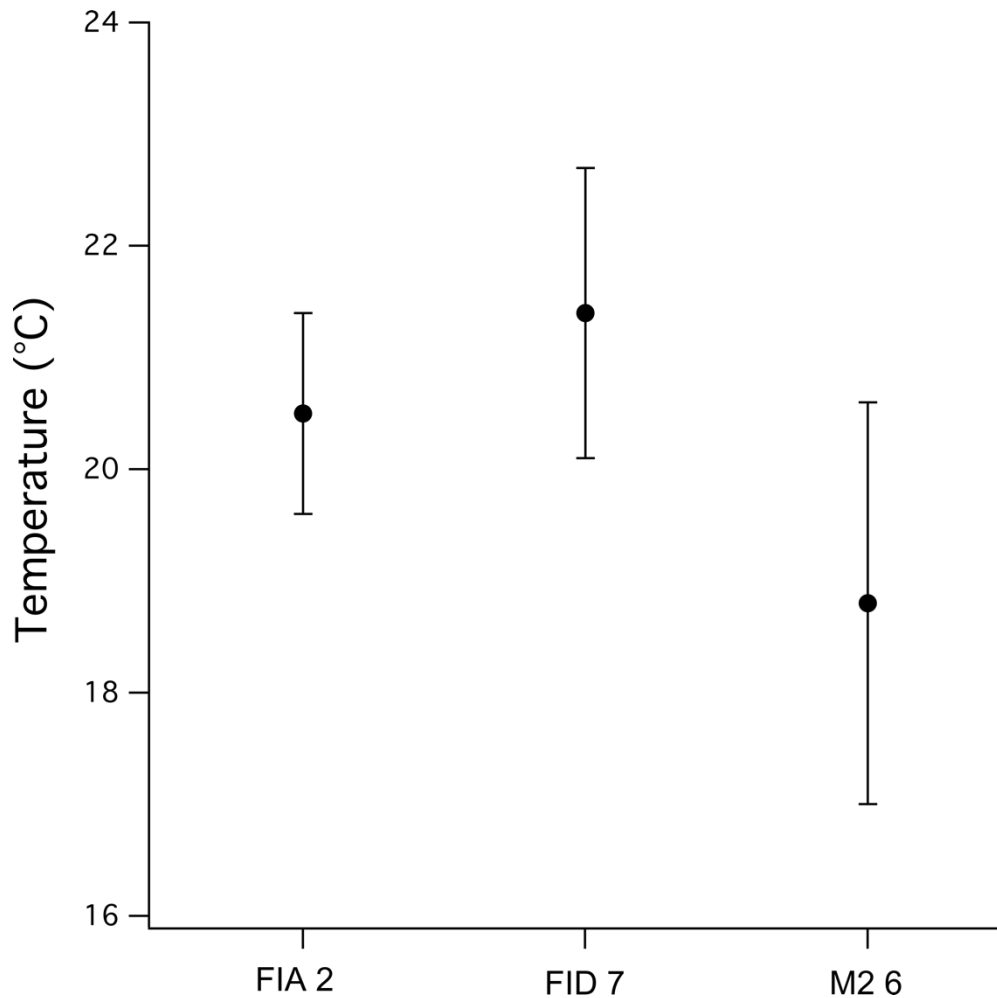


Fig. 6.22 – Accepted temperatures from the error-weighted mean of accepted fluid-inclusion and clumped-isotope temperatures, with their associated error-weighted uncertainty.

Pliocene, in which average temperatures of 3-4 °C warmer than present are associated (Crowley, 1996; Haywood et al., 2009), temperatures for the Nullarbor (with a modern day average temperature of 18 °C) would be 21-22 °C. This is also in agreement with modelled data which suggests temperature increases of 2-3 °C in the Nullarbor (Salzmann et al., 2011). From current models of Pliocene climates, and to allow for variations in temperature throughout the period, a reasonable temperature range of 19-24 °C is expected. Therefore, within error, these temperature estimates are realistic for the Pliocene. Additionally, as previously discussed, it is possible that the variability suggested by the data represents cool and warm maxima within the MPWP. This is very encouraging for future applications of the fluid-inclusion and clumped-isotope methods in deriving palaeotemperatures, as it indicates that the common problems associated with the two methods individually can be overcome with their intensive combined analyses, and realistic temperature estimates can be

produced. However, it is obvious that the precision of measurements in both fluid-inclusion and clumped-isotope methods must be improved for wider applications of these methods in speleothem studies, and the efficient retrieval of the palaeotemperature signals preserved within them. In order to resolve a picture of the temperature variations throughout the MPWP, a great deal more analyses would need to be undertaken in order to obtain enough palaeotemperatures for such interpretations, including the resource-intensive task of identifying and retrieving additional speleothems that grew within the MPWP.

6.5.2. Limitations and Further Research Required

From the results of this study, it is argued that it is possible to obtain reliable palaeotemperatures directly from speleothems, however the current uncertainties and limits of precision greatly restrict their application. This thesis represents one of the first published attempts to use both fluid-inclusion and clumped-isotope analyses to produce palaeotemperatures; therefore these methods are in their infancy and there is much scope for further research. A key step in improving the reliability and accuracy of palaeotemperatures obtained in this way is in improving the accuracy of, and errors associated with, the individual methods. In this study, the reasons for the majority of samples to be excluded were as follows: failed measurements in the laboratory, large analytical uncertainties on individual measurements, and being classed as an anomalous result (as determined by a lack of overlapping errors with replicate analyses). All of these factors could be minimised by advances in the respective method, with aims to improving analytical precision and reproducibility. Additional uncertainties arose from the application of various palaeotemperature and calibration equations. Further attempts at refining these equations will significantly benefit the application of these methods and increase their reliability. If this further research is targeted at modern speleothems from multiple speleothems and cave systems, it may be possible to identify a more specific offset of temperatures calculated from fluid-inclusion and/or clumped-isotope analyses from actual temperatures. If a specific offset can be identified that can be applied to multiple speleothems and cave systems, it may be possible in the future to use a single method (likely clumped-isotope analyses due to the smaller sample sizes required, and the ability to obtain high precision measurement of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ simultaneously to Δ_{47}) to obtain accurate palaeotemperatures, a long-term goal that should be considered by the speleothem science community. In the absence of this, a great deal more analyses would need to be undertaken in order to obtain enough palaeotemperatures to

assess temperature variations in the lifespan of a given speleothem. Additionally, it is noted that a more extensive number of repeat analyses on individual samples/aliquots, as well as samples from multiple speleothems within individual cave systems, and samples from multiple cave systems would be required to assist with more detailed and robust interpretations.

It is also possible, however, that the difficulties in obtaining multiple temperature estimates is a result of the majority of speleothems used in this study not being suited to preserving temperature signatures from the time of deposition. This refers to the clumped-isotope method, which requires speleothem that have grown under true equilibrium – or very close to – conditions. It is therefore possible that the speleothems largely grew under conditions with significant disequilibria to impact upon the Δ_{47} signal preserved. This suggests that future studies attempting to obtain reliable temperatures using these methods will need to effectively screen potential samples for their suitability prior to analyses.

7. Multi-Proxy Pliocene Speleothem Study

7.1. Methods of Stable Isotope Analyses

7.1.1. *Speleothem Sampling*

Samples for stable isotope analyses were obtained using a TAIG CNC micromilling lathe using the software and contamination elimination procedures of (Drysdales et al., 2012a). Samples were drilled using a 1 mm bit at 1 mm resolution running perpendicular to the apex of the visible laminae of the speleothem, along the main growth axis of the stalagmite. Each isotope sample was drilled to a depth of 1.5 mm, and powders collected in individually labelled vials.

To avoid disequilibrium effects in stable isotope analyses, and for stratigraphic simplicity, it is preferable to sample speleothems down the central growth axis. Due to variations in factors such as drip location and drip rate, the direction of growth can vary through time. As such, multiple transects of central growth axis may be identified within a single speleothem. For sample BT (**Fig. 7.1**), a total of 50 central growth axis changes (herein, the segments in between are referred to as ‘transects’) were identified; from these, a total of 1,944 samples for isotope analyses were obtained. For sample M2, a total of 5 transects were identified (**Fig. 7.2**), and a total of 454 samples obtained. In addition, partial profiles were obtained from the additional speleothems for which fluid-inclusion analyses were undertaken (see **Chapter 6**).

7.1.2. *Analyses*

Samples were analysed using an AP2003 continuous-flow stable isotope ratio mass spectrometer following the methods of sample preparation and processing of (Drysdales et al., 2009). Subsamples of between 0.7 and 0.8 mg were weighed into individual glass vials sealed with septum caps and organised into sample racks along with standards. In-house standards (‘new1’, and ‘new12’), and an international reference standard (‘NBS19’) of known isotopic composition were also analysed. Racks were placed onto a hot plate set at 70 °C and each sample was purged with ultra-high purity helium (99.9995%) for 240 seconds prior to acidification to remove all atmospheric gases. Following purging each sample was injected with 0.2 ml of 105% orthophosphoric acid and left for 30 minutes to ensure complete dissolution.



Fig. 7.1 – Images of speleothem BT (top section on the left, bottom section on the right) displaying the central growth axis along which stable isotope samples were drilled (in red), and the locations of Hendy Test samples (in yellow).

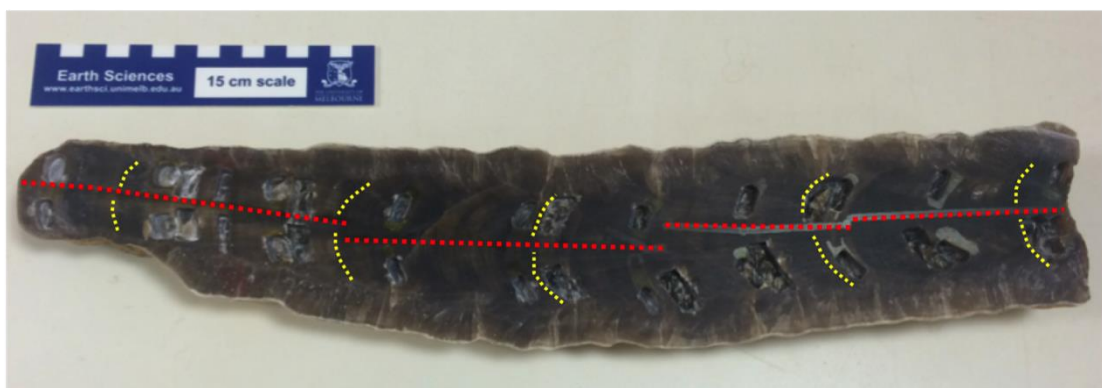


Fig. 7.2 – Image of speleothem M2 displaying the central growth axis along which stable isotope samples were drilled (in red), and the locations of Hendy Test samples (in yellow).

Table 7.1 – Volumes of acid required for differing weights of calcite for trace element analyses.

Sample Weight	Minimum acid (ml)	Maximum acid (ml)
0.1	2	3
0.2	4	6
0.3	6	9
0.4	8	12
0.5	10	12
0.6	12	12
0.7	12	12
0.8	12	12
0.9	12	12
1.0	12	12

* For all samples >0.65mg (acid volumes in red) a second dilution process was required

The CO₂ released from the reaction was introduced to the mass spectrometer in a stream of ultra-high purity helium carrier gas. The output data were reduced using an in-house data reduction program. During this process the instrument results are normalised, corrected for any potential drift and scaling factors, and calibrated to the internationally accepted VPDB scale. This protocol has yielded a long-term analytical reproducibility of 0.05 ‰ for $\delta^{13}\text{C}$ and 0.10 ‰ for $\delta^{18}\text{O}$.

Once the data were reduced, potential outliers were identified as those samples whose values deviated by $>\pm 0.40$ ‰ $\delta^{18}\text{O}$ from those of the adjacent

samples. All identified outliers were re-analyses on the mass spectrometer using remaining powders from the micromilling and then assessed in comparison to the original results prior to identifying the accepted results.

7.1.3. Hendy Tests

For the purpose of assessing quasi-isotopic equilibrium conditions during the growth of each speleothem, a series of Hendy Tests (Hendy, 1971) were conducted. For these analyses individual growth layers, approximately evenly spread down the length of the stalagmite, were selected, and 10 samples were collected from each layer following the same drilling and collection protocol outlined in **section 7.1.1**. For speleothem BT, 19 traverses ($n = 190$ samples) were obtained for Hendy Test analyses (**Fig. 7.1**), and five traverses ($n = 50$ samples) for sample M2 (**Fig. 7.2**). Samples were then run following the analytical procedure outlined in **section 7.1.2**.

7.2. Methods of Trace Element Analyses

Using leftover powders from the stable isotope transects, trace element analyses were undertaken on every fourth sample (i.e. every 4 mm) from speleothems BT and M2 (**Fig. 7.1, Fig. 7.2**), giving a total of 486 samples for speleothem BT, and 114 samples for speleothem M2.

Between 0.1 and 1 mg of powder was weighed into a plastic tube, along with a proportionate volume of a 5% nitric-acid solution (**Table. 7.1**), containing known proportions of the elements Sc, In, and Re, which were used as internal standards. Dilution factors were between 20,000 and 30,000, dependent upon sample weights. Samples were analysed in the School of Earth Sciences at The University of Melbourne on an Agilent 7700x ICP-MS tuned to provide low oxides ($<1\%$ CeO/Ce). Instrument parameters included an uptake time of 30 seconds, a stabilisation time of 35 seconds, and a washout time of 60 seconds. Dwell times were 1 ms for Mg and Ca, 5 ms for Sr, and 25 ms for Ba and U. A reference material of known composition was used for calibration and re-analysed every 20 samples for later drift corrections.

7.3. Stable Isotope Results

7.3.1. Stable Isotope Values

Complete stable isotope profiles ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) were obtained for both speleothems BT (**Appendix 6**) and M2 (**Appendix 7**), while only partial profiles were obtained for additional speleothems (**Appendix 8**). For speleothem BT (**Fig. 7.3**), $\delta^{18}\text{O}$ values ranged from -3.52‰ to -5.49‰ , a total range of 1.97‰ ,

and $\delta^{13}\text{C}$ values ranged from -7.61‰ to -11.21‰ , a total range of 3.6‰ . For speleothem M2 (**Fig. 7.4**), $\delta^{18}\text{O}$ values ranged from -4.38‰ to -5.56‰ , a total range of 1.18‰ , and $\delta^{13}\text{C}$ values ranged from -8.61‰ to -11.48‰ , a total range of 2.87‰ . The combined partial transects of the additional speleothems used in this study show $\delta^{18}\text{O}$ values ranging from -3.23‰ to -6.08‰ , a total range of 2.85‰ , and $\delta^{13}\text{C}$ values ranging from -5.93‰ to -11.84‰ , a total range of 5.91‰ . When broken down into variations between different caves and speleothems, relatively similar ranges and average values can be noted (**Table. 7.2**). **Fig. 7.5** shows that the isotopic ranges evident across all of the speleothems are comparable to those of the Nullarbor bedrock limestones during their first five stages of diagenesis (Miller et al., 2012a), including the fourth and fifth stages (encompassing the Pliocene) at which time the speleothems were forming. Isotopic signatures from later stages of diagenesis have been excluded from the figure, as they post-date the deposition of the speleothems. While there is greater variation between speleothems BT and M2, and the ‘additional’ speleothems, the evident similarities in isotopic values across all samples suggest that they are likely reflective of more regional influences than local influences: if local influences were driving the isotopic variations, a more significant difference in values would be expected between the speleothems from each cave system, as factors such as strong spatial variations in vegetation composition and cover, water pathways through the bedrock (including residence times), and cave microclimate would override regional factors (e.g. temperature and precipitation). As the ranges of values are comparable between the multiple speleothems and cave systems, it suggests that the sampled speleothems recorded regional climate changes.

The primary purpose of the partial profiles obtained from the additional speleothems was for verification and assessment of fluid-inclusion analyses and were discussed in **Chapter 6**; as such only the two complete profiles obtained from speleothems BT and M2 will be discussed henceforth in this chapter.

7.3.2. Hendy Test Analyses

For the Hendy Test analyses, assessments of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variation along individual layers were made (Hendy, 1971), with the multiple-traverse analyses allowing for assessment of potential disequilibrium conditions throughout the growth span of each speleothem. These assessments are used alongside record replications from similar time periods within the same cave system to determine the likelihood of the speleothems having been affected by disequilibrium fractionation.

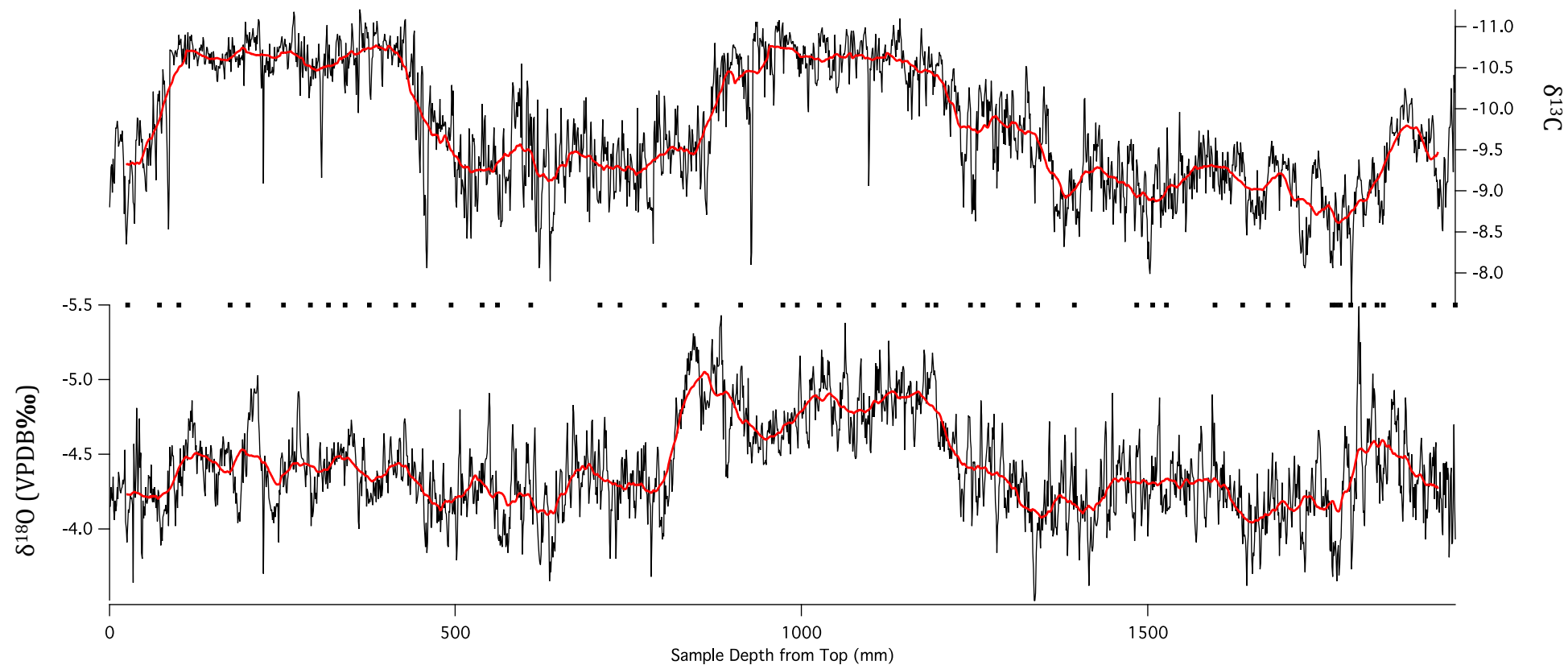


Fig. 7.3 – Stable isotope profile of speleothem BT (in black) and a 50-point moving average (in red). Transect changes are noted by markers in the centre of the graph.

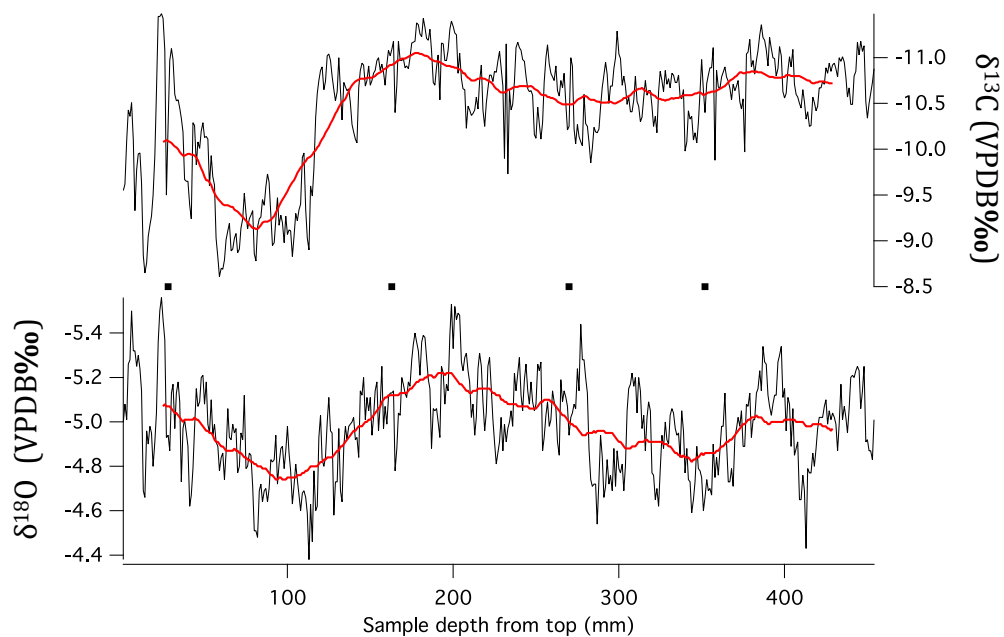


Fig. 7.4 – Stable isotope profile of speleothem M2 (in black) and a 50-point moving average (in red). Transect changes are noted by markers in the centre of the graph.

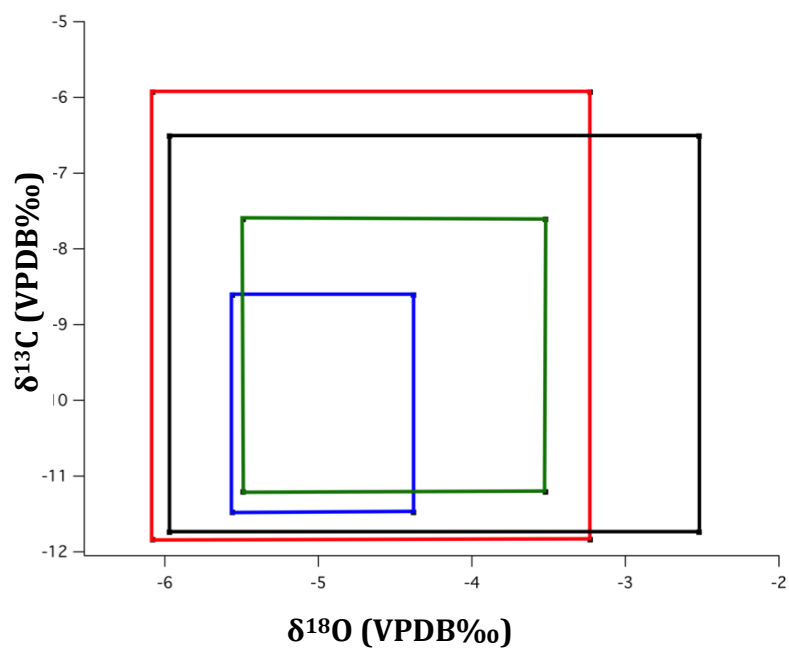


Fig. 7.5 – A visualisation of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ranges of all speleothems used in this study (BT in green, M2 in blue and additional speleothems in red) and of the bedrock limestones during the first five stages of diagenesis analysed in Miller et al (2012) in black.

Table 7.2 – Stable isotope ranges and averages for speleothem BT, M2, and the individual additional speleothems from which fluid-inclusion data were obtained. “Matilda Average” represents all speleothems obtained from this cave (including speleothems BT and M2), and “Additional Average” represents all of the additional speleothems obtained from other caves on the Nullarbor plain.

Speleothem	$\delta^{18}\text{O}$ (ppm)				$\delta^{13}\text{C}$ (ppm)			
	Min Value	Max Value	Range	Average	Min Value	Max Value	Range	Average
FIA	-3.49	-2.95	0.54	-3.34	-8.20	-5.93	2.27	-6.42
FIB	-6.08	-5.66	0.42	-5.82	-10.48	-9.24	1.24	-10.01
FIC	-4.99	-3.36	1.63	-4.21	-7.52	-4.68	2.84	-6.32
FID	-5.42	-3.93	1.49	-4.42	-11.84	-9.53	2.31	-11.12
FIE	-5.54	-4.40	1.14	-5.08	-10.31	-7.74	2.57	-9.57
FIF	-5.25	-3.77	1.48	-4.52	-11.09	-8.65	2.44	-9.92
Additional Average	-6.08	-3.23	2.85	-4.53	-11.84	-5.93	5.91	-9.54
M2	-5.56	-4.38	1.18	-4.99	-11.48	-8.61	2.87	-10.44
BT	-5.49	-3.52	1.97	-4.41	-11.21	-7.61	3.60	-7.61
Matilda Average	-5.56	-3.52	2.04	-4.52	-11.48	-7.61	3.87	-9.90

For each layer evaluations of the relationships between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ were made as well as of changes in $\delta^{18}\text{O}$ values across each layer for both speleothems BT (**Fig. 7.6**) and M2 (**Fig. 7.7**). For the majority of individual layers there is no significant relationship between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, thus indicating that it is probable that the speleothems were not significantly affected by disequilibrium fractionation (Hendy, 1971).

While the Hendy test has traditionally been used in speleothem studies it has known limitations, which have become increasingly acknowledged (Dorale and Liu, 2009). It is now realised that covariance of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ does not definitively indicate that the speleothem was forming under disequilibrium conditions, and may be a result of sampling issues in regards to obtaining, in a precise manner, multiple samples from a single layer (Dorale and Liu, 2009). With these limitations in mind, while the Hendy test has been used in this study and argues against disequilibrium conditions, it is not being solely relied upon to reach this conclusion. An accepted alternative for the Hendy test is record replication; this is one of the several reasons that both speleothems BT and M2 were selected for analyses.

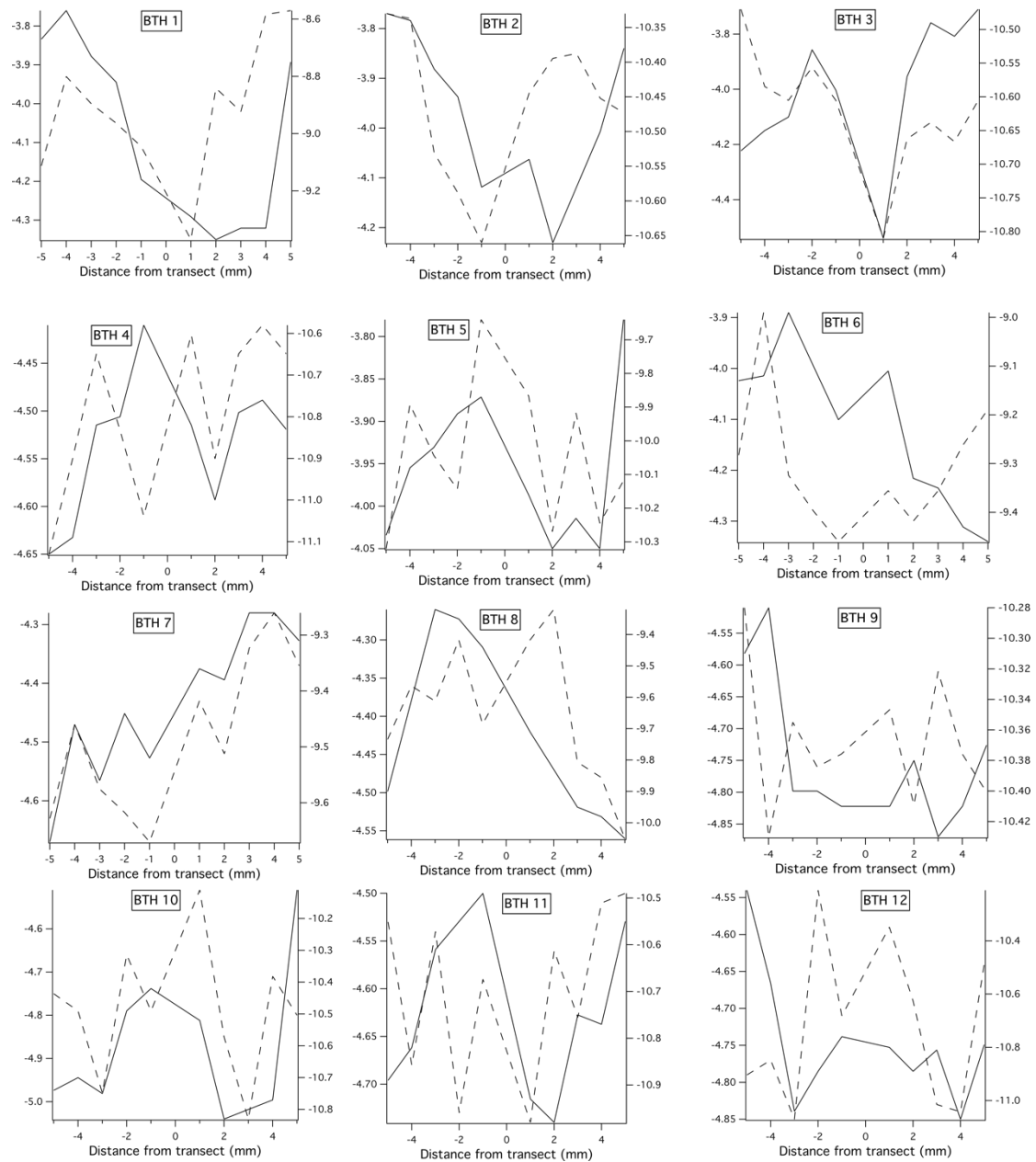
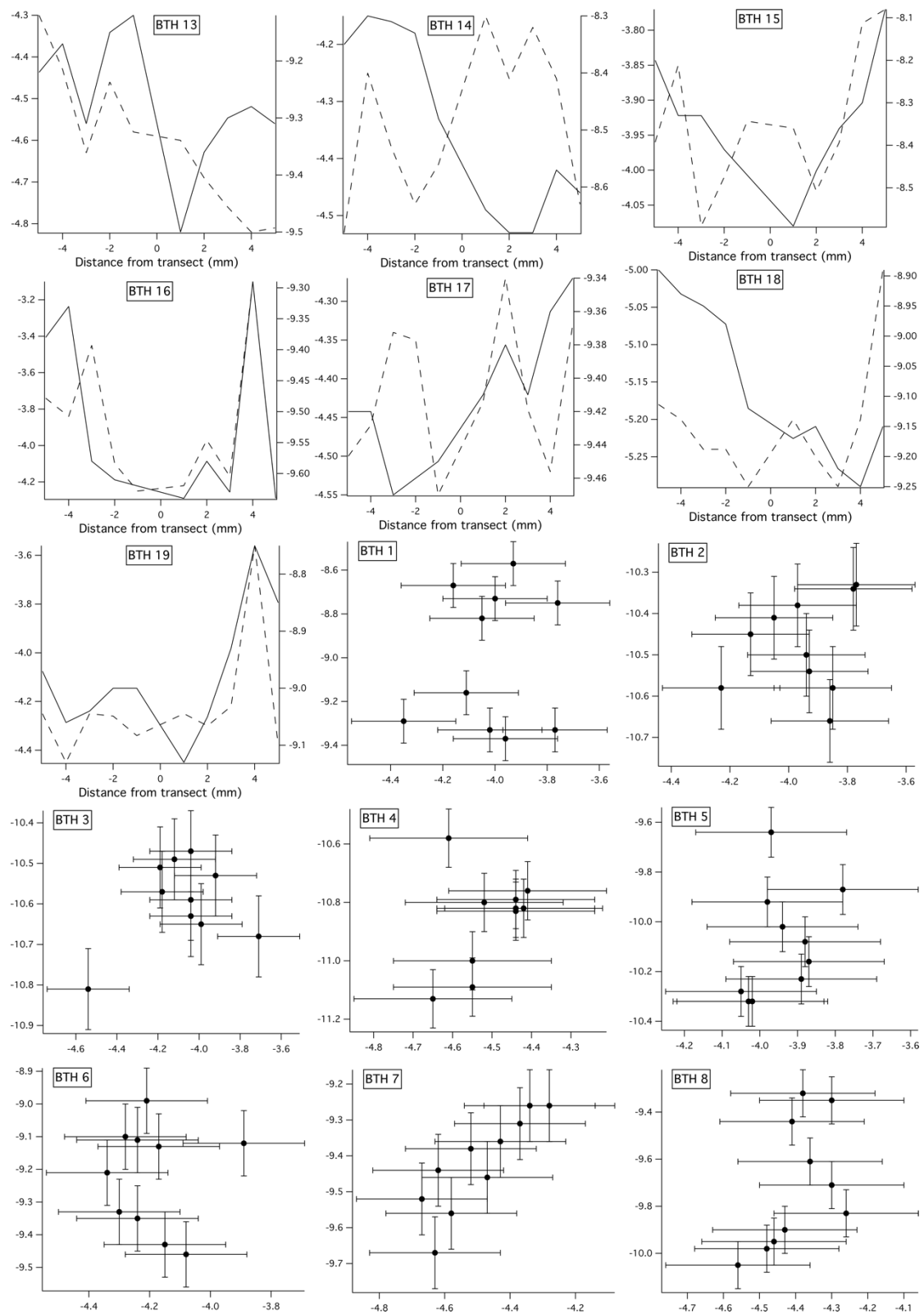
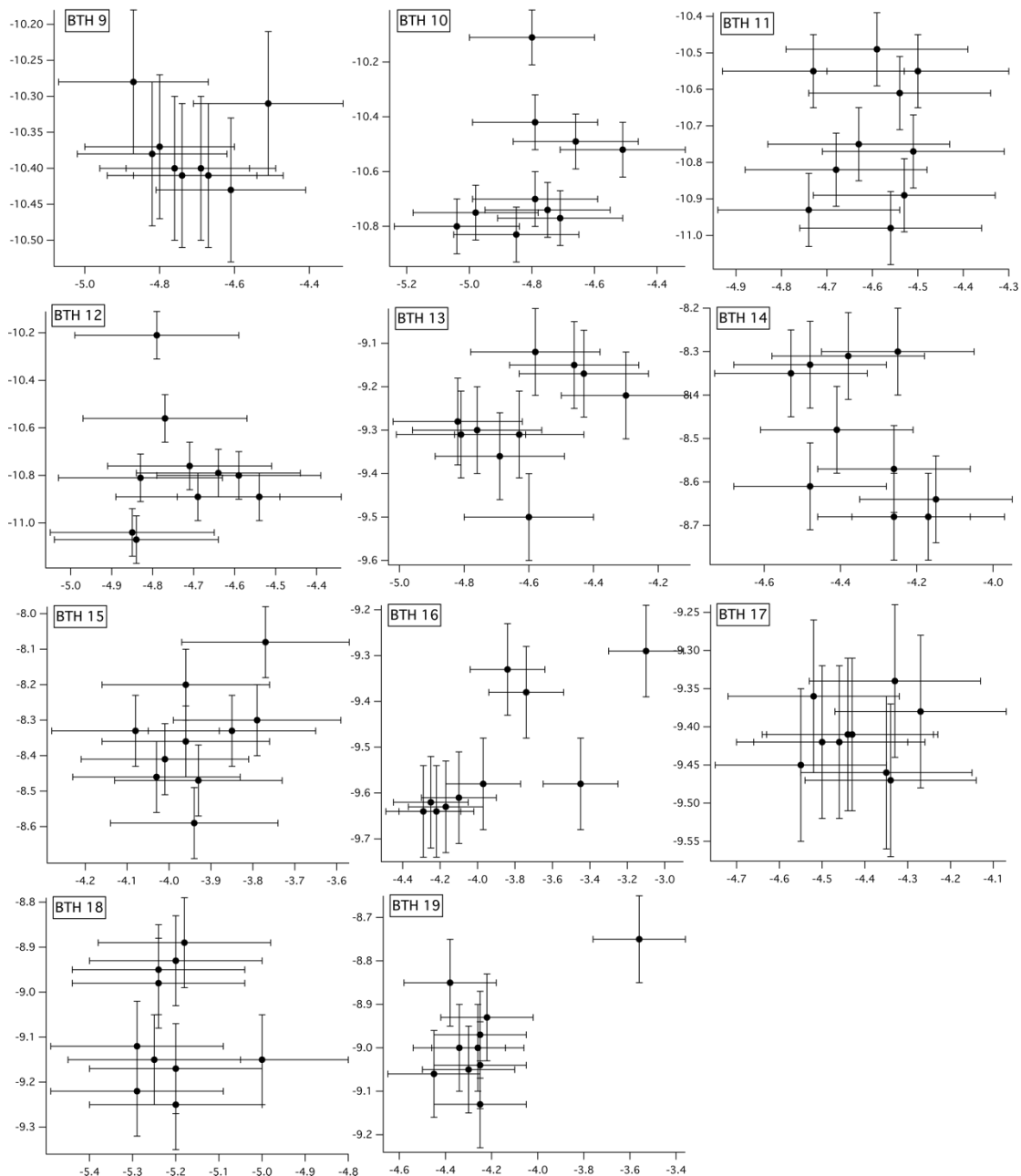


Fig. 7.6 – Visualisations of the Hendy Test analyses of speleothem BT. Graphs 1-19 show the variability across the width of the speleothem for the individual layers with the x-axis showing the distance from the transect (mm), and the y-axes showing $\delta^{18}\text{O}$ (VPDB‰ – left, dashed line) and $\delta^{13}\text{C}$ (VPDB‰ – right, solid line). The following 19 graphs show the correlations of $\delta^{18}\text{O}$ (VPDB‰ – x-axis) and $\delta^{13}\text{C}$ (VPDB‰ – y-axis) for each layer and the associated 1σ errors. Figure continued on the following two pages.





While the two records cannot be compared as overlapping series in a traditional way due to the constraints of the U-Pb dating, the similarity of the isotopic ranges obtained from both speleothems from similar locations within the same cave suggests that both were not significantly affected by disequilibrium fractionation. If prevailing disequilibrium conditions had occurred, a much greater level of variability would be expected between the two records, and potentially a much greater range of isotopic values, particularly $\delta^{13}\text{C}$, as this ratio is most susceptible to processes such as rapid degassing and evaporation. As such it can also be concluded that variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are representative of larger-scale environmental processes than non-equilibrium deposition.

7.3.3. Stable Isotope Analyses and Interpretations

7.3.3.1. Speleothem BT

Shifts in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values were compared to transect changes to assess any correlation between isotopic variation and changes in the orientation of the central growth axis of the speleothem. In speleothem BT, there are two possible incidences where significant shifts in isotope values correspond to growth axis changes. These are at the approximate positions of 800 mm and

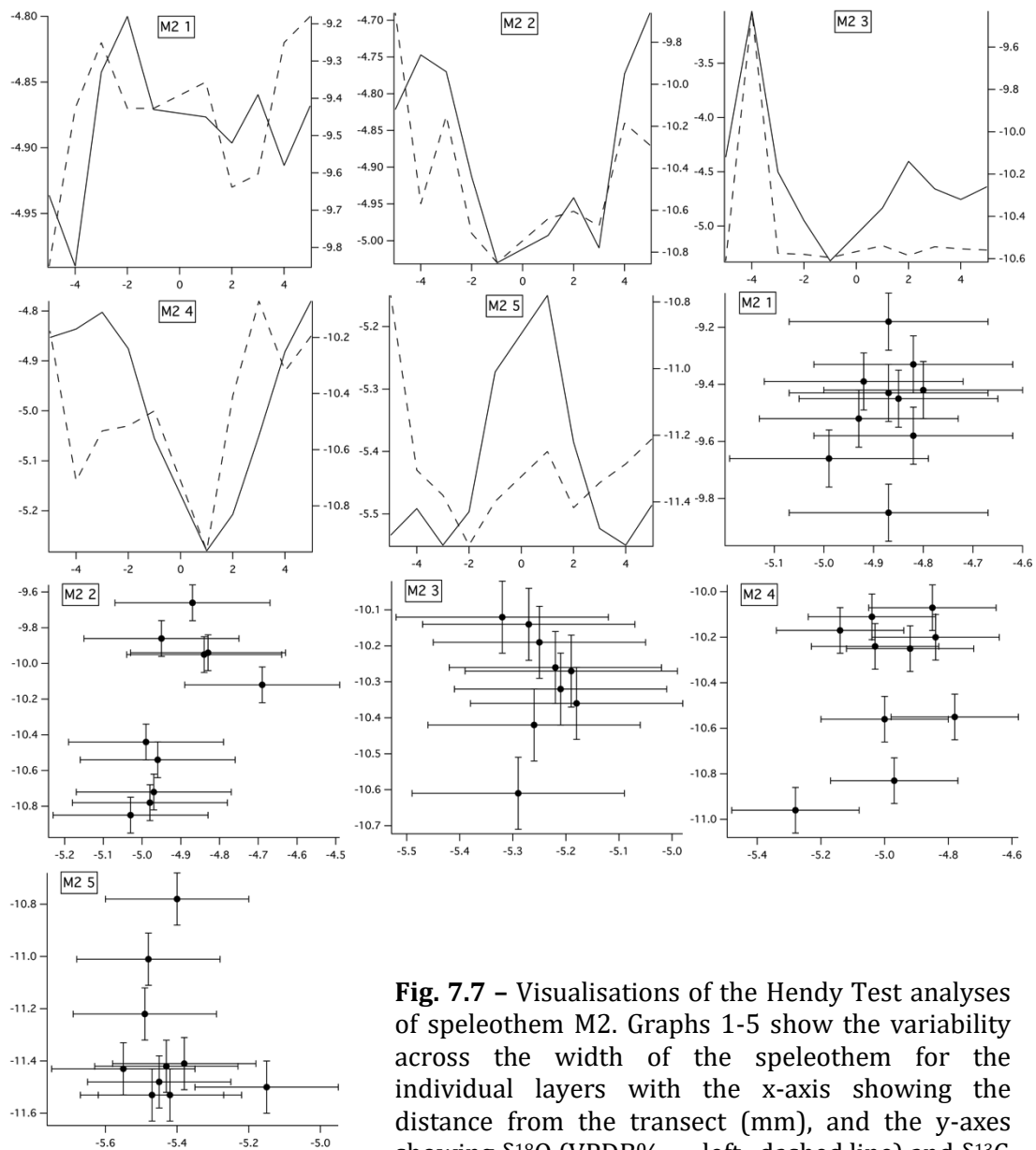


Fig. 7.7 – Visualisations of the Hendy Test analyses of speleothem M2. Graphs 1-5 show the variability across the width of the speleothem for the individual layers with the x-axis showing the distance from the transect (mm), and the y-axes showing $\delta^{18}\text{O}$ (VPDB‰ – left, dashed line) and $\delta^{13}\text{C}$

(VPDB‰ – right, solid line). The following 5 graphs show the correlations of $\delta^{18}\text{O}$ (VPDB‰ – x-axis) and $\delta^{13}\text{C}$ (VPDB‰ – y-axis) for each layer and the associated 1 σ errors.

1200 mm. As the shifts originating at these points are progressive, occurring over multiple samples (**Fig. 7.8**), it is unlikely that they represent substantial growth hiatuses, which are usually represented by large isotopic changes between two adjacent samples. This is somewhat supported by the U-Pb dates, as there is little room within the age uncertainties to accommodate long-term growth hiatuses. While it is still deemed unlikely due to the shifts occurring over multiple samples, it is possible that there were short-term growth hiatuses at these points.

As discussed in **Chapter 4**, it was not possible to develop internal chronologies so it is unfortunately not possible within the scope of this study to prove or disprove the occurrence of growth hiatuses within this speleothem. A 50-point moving average was calculated for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (**Fig. 7.3**) for the purposes of removing the high-frequency variability, thus better highlighting the similarities between the two isotopic profiles. The low-frequency variations throughout both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles are generally coeval; however, there are considerably larger variations in the $\delta^{13}\text{C}$ profile, suggesting that vegetation above the cave may be an important influence on the geochemical signals preserved in the speleothem. Although the two profiles generally co-vary there is a distinct deviation from this, as emphasised by the moving average, in the uppermost section of the speleothem (0 mm to 100 mm), where there is a distinctive depletion in the $\delta^{13}\text{C}$ values, which is not as apparent in the $\delta^{18}\text{O}$ values. This may result from a number of different influences, including increased aridity, reduced vegetation productivity above the cave, or the decreased drip rates commonly associated with the end of a speleothem's lifespan, and the resultant enhanced degassing occurring (Fairchild and Baker, 2012). Alternatively, it may be a result of the $\delta^{13}\text{C}$ shift preceding that of $\delta^{18}\text{O}$, a trend apparent at other significant shifts in the profile, e.g. at approximately 1400 mm and 800 mm in speleothem BT. There are several possible reasons for such delays to long-term shifts in the $\delta^{18}\text{O}$ profile in comparison to those of the $\delta^{13}\text{C}$ profile, which are presented here:

Possibility One:

Where moisture source is a key driver in precipitation $\delta^{18}\text{O}$, as is the case in modern Nullarbor precipitation (**see Chapter 5**), increased/decreased precipitation from an individual moisture source and resultant increase/decrease in vegetation cover may only be evident in the comparatively depleted/enriched $\delta^{13}\text{C}$ signal (Fairchild et al., 2006; Wong and Breecker, 2015; Yin et al., 2017). If increased precipitation from an individual moisture source is

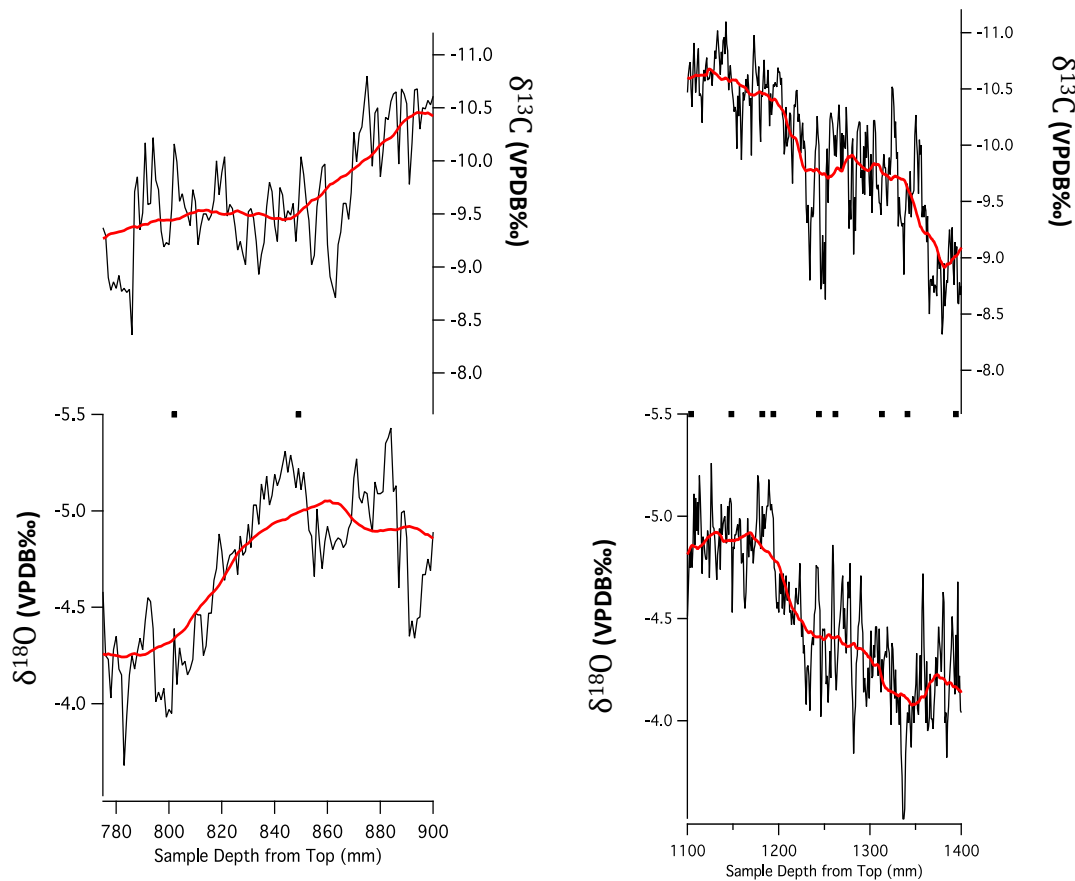


Fig. 7.8 – Examples of the multi-point isotopic shifts in speleothem BT at approximately 800cm (left) and 1200cm (right). Individual analyses tracked in black, a 50-point moving average (from the complete dataset) marked in red, and transects changes shown by the central markers.

a precursor to larger changes in the precipitation regime of a region in which significant changes in moisture source follow (for example, the increased precipitation evident in North America since 1910 (Karl and Knight, 1998; Trenberth et al., 2003) followed by increased frequency of high-intensity hurricanes from the 1970s (Webster et al., 2005), this may result in $\delta^{18}\text{O}$ shifts lagging the $\delta^{13}\text{C}$ shifts in a speleothem record. To date, no speleothem research has identified this, as it is unusual for such a lag to be evident unless on rapid (centennial-millennial) timescales. Therefore, this assumption cannot be made with confidence. However, it may be highlighted as an area for future research of modern stalagmites where reliable moisture source data is available, and internal chronologies are developed.

Possibility Two:

Alternatively, when increases in precipitation result in increases in vegetation density and diversity (Barbour and Diaz, 1973; Holmgren et al., 2001;

Eklundh and Olsson, 2003), it may also result in significant increases in evapotranspiration where the increased plant activity induces a significantly higher uptake of soil moisture and trace elements as a result of the increased soil moisture availability associated with higher rainfall frequency and amounts (Xu et al., 2004). Increased plant respiration has been shown to lead to increased soil biogenic CO₂ production and microbial activity, thus resulting in increasingly depleted $\delta^{13}\text{C}$ values (Liang et al., 2003; Fairchild et al., 2006; Perez-Mejias et al., 2017). Such moisture uptake may happen to the extent that it influences the amount of water infiltrating the cave (Green et al., 2015), especially when increases in precipitation are related to an increase in the number of low-rainfall events. In such cases, despite sufficient moisture for vegetation cover to increase, the resultant increased moisture uptake may not correspond with increased percolation waters into the cave, ultimately resulting in $\delta^{13}\text{C}$ variations becoming evident prior to $\delta^{18}\text{O}$ variations in the speleothem record. Once vegetation growth stabilises, often less moisture uptake from the soil is required to maintain the vegetation as alternative factors such as CO₂, light intensity begin to limit photosynthesis and respiration (Smith, 1938), therefore greater volumes of water will then percolate into the cave. It is at this stage that the variations in $\delta^{18}\text{O}$ associated with increased and/or altered precipitation dynamics will become evident in the speleothem record.

Possibility Three:

An alternative but similar explanation for the $\delta^{13}\text{C}$ shifts preceding $\delta^{18}\text{O}$, is that rather than moisture availability (and therefore precipitation), alternative controls on plant growth, for example, temperature, may have altered as a primary response to changing climates (Smith, 1938; Xu et al., 2004). Under a constant moisture regime, temperature has been shown to account for large percentages of soil CO₂ efflux (in the long-term, representative of soil respiration from microbes and plant roots (Maier et al., 2011)). In this case, vegetation above the cave may have increased/decreased as an immediate response to other climatic changes such as an increase/decrease in temperature, thus influencing the soil and vegetation above the cave, and therefore the $\delta^{13}\text{C}$ signal (Yin et al., 2017). Despite these changes in $\delta^{13}\text{C}$, under these circumstances the $\delta^{18}\text{O}$ may remain unchanged until significant changes in precipitation occurred as a result of on-going large-scale climatic changes. Therefore, this may also explain the apparent delay in $\delta^{18}\text{O}$ shifts following $\delta^{13}\text{C}$ shifts.

Summary:

At this stage it is not possible to further evaluate which of the three possibilities is most likely, as there is not sufficient evidence to do so. The discussion will be revisited later in this chapter where conclusions can be supported by additional evidence from trace element and modern precipitation data. However, it is clear that vegetation above the cave has had a strong influence on the geochemical signals preserved in the speleothem.

7.3.3.2. Speleothem M2

As with speleothem BT, shifts in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for speleothem M2 were compared to transect changes to assess any correlation between isotopic variation and changes in the central growth axis of the speleothem. There is one isotopic shift that coincides with a change in the central growth axis: at the approximate position of 30 mm. At this depth, both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ become rapidly enriched before again becoming increasingly depleted.

This is the largest short-term variation throughout the profile and could represent a number of influences to be discussed later. As with the corresponding shifts in speleothem BT, this shift in isotopic values also occurs over multiple samples (**Fig. 7.9**), thus reducing the likelihood that it relates to a significant growth hiatus.

A 50-point moving average was also calculated for this speleothem, for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (**Fig. 7.4**), in order to assess any low-frequency correspondence between the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles. The moving average further exemplifies the distinctive shift at approximately 200 mm towards more enriched samples followed by a shift back towards more depleted values at approximately 100 mm. These shifts are evident in both the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles. There does also appear to be a general trend, from approximately 350 mm, of increasingly depleted values; however, this is more apparent in the $\delta^{18}\text{O}$ profile.

It could be argued that the corresponding trend in the $\delta^{13}\text{C}$ values has a delayed response starting at approximately 300 mm. However, the degree of depletion is less significant in relation to the complete profile compared to the corresponding trend in the $\delta^{18}\text{O}$ profile. There are several reasons that $\delta^{18}\text{O}$ variation may precede that of $\delta^{13}\text{C}$, in particular where the $\delta^{13}\text{C}$ variation is driven by changes in vegetation above the cave and $\delta^{18}\text{O}$ is largely temperature and/or moisture driven. In this case the $\delta^{18}\text{O}$ signal variations will become apparent more immediately, with a time delay in $\delta^{13}\text{C}$ variations relating to the time delay in vegetation responses to the changing climate above the cave.

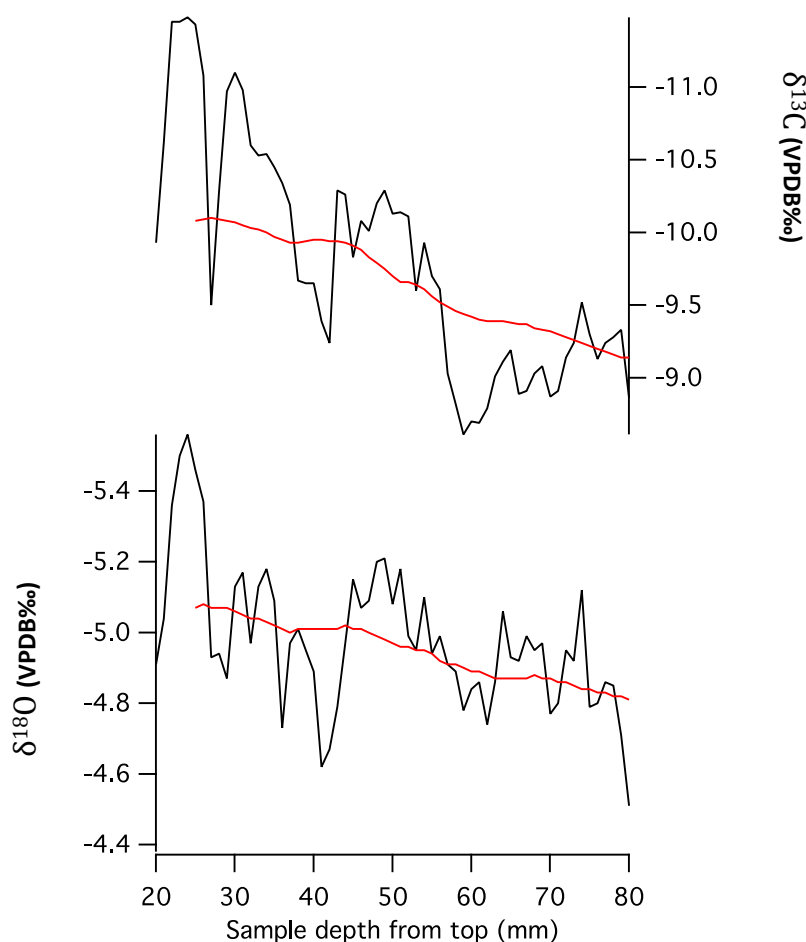


Fig. 7.9 – Example of the multi-point isotopic shifts in speleothem M2 at approximately 30 mm. Individual analyses tracked in black, a 50-point moving average (from the complete dataset) marked in red, and transects changes shown by the central markers.

7.3.3.3. All speleothem analyses

Due to the apparent similarities between the isotopic records of the two speleothems (in regards to $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ranges and coeval trends), and their growth locations within the same cave system, further interpretation of the range of values and apparent variations and shifts throughout the profile will focus on both samples simultaneously. Unfortunately, they cannot be directly compared as time series due to the overlapping age determinations throughout the speleothem.

There is a high level of understanding of the factors influencing speleothem $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. As such, interpreting the dominant processes influencing a speleothem at a given site is a matter of disentangling the evidence to eliminate certain factors, and identify others that are likely dominating the isotopic signal. In general terms, there are both high and low frequency variations evident in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles of both speleothems. It is most

likely that the low-frequency variations are related to global or regional-scale climate variations, perhaps of orbital origin, such as precession or obliquity-driven changes in insolation. This is suggested by the apparent covariation of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ low-frequency profiles (highlighted by the moving average profiles), indicating that larger-scale forces are driving the long-term isotopic variation. It is further supported by evidence provided in other speleothem studies in which speleothems are shown to be reliable records of orbital-scale climate changes (Wang et al., 2008; Drysdale et al., 2009; Hopley et al., 2018).

Without a robust time frame on which to base the low-frequency variations, it is not possible to confidently relate the isotopic profiles obtained in this study to other Pliocene reconstructions (e.g. Cliff et al., 2007; Ballantyne et al., 2010; Csank et al., 2011; Hill et al., 2011; De Schepper et al., 2014; Sniderman et al., 2016), or to any specific orbital parameters (e.g. Naish et al., 2009; Dolan et al., 2011; Willeit et al., 2013). Generally speaking, the low-frequency variations may possibly represent larger scale influences, it must be noted that overall isotopic variation will also be influenced by local-scale factors such as precipitation and vegetation. The differences between the extent and frequencies of these variations are suggested to result from the prevalence of different forcing mechanisms such as dominant regional climate modes on annual to centennial scales. While the resolution at which these isotope profiles were obtained obscures any potential annual-scale variations, the high-frequency variation may still reflect changes in the mean climate state over decadal scales. A high-resolution internal chronology would be required to reliably ascertain if this is the case or not, however, the profiles and level of variation within them for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles provides significant indications as to the mean climate state in the region at this time.

This problem highlights the need for further advances in Pliocene speleothem research and U-Pb dating capabilities. However, by assuming the maximum growth period of the speleothems (as tentatively derived from the ages and associated errors), and a constant growth rate, a maximum frequency for these variations can be developed (**Fig. 7.10, Fig. 7.11**). As discussed in **section 4.3.2** it is highly unlikely that the maximum growth periods provide a reliable timeframe for the records as it would suggest average growth rates of 0.00972 mm/yr and 0.00076 mm/yr for speleothem BT and M2 respectively, considerably lower than typical speleothem growth rates globally (**Table 4.4**). However, based on this timeframe, low-frequency variations appear to occur over periods of approximately 90 kyr in speleothem BT and 30 kyr in speleothem M2, with the low frequency variation being significantly more

variable in both speleothems. More detailed analyses based on this timeframe are not undertaken due to the improbability of it being a true representation of the growth of the speleothem. For a more realistic estimate the growth rate from Hesheng Cave, China (Johnson et al., 2006) has been applied. This has been selected as a location at a similar latitude to the Nullarbor, with a monsoon climate, thus precipitation amounts similar to those predicted for the Nullarbor region during the Pliocene. The average growth rate of the speleothems from Hesheng cave of 0.035 mm/yr, suggest a growth period of approximately 55,500 years for speleothem BT and approximately 13,000 years for speleothem M2. This in turn suggests that the low-frequency variations occurred over approximately 25,000 years in speleothem BT and 6000 years in speleothem M2. This suggests that it is within the realms of possibility that the low-frequency variations of $\delta^{18}\text{O}$ in speleothem BT are driven by cycles of precession, which has a mean period of approximately 26,000 years; this has been identified as a driver of $\delta^{18}\text{O}$ variations in well-dated speleothems elsewhere (Hopley et al., 2018). While this is an interesting possibility, it is not possible to reliably assess its likelihood without a robust age model for the growth of the speleothem. As such, it will not be considered further in this thesis.

While it is not possible to ascertain the timings of the variability evident, it is possible to consider the multiple possible drivers of this variability. Focusing solely on the $\delta^{18}\text{O}$ record presented by the two speleothems, there are several known influences on their isotopic values. These can be grouped into three categories: precipitation above the cave, the soil and epikarst zone processes, and temperature (both atmospheric and cave). The processes affecting the $\delta^{18}\text{O}$ of precipitation prior to its deposition at the cave site were discussed in detail in **Chapter 5**, and will be further discussed later in this chapter. A lack of significant regional tectonism precludes any effect of altitudinal change on $\delta^{18}\text{O}$ (Ghosh et al., 2006b). It is possible that changes in the physical properties of the soil account for some of the observed variation. There is also the possibility that changes in atmospheric and cave temperatures have controlled some of the variation. However, the range of $\delta^{18}\text{O}$ values found in these speleothems would require a temperature change beyond the realms of likelihood. In order to calculate the temperature change theoretically required, the minimum and maximum $\delta^{18}\text{O}$ values were input into the palaeotemperature equation of Tremaine et al. (2011), alongside the average $\delta^{18}\text{O}$ value derived from the complete fluid-inclusion dataset (**Table 7.3**). It is more reliable to use an average value for the $\delta^{18}\text{O}_{\text{water}}$ due to the uncertainties associated with the fluid-inclusion analyses. From this, it is calculated that the range of $\delta^{18}\text{O}$ values would

theoretically represent a temperature change of approximately 12 °C within the growth period of the speleothem. Therefore, it is highly unlikely that temperature would be the dominant influence on $\delta^{18}\text{O}$ variation. It is most likely that the $\delta^{18}\text{O}$ variations are largely driven by changes relating to precipitation, the details of which will be discussed later. However, the influence of temperature cannot be entirely discounted at this stage, and it is possible that the isotopic signals of the speleothem represent a combination of precipitation and temperature changes throughout its growth period.

There are other potentially influential factors, which are also important to consider. For example, as the precipitation percolates through the soil and bedrock, evaporation and the mixing of multiple precipitation events can influence the $\delta^{18}\text{O}$ signal ultimately preserved within the speleothem. The degree of influence of these factors cannot be accurately identified through stable isotope analysis alone, hence the need for a multi-proxy approach, which will be discussed in the following section. While $\delta^{13}\text{C}$ is less commonly applied in speleothem research than $\delta^{18}\text{O}$ due to the greater complexity of the underlying processes, there exists adequate knowledge to attempt to disentangle these potential influences. As with $\delta^{18}\text{O}$, we observe both low- and high-frequency variations in the $\delta^{13}\text{C}$ profiles of both speleothems. In comparison to the $\delta^{18}\text{O}$ values, there is a significantly larger range of $\delta^{13}\text{C}$ values evident in both speleothems; this can be attributed to the significantly larger carbon isotope variations evident in nature (McDermott, 2004; Fairchild and Baker, 2012).

The range of values is generally consistent with those typical where C3 vegetation is dominant above the cave (McDermott, 2004); as such, it is suggested that C3 vegetation types dominated the region during the period of speleothem growth. While intervals dominated by enriched $\delta^{13}\text{C}$ values may suggest an increase in the presence of C4 vegetation above the cave, there is little evidence in the literature that C4 vegetation had reached Australia by the Pliocene (Sniderman et al., 2016), therefore this factor can be discounted. While data are scarce, this conclusion is supported by current knowledge of the global progression of C4 vegetation (Osborne and Beerling, 2006; Edwards et al., 2010); assuming significant abundances of C4 vegetation arising in east Asia during the Pliocene-Quaternary transition (Zhou et al., 2014), it is highly unlikely that such vegetation would have been dominant in the Nullarbor region during the MPWP. This conclusion is further supported by the fact that for C4 to be the cause for enriched $\delta^{13}\text{C}$, one might expect to see a larger range of values than those apparent in these speleothems $\delta^{13}\text{C}$ profiles.

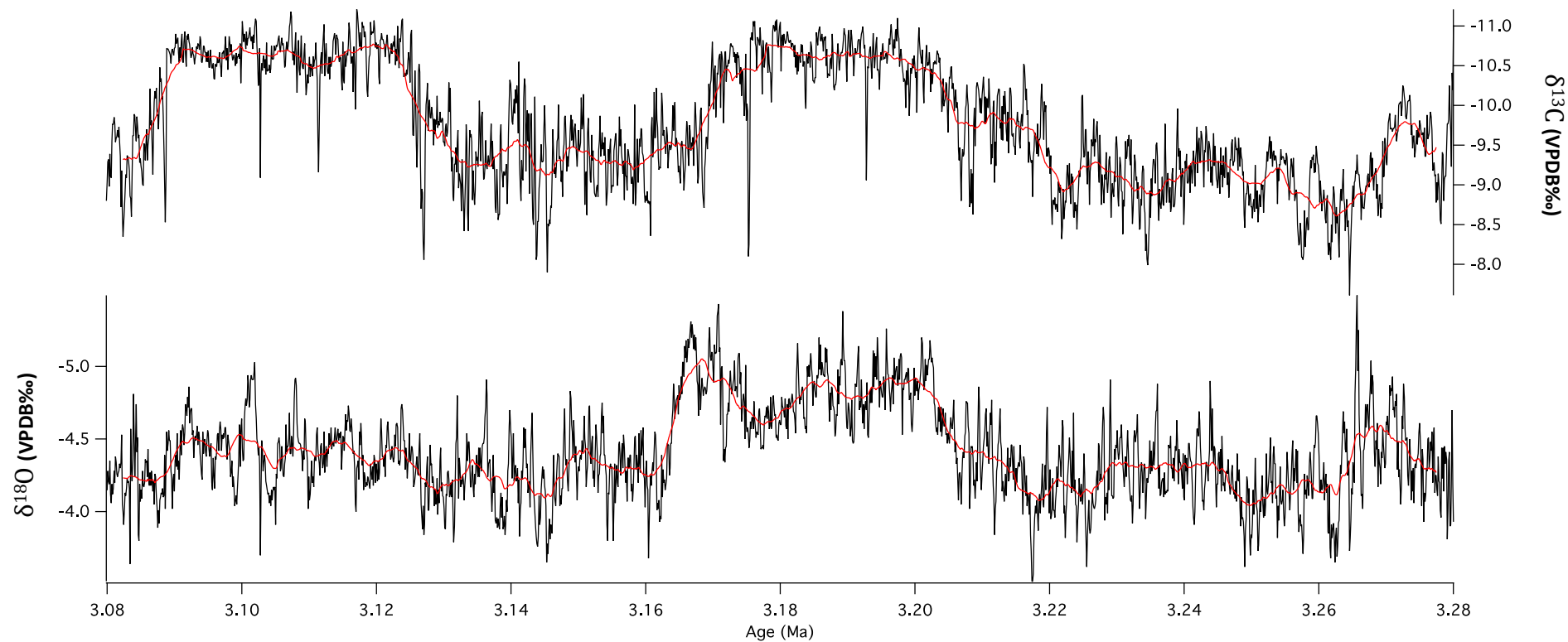


Fig. 7.10 – Stable isotope profile of speleothem BT (black) and a 50-point moving average (red), plotted on an age line determined from a maximum growth period/rate of the speleothem as determined by U-Pb ages and associated errors (**Fig 4.7**).

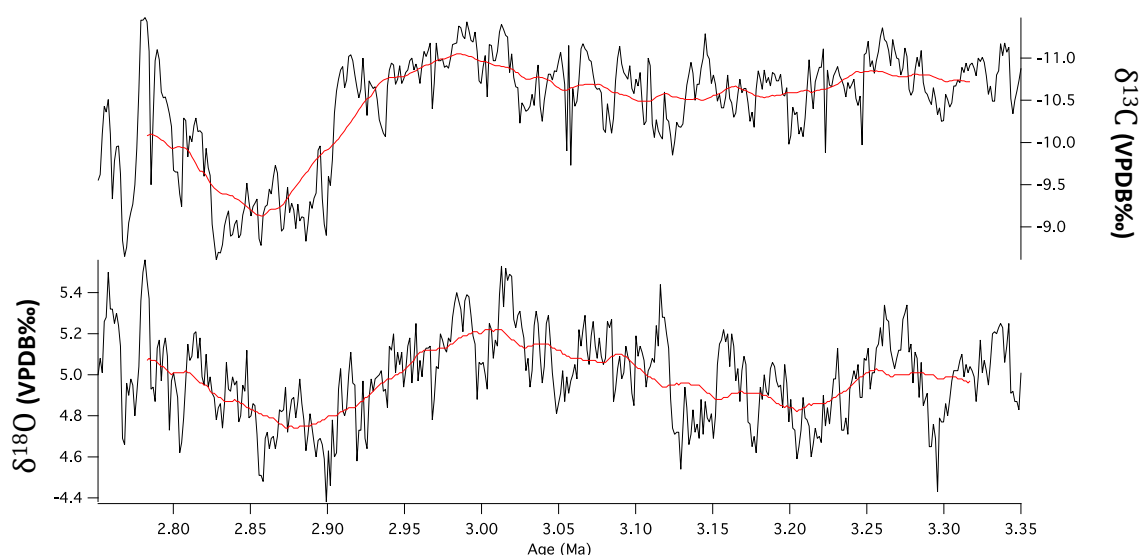


Fig. 7.11 – Stable isotope profile of speleothem M2 (black) and a 50-point moving average (red), plotted on an age line determined from a maximum growth period/rate of the speleothem as determined by U-Pb ages and associated errors (**Fig 4.8**).

Table 7.3 – The calcite and fluid-inclusion values used to calculate the theoretical temperature difference required to explain the $\delta^{18}\text{O}$ range evident in speleothems BT and M2. The fluid-inclusion $\delta^{18}\text{O}$ value used for calculating both temperatures is the average value from all successful fluid-inclusion analyses. Temperature has been calculated using the equation of Tremaine et al. (2011) for ease of comparison to the temperatures calculated in Chapter 6.

	Calcite $\delta^{18}\text{O}$ (VPDB‰)	Fluid-inclusion $\delta^{18}\text{O}$ (VSMOW‰)	$\delta^{18}\text{O}_c - \delta^{18}\text{O}_w$	Temperature (°C)
Max. Value	-3.52	-3.08	-0.44	21.7
Min. Value	-5.56	-3.08	-2.48	33.2

There are several other possible explanations for the variability evident. Bioproductivity in the overlying soil has been known to cause significant variability in the $\delta^{13}\text{C}$ profiles of speleothems (McDermott, 2004; Lambert and Aharon, 2011); here, increases in vegetation activity result in more depleted $\delta^{13}\text{C}$ values (Huguet et al., 2018). As vegetation amounts often relate closely to available moisture (Xu et al., 2004; Fairchild et al., 2006; Yin et al., 2017), it can be inferred that with increasing moisture one would expect increasing vegetation cover, and that this would translate into increasingly lower speleothem values of both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (although the $\delta^{18}\text{O}$ signal may be disguised by changes in rainfall regimes that increase $\delta^{18}\text{O}$ values). This is

supported by the apparent correspondence between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ profiles of both speleothems.

Additionally, pollen evidence in the region suggests that for much of the Pliocene, mesic forests of Eucalyptus, Myrtaceae, Proteaceae and Doryanthaceae existed in the Nullarbor region (Sniderman et al., 2016). These vegetation types are today restricted to the wetter climates of Australia's east coast and are largely reliant on high precipitation with significant summer rain (Groves, 1994), further supporting the hypothesis of precipitation being a key driver of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variations evident. However, using stable isotope analyses alone, it is not possible to confidently identify or exclude all of the potential influences on the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles observed in the two speleothems. The results of these analyses will be discussed henceforth.

7.4. Trace Element Results

7.4.1. Trace Element Variability

Data were obtained for the elements Mg, Fe, Cu, Sr, Y, Ba, La, Ce, Pr and U, all displayed as ratios to Ca, for both speleothems BT (**Appendix 9**) and M2 (**Appendix 10**). The elements Mg, Sr, Ba, and U are most commonly used in speleothem research and form much of the following discussion. While the other measured elements of Fe, Cu, Y, Le, Ce, and Pr have been cited as environmental proxies in the literature, for example Cu and Y as indicators of vegetation change (Borsato et al., 2007), they have been far less studied and as such there is significantly less confidence in their interpretations in a Pliocene context where internal chronology is poorly constrained. For this reason, they have largely been omitted from further discussions and interpretations, with the exception of a brief analysis that might encourage further investigation into these elements.

While the maximum values, minimum values and ranges of all key elements for both speleothems BT (**Table. 7.4**) and M2 (**Table. 7.5**) are largely similar, there are notable differences, with the values of speleothem BT being consistently higher with a wider range (**Fig. 7.12**). This is likely a factor of the significantly greater number of samples measured, the longer growth span of speleothem BT, and the potential for growth to have occurred over different time periods, thus representing different climate states. This level of variation between the two speleothems is to be expected and could relate to a number of factors including varying transition times and/or paths through the overlying soils and bedrock. However, overall the variations in all key trace elements vary over the same order of magnitude. This suggests that there are similar influencing mechanisms on the incorporation of trace elements in both

speleothems, further enforcing their use as duplicate samples from the same cave system during the same climatic phase of the Pliocene.

7.4.2. Trace Element Analyses and Interpretations

Moving averages were calculated for each element to coincide with those of the stable isotope profiles (**Fig. 7.13** and **Fig. 7.14**). Eliminating high-frequency variations reveals distinctive trends in individual elements. Pearson r correlation coefficients were calculated on both the raw values and moving averages (**Table 7.6**). Analysis of the raw values identifies relationships on a high-resolution scale, usually reflective of local variations, whereas analyses of the moving average targets low-frequency relationships in each of the elements, with the aim of identifying larger, potentially global trends.

Conventional statistical significance has the potential to be somewhat misleading when considering such complex natural systems, where traditional boundaries of significance become either unrealistic, or discount relationships that may not be statistically significant, but do hold significance in an environmental setting.

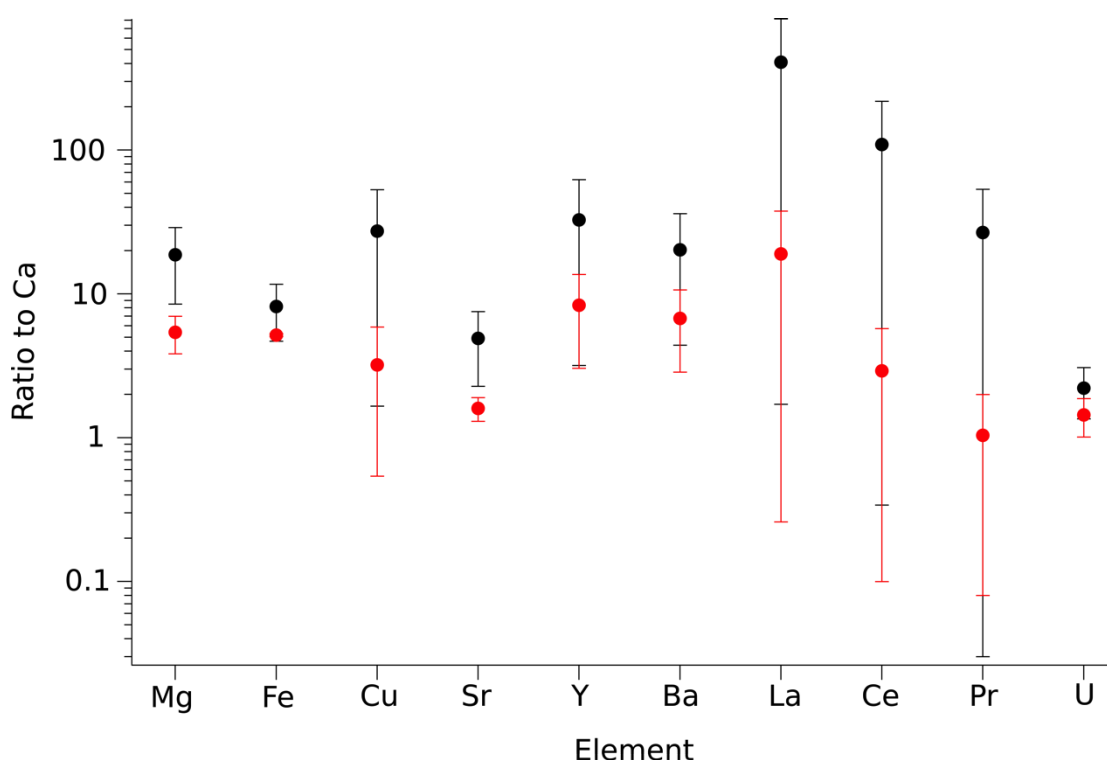


Fig. 7.12 – A comparison of the range of values in speleothems BT (black) and M2 (red) of each measured trace element. The error bars represent the minimum and maximum values, with the markers representing the median value. Each element has been multiplied by different factors for ease of comparison as follows: Mg ($\times 10^{-3}$), Fe ($\times 10^{-3}$), Cu ($\times 10^{-6}$), Sr ($\times 10^{-4}$), Y ($\times 10^{-9}$), Ba ($\times 10^{-6}$), La ($\times 10^{-9}$), Ce ($\times 10^{-8}$), Pr ($\times 10^{-9}$), and U ($\times 10^{-6}$).

Table 7.4 – The minimum values, maximum values, averages and ranges of trace element ratios to Ca in speleothem BT, multiplied by different factors for ease of comparison.

Element	BT (ratios to Ca)			
	Min	Max	Range	Average
Mg ($\times 10^{-3}$)	8.51	28.95	20.44	19.05
Fe ($\times 10^{-3}$)	4.69	11.67	6.99	4.93
Cu ($\times 10^{-6}$)	1.66	53.06	51.40	7.30
Sr ($\times 10^{-4}$)	2.28	7.54	5.26	4.10
Y ($\times 10^{-9}$)	3.18	62.30	59.12	19.71
Ba ($\times 10^{-6}$)	4.40	36.13	31.72	11.58
La ($\times 10^{-9}$)	-1.70	-816.81	-815.11	-111.92
Ce ($\times 10^{-8}$)	0.34	218.39	218.05	17.82
Pr ($\times 10^{-9}$)	0.03	53.47	53.44	2.68
U ($\times 10^{-6}$)	1.36	3.07	1.71	2.21

Table 7.5 – The minimum values, maximum values, averages and ranges of trace element ratios to Ca in speleothem M2, multiplied by different factors for ease of comparison.

Element	M2 (ratios to Ca)			
	Min	Max	Range	Average
Mg ($\times 10^{-3}$)	3.84	6.99	3.15	4.91
Fe ($\times 10^{-3}$)	5.04	5.30	0.26	5.12
Cu ($\times 10^{-6}$)	0.54	5.88	5.34	1.86
Sr ($\times 10^{-4}$)	1.29	1.90	0.61	1.50
Y ($\times 10^{-9}$)	3.03	13.66	10.63	26.92
Ba ($\times 10^{-6}$)	2.86	10.66	7.80	4.06
La ($\times 10^{-9}$)	0.26	37.72	37.46	18.51
Ce ($\times 10^{-8}$)	0.10	5.74	5.64	2.82
Pr ($\times 10^{-9}$)	0.08	2.00	1.92	3.21
U ($\times 10^{-6}$)	1.01	1.87	0.86	1.36

For this reason, while statistical significance is noted, it is applied to interpretations with caution. For 484 samples with 2 degrees of freedom, a critical value of r of 0.15 is required for significance at the 0.05 level, indicating that in speleothem BT, all apparent correlations with the exception of those

between $\delta^{18}\text{O}$ and Sr and U are statistically significant. In contrast, in speleothem M2 there are several insignificant relationships including those between Mg and Sr, and $\delta^{18}\text{O}$ and Ba. In both speleothems there are significant correlations between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, whereas the trace elements are consistently more significantly correlated with $\delta^{13}\text{C}$. This suggests that there are common drivers of the $\delta^{13}\text{C}$ and trace element signals, whereas the $\delta^{18}\text{O}$ signal, while still related to the $\delta^{13}\text{C}$ and trace elements is more independent and influenced by alternative factors that do not directly impinge on the trace elements. From the relationships and variability of the $\delta^{13}\text{C}$ and specific trace elements, it is possible that the higher variability is a result of local signals such as vegetation changes above the cave. Due to the correlations between $\delta^{13}\text{C}$ and the aforementioned trace elements, this conclusion is supported by the well-understood influences of vegetation on $\delta^{13}\text{C}$ due to respiration and CO_2 uptake of vegetation for photosynthesis (Liang et al., 2003; Fairchild et al., 2006; Wong and Breecker, 2015; Yin et al., 2017). It is argued that due to these relationships, it is likely that there was a sufficient residence time in the soil to incorporate the $\delta^{13}\text{C}$ and trace element signals from the soil in the percolation waters. From this it can be suggested that while there is a regional signal in both the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, the $\delta^{13}\text{C}$ and trace element signals are then complicated and disturbed by local drivers such as vegetation dynamics.

In speleothem BT, the trace elements most significantly correlated with $\delta^{13}\text{C}$ are Mg and Ba, whereas in speleothem M2 they are Mg and U. The strongest correlations between trace elements are Sr and U, and Mg and Ba in speleothem BT, and Mg and U in speleothem M2. Such differences between the two speleothems are not unexpected, as they may not represent identical periods of time of speleothem deposition. Even if there is overlap in the growth time periods, variations may still result due to percolation pathways through the bedrock and other factors associated with differing drips feeding speleothem growth. In this regard, it is important to consider the overall relationships between the various elements and the conditions that they likely represent rather than placing too much focus on the specific measured values. It is the relationships between particular elements and the overall shifts in values that provide clues to the processes driving the inferred environmental changes they represent. This will now be the focus of further discussion. The following discussion will aim to determine the most likely influences on each of the significant trace elements (Mg, Sr, Ba, U) in order to better understand the climatic information recorded in the geochemistry of speleothems BT and M2.

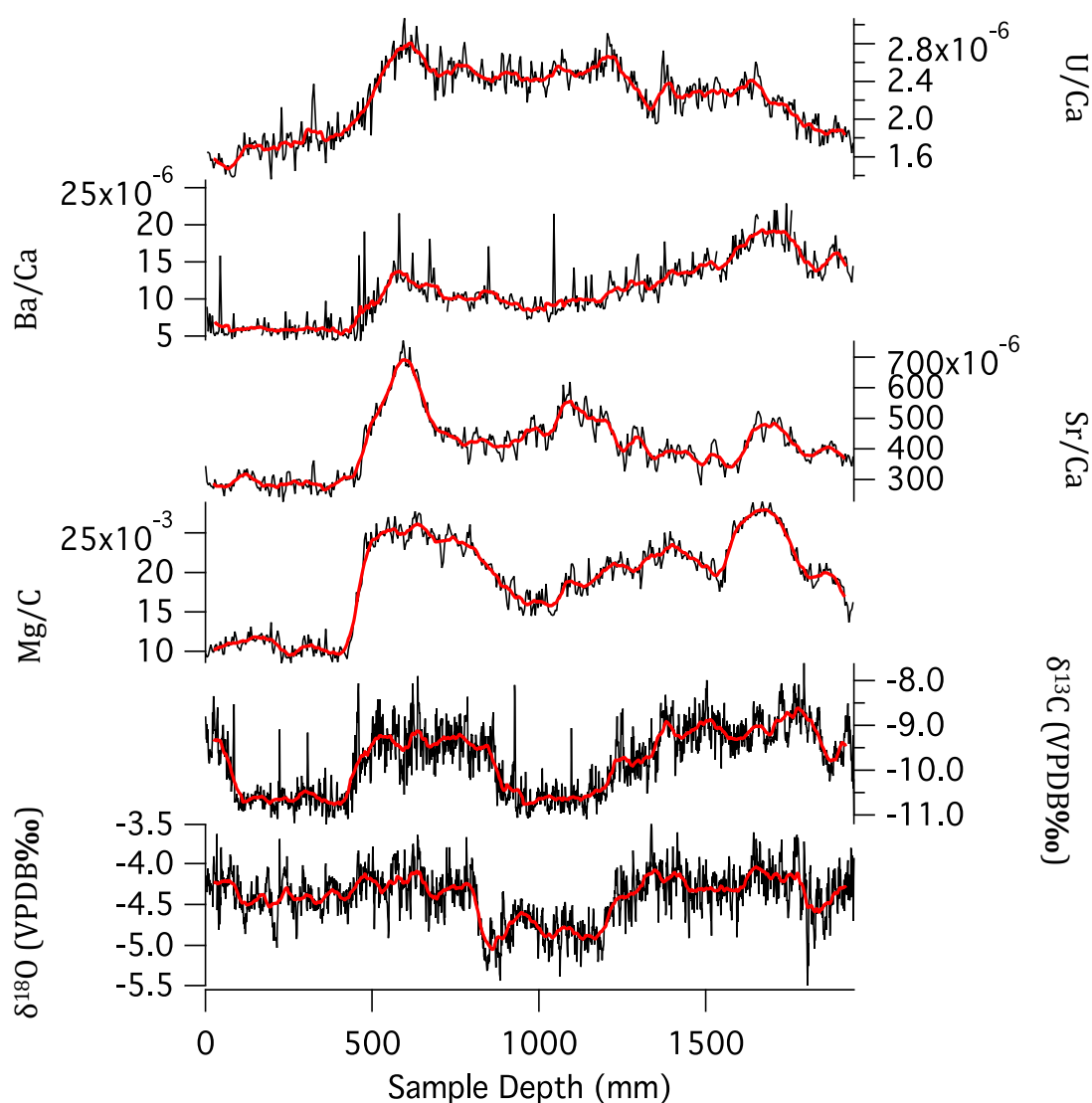


Fig. 7.13 – Stable isotope (VPDB‰) and trace element (ratios to Ca) profiles of speleothem BT (a 50-point moving average for each is displayed in red).

7.4.2.1. *Mg*

Mg is conventionally the most abundant trace element in speleothems as a consequence of Mg being the most prevalent cation in limestone after Ca (Tucker and Wright, 2009). This is the case in both speleothems BT and M2. The Mg/Ca values obtained in this study have been compared to a global collection of speleothems (**Table 7.7**). It is evident that the concentration of Mg of the Nullarbor speleothems is a little lower than the average of the studies compared in **Table 7.7**; this is in keeping with the extensive low-Mg calcite cement dominating the Nullarbor limestone (Miller, 2012; Miller et al., 2012a). As Mg is primarily derived from the bedrock (Fairchild and Treble, 2009b; Tremaine and Froelich, 2013; Rutledge et al., 2014; Vaks et al., 2018), this accounts for the

relatively low concentrations measured in the speleothems in this study. As there are lower than usual concentrations of Mg present, it must be noted that some signals may be obscured or appear insignificant in comparison to other studies. However, their variations and relationships with other trace elements remain indicative of climatic changes at the time of speleothem formation.

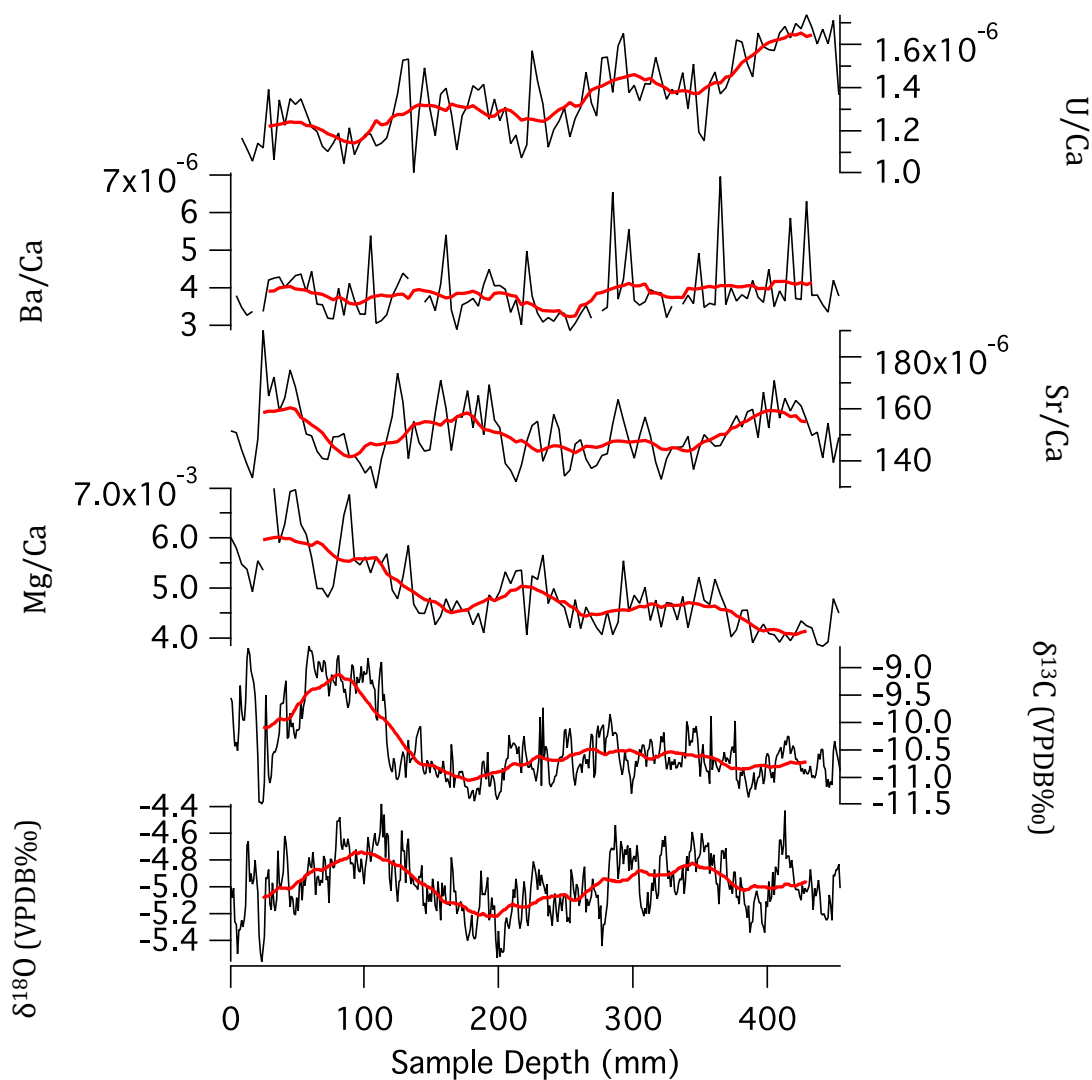


Fig. 7.14 – Stable isotope (VPDB‰) and trace element (ratios to Ca) profiles of speleothem M2 (a 50 point moving average is displayed in red).

Table 7.6 – *r* values obtained from Pearson correlations of isotope and trace element values. The tables present the correlations of all measured values and of moving average values for speleothem BT (left) and speleothem M2 (right); *r* values greater than 0.15 indicate statistical significance at the 0.05 level.

BT All	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Mg	Sr	Ba
$\delta^{13}\text{C}$	0.52				
Mg	0.25	0.62			
Sr	-0.05	0.20	0.66		
Ba	0.23	0.60	0.72	0.38	
U	-0.12	0.21	0.65	0.78	0.35
BT M.A.	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Mg	Sr	Ba
$\delta^{13}\text{C}$	0.61				
Mg	0.33	0.76			
Sr	-0.07	0.26	0.69		
Ba	0.35	0.78	0.82	0.41	
U	-0.20	0.24	0.71	0.82	0.37

M2 All	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Mg	Sr	Ba
$\delta^{13}\text{C}$	0.49				
Mg	0.22	0.48			
Sr	-0.28	-0.41	0.03		
Ba	0.00	-0.13	0.04	0.33	
U	-0.16	-0.48	-0.63	0.43	0.25
M2 M.A.	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Mg	Sr	Ba
$\delta^{13}\text{C}$	0.65				
Mg	0.27	0.72			
Sr	-0.33	-0.16	0.09		
Ba	0.04	-0.12	-0.02	0.53	
U	-0.10	-0.53	-0.64	0.41	0.50

Table 7.7 – A comparison of published Mg ranges in speleothems grown in various host limestones (or *partially dolomitised limestone).

Reference	Location	Mg Range (ppm)
This study	Australia	900-1,700
(Hellstrom and McCulloch, 2000)	New Zealand	300-550
(Treble et al., 2003)	Australia	3,000-6,000
(Johnson et al., 2006)	China	3,500-5,500
(Huang et al., 2001)	Italy	500-1,300
(Roberts et al., 1998)*	England	1,500-2,500
(Woodhead et al., 2010)	USA	600-2,000
(Cruz et al., 2007)	South Brazil	5,000-11,000

The covariance of Mg and $\delta^{13}\text{C}$ at key intervals such as at ~1500 mm, ~1000 mm, and ~500 mm in speleothem BT and ~150 mm in speleothem M2 suggest that where there are decreases/increases in both Mg and $\delta^{13}\text{C}$ values, it reflects increased/decreased rainfall and increased/decreased vegetation cover (signalled by decreases/increases in $\delta^{13}\text{C}$ values), and therefore decreased/increased residence time in overlying soils and bedrock (signalled by decreases/increases in Mg). In particular, the residence time in the bedrock has

been shown to result in strong correlations between Mg and $\delta^{13}\text{C}$ due to the differing extents of CO_2 degassing prior to speleothem deposition (Fairchild et al., 2000a; Drysdale et al., 2006).

It is still important, however, to consider alternative drivers of variations in the Mg profiles. The finding of early studies suggested that, in theory, Mg can be a direct indicator of cave temperature at the time of deposition, by which increasing temperatures result in increasing concentrations of Mg (Katz, 1973). This relationship is determined by the positive correlation between the Mg distribution coefficient and temperature. Based on this relationship there are Mg distribution coefficient ranges for both experimental (Tremaine and Froelich, 2013) and field measurements (Huang and Fairchild, 2001) for given temperatures. However, this relationship is dependent upon temperature being the sole influence on Mg incorporation and constant Mg/Ca ratios in the percolation waters. Where alternative source controls are found to be important in Mg, for example where Mg/Sr correlations indicate a strong bedrock component, Mg cannot be argued to be a function of temperature (Zhao et al., 2017), rather of changes in the Mg/Ca ratios of the dripwaters.

Variations in Mg, as well as Sr, have also previously been shown to be driven by the occurrence of prior calcite precipitation (PCP) in percolation waters (Fairchild et al., 2000a; McMillan et al., 2005; Zhao et al., 2017). This is a consequence of PCP reducing the Ca concentrations of percolating waters, as the Ca is lost to calcite deposition upstream of the speleothem (Fairchild and Baker, 2012). The resulting increase in the ratio of Mg:Ca (and Sr:Ca) in the percolation water eventually leads to elevated ratios in the speleothem (Sinclair, 2011). Therefore, where PCP is consistently occurring, it is expected that there will be a positive correlation between Mg:Ca and Sr:Ca (Sinclair et al., 2012). However, where PCP is occurring as a consequence of drier conditions and long residence times in the bedrock, there can be an anti-correlation between Sr and Mg (Tremaine and Froelich, 2013; Belli et al., 2017). This is due to lower rates of percolation, which can enhance the leaching of Mg from the bedrock at a greater rate than that at which the Mg and Sr in the percolating waters are deposited in PCP (Baker et al., 2008); where this is the case there is an overall increase in Mg, compared to a decrease in Sr. As such, the anti-correlation of Mg and Sr in speleothems can also be inferred to be a result of PCP, in particular that which is associated with long residence times of the percolating waters (Johnson et al., 2006). There is no evidence of either positive or inverse correlations between Mg and Sr in speleothem M2, and as such it is a justifiable assumption that PCP is either not occurring, or due to the geochemical complacency of this speleothem.

Speleothem BT, however, does display a positive correlation (**Fig. 7.15**), with an r value of 0.66 (**Table 8.6**), which is significant at the 0.05 level. As such, these effects of PCP on the Mg and Sr ratios must be considered as a potential influence on the geochemistry of speleothem BT unless it can be otherwise ruled out by other proxies.

Where it is determined that temperature and/or PCP effects are not the key drivers of Mg (and Sr) variation, it can be suggested that the Mg composition of the initial percolation waters (i.e. the precipitation above the cave) are the most significant influence. However, it is also important to consider other potential exogenic inputs such as aerosols. Due to the higher sea levels of the Pliocene (during the deposition of the Roe Plain), it is important to consider the potential impacts of the cave system being closer to the coastline. Commonly sea salt aerosols can be a significant influence on Mg and Sr abundances (Roberts et al., 1998) (Ayalon et al., 1999; Rutledge et al., 2014; Nagra et al., 2017), however if this were occurring at the time of the deposition of speleothems BT and M2, it would be expected that there would be a stronger correlation between the two elements. This correlation would only be apparent if the influx of Mg and Sr from sea-salt aerosols were significant enough to override sources of trace elements. As such correlations are not evident, it can be assumed that the more coastal location of the caves during the Pliocene in comparison to today was not a key influence on Mg abundances and variations. Therefore, it can be argued that the key drivers of such variations would have been changes in precipitation amount, resulting in variable residence times in the overlying soils and bedrock.

7.4.2.2. *Sr*

In addition to the previously discussed influences on Sr variation (residence time in the bedrock (Fairchild et al., 2006), temperature (Zhao et al., 2017), and sea spray (Ayalon et al., 1999; Rutledge et al., 2014; Nagra et al., 2017), increases in Sr concentrations have also been commonly shown to reflect increases in growth rate (Gabitov and Watson, 2006), as shown by the tendency for Sr to be adsorbed onto the lattices of actively growing speleothem calcite (Huang and Fairchild, 2001; Fairchild and Baker, 2012). Therefore, it can be suggested that variations in Sr concentrations may relate to variations in the growth rates of both BT and M2. However, it is not possible to determine whether or not this is the case without internal chronologies or detailed petrography for either speleothem. As such, the focus will remain on the influences that can be delineated within the constraints of this study. With the exclusion of factors impossible to discern without either knowledge of the composition of above-cave soil at the time of speleothem deposition or modern

speleothem comparisons such as the influences of exogenic inputs such as dust-borne particulates and sea spray (Ayalon et al., 1999; Vaks et al., 2018) and assuming consistent PCP, it can be argued that precipitation and karst hydrology must have been key influences on Sr variability. From this, variations in Sr are reflective of variable residence times in the overlying soils and bedrock, resulting in more/less incorporation of trace elements, including Sr, into the percolating waters. This conclusion is supported by the general covariance of Sr and Mg, whose variations have previously been attributed largely to changes in precipitation and therefore residence times in overlying soils and bedrock.

7.4.2.3. *Ba*

As with Mg and Sr, Ba concentrations are also influenced by a number of factors including speleothem growth rate, exogenic inputs and local precipitation and hydrology (Ayalon et al., 1999; Hellstrom and McCulloch, 2000). Previous research has indicated that where Ba and Sr closely correlate there is a likely strong influence of exogenic inputs and/or bedrock, particularly under periods of high precipitation where there is enhanced weathering of overlying soils and host rock (Ayalon et al., 1999). While this is somewhat the case in this study, one would also expect to see stronger covariation of Sr and Ba if exogenic inputs were the dominating factor in elemental variations, as a dominating common input would be expected to weaken any signal from other factors such as growth rate. From this it can be concluded that while exogenic inputs may have had some influence on Ba variations, it is likely that this was not a dominant influence. It is therefore suggested that the primary influence of Ba variation in speleothems BT and M2 is precipitation and local hydrology. Leaching rate in the soil zone and bedrock have previously been shown to have significant influences on Ba variation by which increased precipitation promotes increased vegetation cover, thus increasing soil pCO₂ with corresponding increases in carbonic acid concentrations thus enhancing the amount of leaching occurring (Yin et al., 2017). Previous studies have found the influence of overlying vegetation supported by negative correlations between Ba and $\delta^{13}\text{C}$ (Hellstrom and McCulloch, 2000). However, this is not the case in this study, where this is in fact a slight positive correlation evident in BT, and no correlation in M2 (**Table 7.6**).

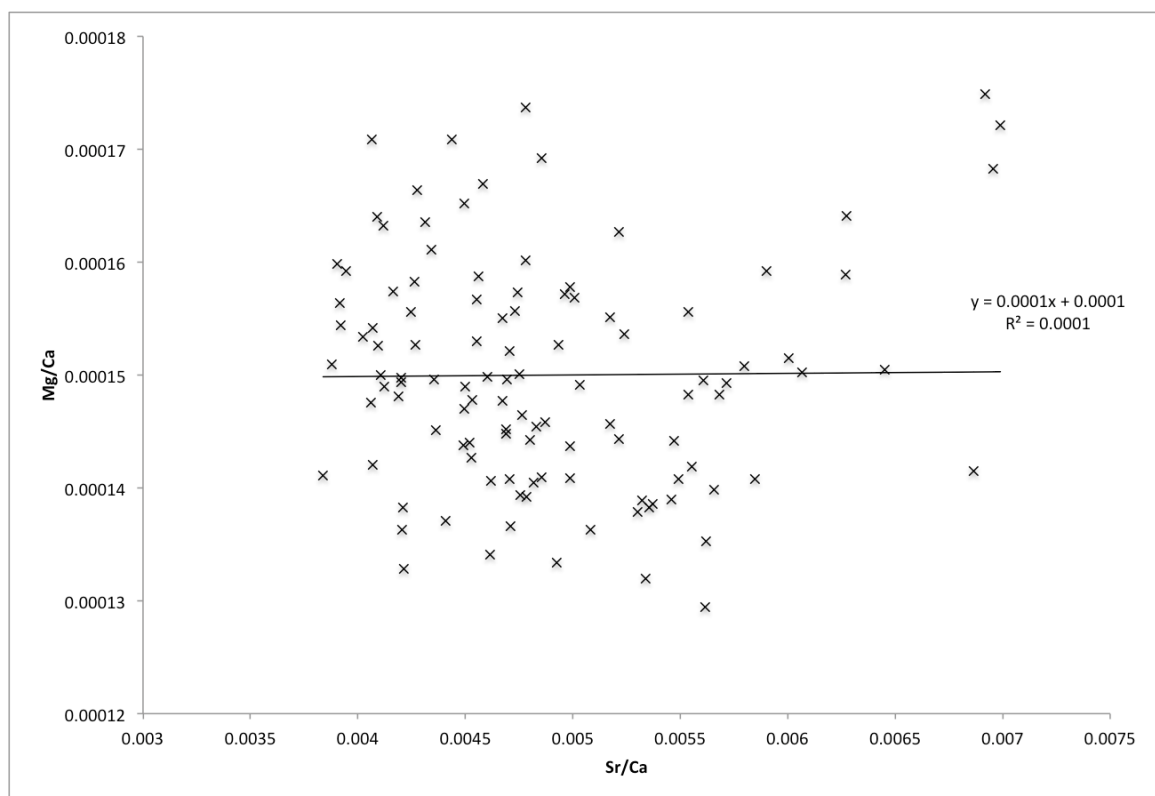
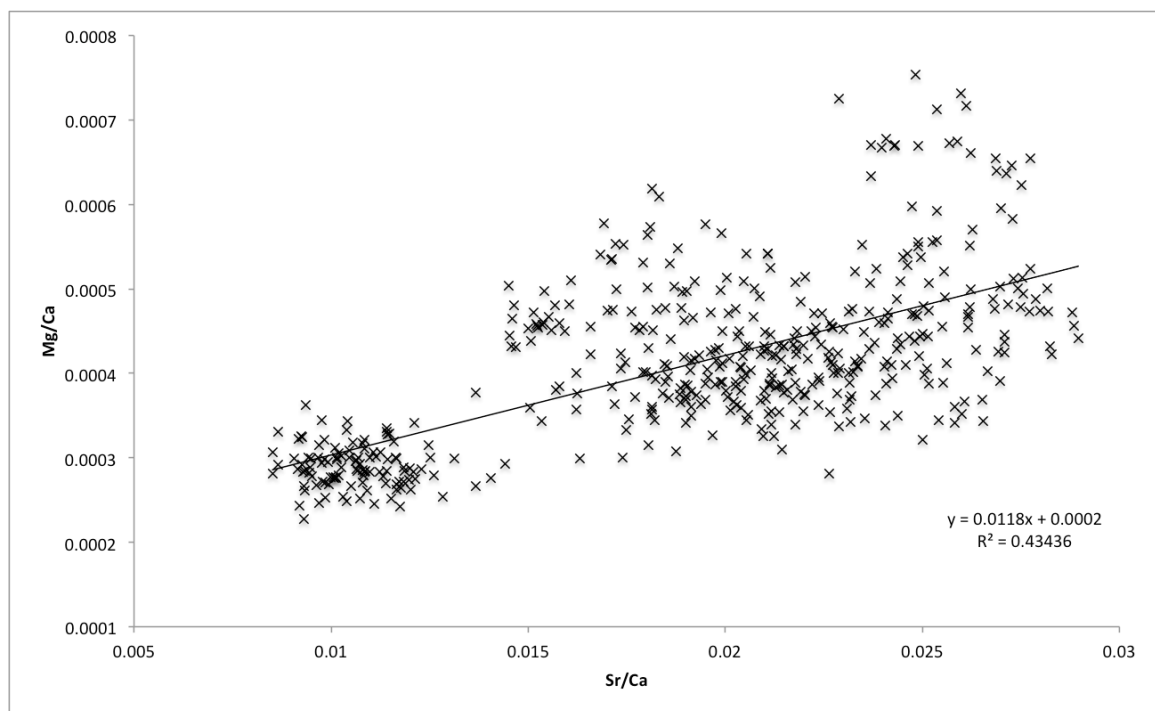


Fig. 7.15 – Correlations between Mg/Ca and Sr/Ca in speleothem BT (top) and speleothem M2 (bottom).

This may be indicative of thin soils, reducing the influence of the soil zone and increasing the influence of the bedrock, and also be an artefact of the lack of Ba-bearing mineral phases evident within the bedrock, which are required for such leaching to occur. From this it can be suggested that while vegetation had little impact on the Ba signal, precipitation was a key driver of variation. The positive correlation between Ba and $\delta^{13}\text{C}$ in speleothem BT does, however, further support the conclusion that precipitation and bedrock residence times, and potential PCP, are key influences of the geochemical signal in these speleothems, as suggested by the relationships between $\delta^{13}\text{C}$ and Mg, and Mg and Sr.

7.4.2.4. *U*

While U is less commonly reported than the previously discussed trace elements, there have still been discussions of its incorporation into speleothems in the literature (Ayalon et al., 1999; Treble et al., 2003), and has been suggested to provide a climate related signal in some cases (Ayalon et al., 1999). For example, in Soreq Cave, where U variations in speleothems are linked to transitions from colder and drier, to warmer and wetter climates, reflective of the resultant shift in relative proportions of bedrock-originating and soil zone-originating U. Indeed, most commonly in the literature, U variations have been attributed to water residence times in the bedrock (Ayalon et al., 1999; Nagra et al., 2017), and changes in vegetation cover, by which decreased U reflects decreased precipitation and vegetation cover (Treble et al., 2003). This has been related to the importance of U transported with organic matter (Baker et al., 1993). As both residence times in the bedrock and vegetation changes above the cave are essentially a function of changes in precipitation, whereby increased/decreased precipitation results in shorter/longer residence times and increased/decreased vegetation cover, precipitation is here deemed to be a primary driver of U variations. This is supported by the lack of other significant influences on U concentrations cited in literature. Regarding speleothems BT and M2, the conclusion of precipitation, and the resulting variations in bedrock and soil layer residence times, being a key driver of U (and other trace element) variations is supported by the high organic contents common in Nullarbor speleothems (Caldwell et al., 1982; Blyth et al., 2010; Sniderman et al., 2016). The high organic content is also evident in the uncommonly dark colourations of all speleothems studied in this thesis. The organic matter in speleothems has been shown to largely relate to the composition of overlying soils, suggesting that variations in residence times in these soils would have a notable impact on not only the organic content of the speleothems, but also on trace elements

obtained from these soils. Additionally, as the trace element signals of Mg, Sr and Ba all appear to indicate a strong palaeohydrological influence, thus increasing confidence in this conclusion.

7.4.2.5. Other trace elements

Although less well understood, the additional trace elements measured warrant some discussion. The trace elements Fe, Cu, Y, La, Ce and Pr have been compared to the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records of both BT (**Fig. 7.16**) and M2 (**Fig. 7.17**). While there are no strong correlations between any of these elements and the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles, there are some notable relationships and variations. While there is no consistent relationship between $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and Fe, there is a notable excursion in Fe values that appears to relate to the period of depleted $\delta^{13}\text{C}$ values from 500 mm in speleothem BT and from 75 mm in speleothem M2. This suggests that at this time, there may have been a change in the dynamics controlling the element variability related to the factors driving the $\delta^{13}\text{C}$ variation. The evidence suggests that there was increased in wind-blown particles either above the cave, being transported through the soil and bedrock, or directly into the cave at this time, as Fe is primarily sourced from such particles (Fairchild and Baker, 2012; Zhao et al., 2017); however, as this also coincides with a distinct decrease in Mg, which is also associated with aeolian particles as well as solutes (Fairchild and Baker, 2012), there must have been other factors involved. Additionally, as similar changes in $\delta^{13}\text{C}$, such as at ~1400 mm, show no response in the Fe profile and as there is no consistent correlation with the $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ profiles, it is not possible from these data alone to further decipher the factors, or change in factors, driving the Fe variability in either speleothem. However, the combined decrease in $\delta^{13}\text{C}$ alongside Mg and Sr are indicative of increased precipitation from around 500 mm and resulting reductions in residence times in the overlying soil and bedrock. Assuming a dominance of the bedrock Mg signal in speleothem BT, this may explain the discrepancy between Mg and Fe during this period, as there may have been an increase in aeolian particles, which is evidenced in the Fe profile, while the Mg signal of this occurring is overridden by the bedrock Mg signal.

While not statistically correlated, there does appear to be some similarities between the profiles of elements Cu, Y, La, Ce and Pr, suggesting that a common driver in their variations (i.e. their atomic configuration resulting in near identical behaviours) is being overridden by other, unrelated, variations. Among other elements, Y and Cu have been found to correlate with the seasonal flushing of colloidal particles into the cave system, and also to changes in vegetation above the cave, by which their concentrations increase with

decreased vegetation cover (Borsato et al., 2007). However, if that were the case in this study, a stronger correlation between these elements would be expected. Additionally, the similarities of these profiles do not correspond with the $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ profiles, complicating further delineation of the drivers of their variations. Despite this, these tenuous relationships are significantly more evident in speleothem BT, with corresponding excursions in all of these elements at approximately 550 mm and 1900 mm. These excursions could be argued to correspond with shifts in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ profiles, however at 550 mm, the excursions precede a depletion in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ profiles, whereas at 1900 mm they precede an enrichment in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ profiles. This further suggests that there are other processes driving the variations in these elements, or that they are not dominated by any of the same processes as those dominating the variations of other elemental profiles.

While some suggestions can be made about the processes driving variations in some of these elements (Borsato et al., 2007; Hartland et al., 2012), it is important to note that these are suggestions based purely on the relationships with better-understood elements. A great deal more research is required into how these elements are transported to and represented within speleothems in order to be able to use these elements for robust palaeoclimatic interpretations.

7.4.2.6. Summary

This thesis emphasises that further research into the mechanisms by which trace elements are transported through the atmosphere, soils, karst system, and eventually incorporated into speleothems is of high importance to allow for more reliable interpretations of their variations and relationships. Overall, it can be argued that precipitation is likely the most influential factor on variations in Mg, Sr, Ba and U, further supported by the apparent co-variations with $\delta^{13}\text{C}$ discussed above. While there is no time scale on which to apply these variations, this study suggests that despite consistently warmer and wetter conditions during the MPWP, there was still significant climatic variability present in the Nullarbor region, particularly regarding precipitation amounts. As precipitation is consistently deemed a significant influence on the geochemical variability apparent in speleothems BT and M2, additional discussion will focus on further assessing and interpreting the likely changes in precipitation in the region throughout the Pliocene.

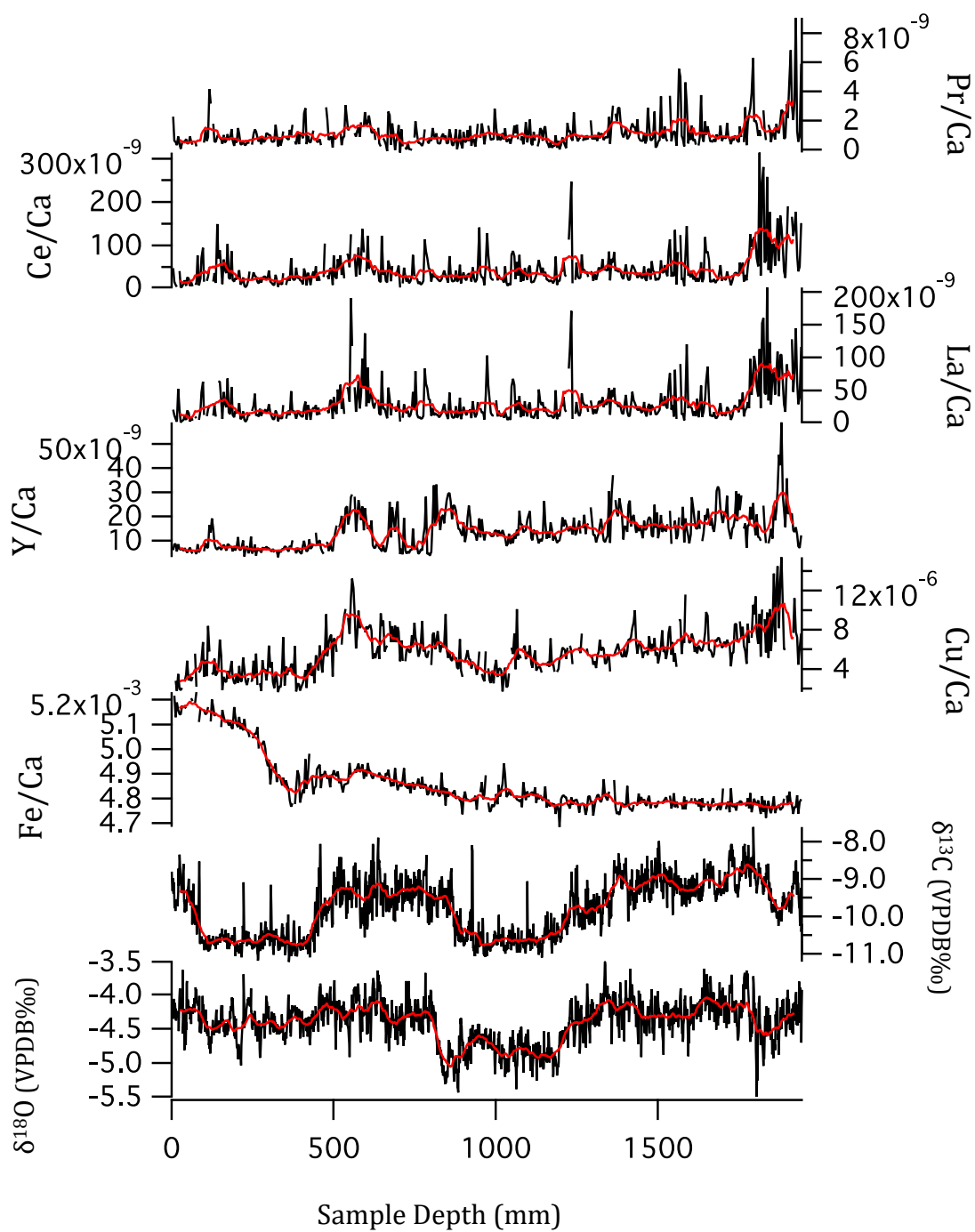


Fig. 7.16 – Profiles for the additional trace element to Ca ratios (and stable isotopes for reference) in speleothem BT.

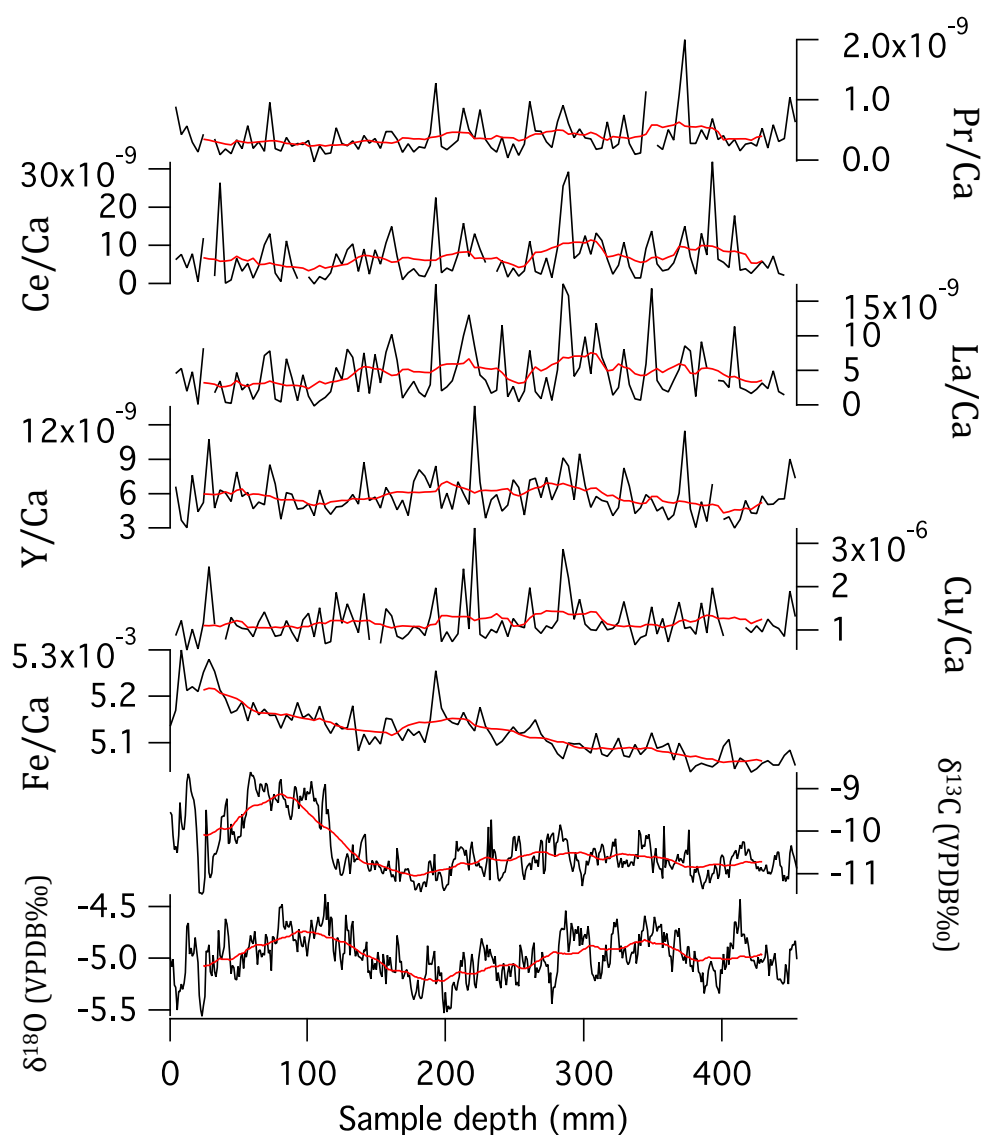


Fig. 7.17 – Profiles for the additional trace element to Ca ratios (and stable isotopes for reference) in speleothem M2.

7.5. Further Fluid-inclusion Interpretations

As precipitation has been identified as a major influence on the variation of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and trace elements evident in both speleothem BT and M2, it becomes important to consider fluid-inclusions as a recorder of precipitation $\delta^{18}\text{O}$ in addition to temperature. As discussed in **Chapter 2**, fluid-inclusions are potentially representative of the percolation water from which the speleothem was formed, thus representing the isotopic signature of the precipitation of the region at the time of deposition. As speleothem BT was found to have water contents too low for reliable results, data from the additional speleothems were

obtained and used for palaeotemperature analyses (**Chapter 6**) to augment the data from speleothem M2.

The range of isotopic values of fluid-inclusion $\delta^{18}\text{O}$ measurements obtained from all speleothems is -6.65 to -2.14 (measured) and -11.52 to -7.26 (predicted from δD , as presented in **Chapter 6**), in comparison to the total calcite $\delta^{18}\text{O}$ range of -6.08 to -2.95. As with the palaeotemperature analyses, the measured $\delta^{18}\text{O}$ values are used for these analyses as opposed to calculated $\delta^{18}\text{O}$ values from δD . The fluid-inclusion measurements of speleothem M2 have been directly compared to the complete calcite profile (**Fig. 7.18**), where a weak co-variation is observed. This co-variation appears to be reflected in the positive correlation ($r = 0.40$) between $\delta^{18}\text{O}_{\text{calcite}}$ and $\delta^{18}\text{O}_{\text{water}}$ from all accepted analyses (**Fig 7.19**). However, as this is insignificant at a 0.05 significance level (the critical value of r is 0.49), caution must be applied in interpretations. As there is a known relationship between $\delta^{18}\text{O}_{\text{calcite}}$ and $\delta^{18}\text{O}_{\text{water}}$ it can be deemed that the results presented here do in fact represent an important co-varying relationship, which has been obscured, firstly, by the complexity of the processes of preserving and measuring $\delta^{18}\text{O}_{\text{water}}$ values, and secondly, by the disproportionate inclusion of fluid-inclusions within growth layers (as discussed in **Chapter 6**). Therefore, although the $\delta^{18}\text{O}_{\text{calcite}}$ and $\delta^{18}\text{O}_{\text{water}}$ relationship is somewhat obscured, the $\delta^{18}\text{O}_{\text{water}}$ values obtained from fluid-inclusion analyses are argued to have potential applications in the interpretation of precipitation during the period of speleothem growth, when used with caution. As such, the application of modern precipitation analyses to interpreting palaeoprecipitation becomes of increasing importance.

In comparison to modern precipitation, it appears that the fluid-inclusion water is on average more depleted in comparison to the modern LMWL (**Fig. 7.20**). As it has been determined that the $\delta^{18}\text{O}$ of modern precipitation is largely driven by moisture source, the range of fluid inclusion $\delta^{18}\text{O}$ values (-6.67 to -2.19) and amount-weighted mean (-5.17) is comparable to the Southern Ocean and Southern Ocean / NCB interaction moisture sources in modern precipitation (**Table 7.8**). Caution must be applied in this interpretation, however, as it is possible that the discrepancy between the fluid-inclusion $\delta^{18}\text{O}$ and LMWL indicates post-depositional alterations in the fluid-inclusion $\delta^{18}\text{O}$ compositions, as it has been identified that exchange with the surrounding calcite can result in unexpectedly low fluid-inclusion $\delta^{18}\text{O}$ compositions (Demény et al., 2016). While significant processes of diagenesis can largely be ruled out due to the nature of the U-Pb analyses (see **section 4.3**), detailed petrographic analyses would be required to fully assess this possibility. For this reason, conclusions will only be

made regarding the comparatively depleted nature of the fluid-inclusion $\delta^{18}\text{O}$ alongside the interpretations of other proxies in the conclusions of this chapter. Such a multi-proxy approach greatly improves the reliability of any palaeoclimate interpretations, especially in the case of such ancient speleothems where individual analyses are associated with significant limitations.

7.6. Interpretations Based on Modern Precipitation Analyses and Palaeotemperature Estimates

Through the application of modern precipitation analyses, it is possible to identify the likely causes of isotopic variation in palaeoprecipitation. Under the basic assumption that the broad elements of the modern climate system driving and controlling precipitation behaved in the same way during the Pliocene, it can be argued that the causes of isotopic variation in modern precipitation are directly comparable to past isotopic variations. However, such direct comparisons must be treated with some caution, as it is possible that the isotopic signals of precipitation were influenced by factors not apparent today. For example, under the warmer and wetter climates evident in the Pliocene, differing degrees of evaporation, transpiration and rainfall recycling (by which rainfall collects on the earth's surface, is evaporated, and then precipitated again, similarly to the continental effect) may have been present and thus altered the isotopic signatures of precipitation in comparison to today. Despite this, it is reasonable to assume that the more extreme isotopic variations are likely responding similarly to the modern day precipitation isotopes, where moisture source, rather than temperature or rainfall amount, has been shown to be the primary driver of isotopic variation.

As precipitation, along with vegetation is suggested to be the most significant driver of geochemical variation in speleothems BT and M2, these speleothems theoretically represent a record of variations in precipitation in the Nullarbor region during the MPWP. The evidence presented thus far in this chapter suggests significant variations in precipitation and vegetation coverage throughout the growth of the speleothems, with $\delta^{13}\text{C}$ variations being a response to changes in both precipitation and vegetation coverage and composition, and with $\delta^{18}\text{O}$, and trace elements including Mg, Sr, Ba and U, being more directly driven by changes in precipitation.

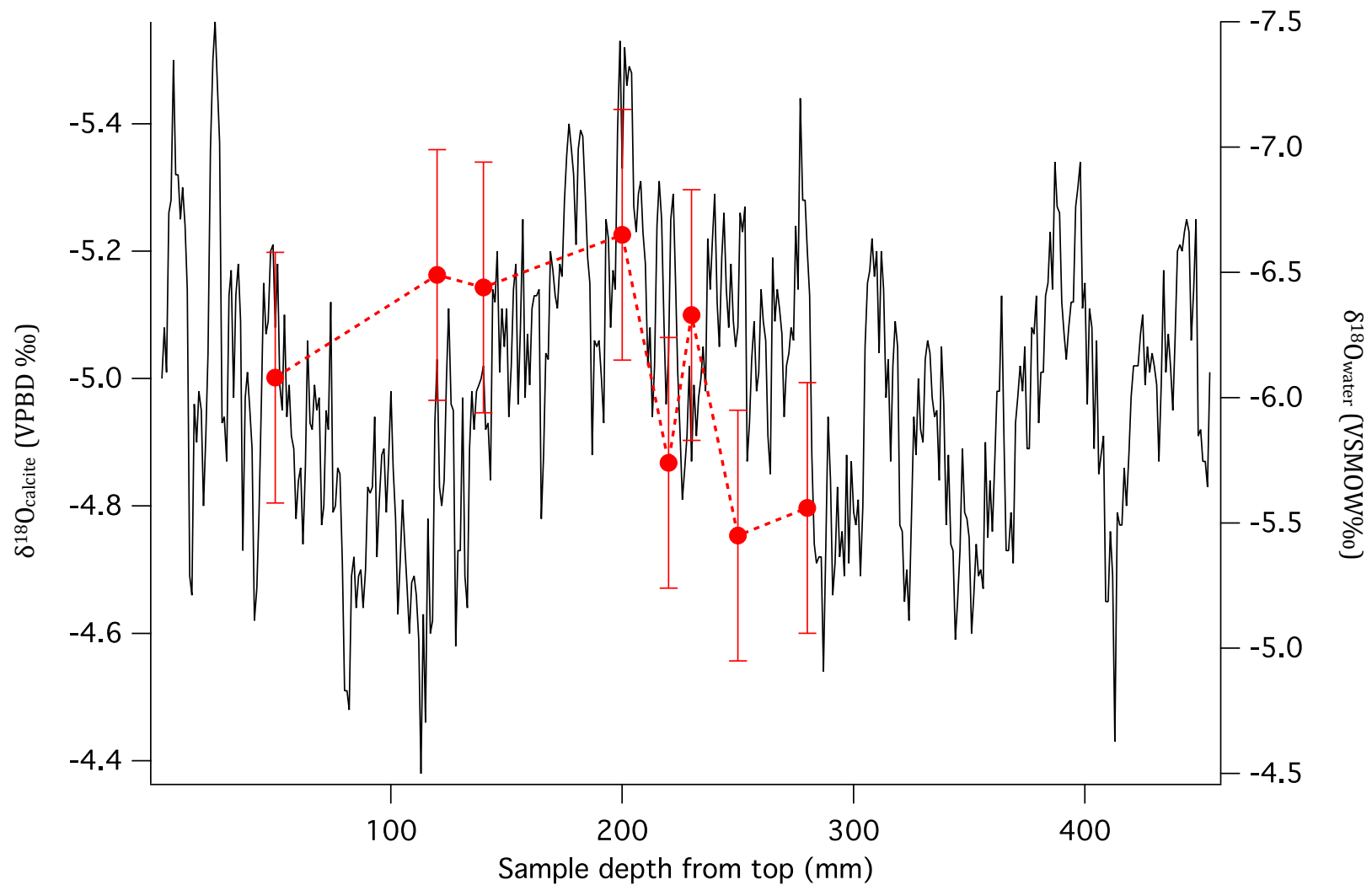


Fig. 7.18 – A comparison of the $\delta^{18}\text{O}_{\text{calcite}}$ profile from stable isotope analyses (in black) and the $\delta^{18}\text{O}_{\text{water}}$ measurements (in red, with 0.5‰ error shown) obtained from fluid-inclusion analyses from speleothem M2.

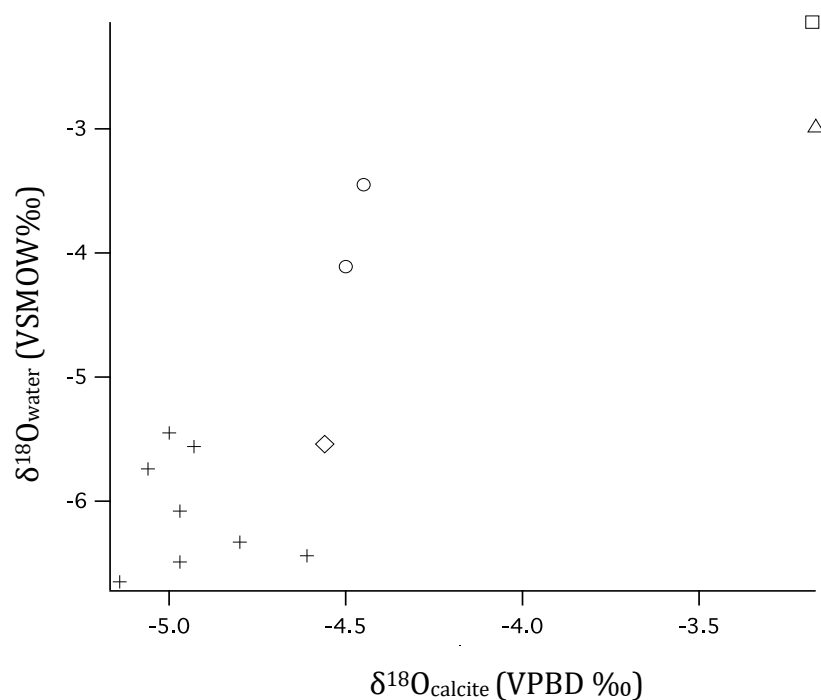


Fig. 7.19 – The correlation between measured values of $\delta^{18}\text{O}_{\text{calcite}}$ and $\delta^{18}\text{O}_{\text{water}}$. Samples from different speleothems identified by the markers: cross (M2), circle (FID), diamond (1411-11), square (2200-4), and triangle (FIA).

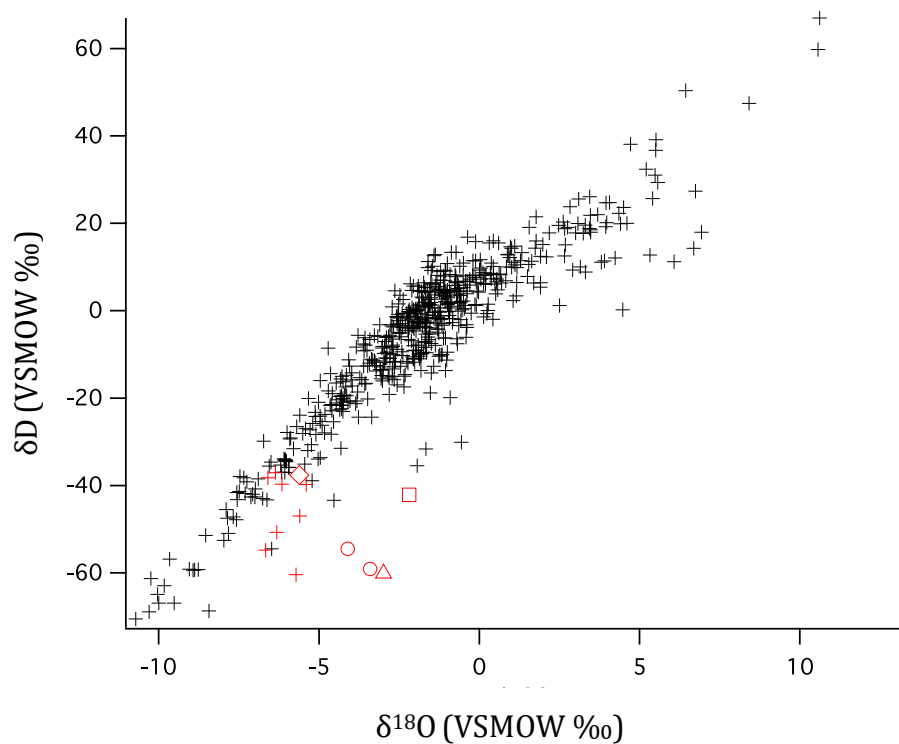


Fig. 7.20 – A comparison of $\delta^{18}\text{O}$ and δD compositions of fluid-inclusion water and modern precipitation. All accepted fluid inclusion samples in red (cross – M2, circle – FID, diamond – 1411-11, square – 2200-4, and triangle – FIA). in relation to the modern precipitation data (black crosses).

Table 7.8 – Minimum, maximum and weighted-average $\delta^{18}\text{O}$ values of the 4 moisture sources identified in the modern precipitation analyses, and of all accepted fluid-inclusion data.

Source	Minimum $\delta^{18}\text{O}$ (VSMOW ‰)	Maximum $\delta^{18}\text{O}$ (VSMOW ‰)	Weighted Average $\delta^{18}\text{O}$ (VSMOW ‰)
Southern Ocean	-10.72	1.28	-5.83
Southern Ocean / NCB interactions	-10.00	6.93	-5.48
Tropical	-8.93	13.18	-1.10
Tasman influenced	-7.47	3.80	-1.21
Speleothem fluid-inclusion	-6.67	-2.19	-5.17

While it is not possible to absolutely determine the details of these variations, it is possible using the modern precipitation analyses to deduce the most likely influencing factors. The analyses presented in **Chapter 5** suggest that there are significant relationships between moisture source and both temperature and $\delta^{18}\text{O}$, as well as moisture source and rainfall amount (**Table 5.20**). This suggests that the apparent increase in precipitation in the Nullarbor region during the Pliocene may have resulted from an increase in the prevalence of precipitation with either a tropical or NCB influenced moisture source. It is also possible that increased precipitation during the Pliocene is a reflection of a northward shift in the subtropical ridge. In the latter scenario, it becomes possible for mid-latitude storms to move further north, thus bringing more frontal systems and increased precipitation into southern Australia (Simmonds, 1990; Murphy and Timbal, 2008). While there is significant disagreement between models regarding the precise response of Australian precipitation to such atmospheric shifts (Maher and Sherwood, 2016), the general correlation between the position of the subtropical ridge and Australian precipitation is relatively well understood, i.e. a northward shift in the subtropical ridge is associated with increased precipitation sourced from (Timbal and Drosowsky, 2013). If such a shift occurred during the Pliocene, it would have resulted in more decaying cyclones reaching the Nullarbor region, with the associated low-pressure systems bringing higher rainfall to the region. Based on the isotopic

variation and signature of such systems in modern precipitation in the Nullarbor region, tropically sourced rainfall is consistently represented by anomalously enriched $\delta^{18}\text{O}$ values (**Table 5.21**). Therefore, based on modern precipitation, a significant increase in precipitation from this source would be represented by an enriched $\delta^{18}\text{O}$ signal in comparison to the average $\delta^{18}\text{O}$ signal of modern precipitation in the region, which is not the case in the palaeo data.

Where northern cloud bands are drawn towards southern Australia it may also be a result of the westerlies deflecting the conventional path of the Hadley circulation (Chen and Held, 2007). A contraction/expansion of the westerlies would result in fewer/higher amounts of northern cloud bands being diverted to southern Australia and thus potentially impacting significantly on precipitation amounts (England et al., 2006). A contraction of the Westerlies also extends the flow of the warmer waters of the Leeuwin Current further south (De Deckker et al., 2012), suggesting that it may have been a contributing factor to the overall warmer Southern Ocean (Passchier, 2011), and thus the smaller East Antarctic ice sheets in the Pliocene in comparison to present (De Schepper et al., 2014). Additionally, the presence of anomalously warm SSTs in the oceanic regions to the northwest of Australia enhances atmospheric circulation conducive to the development of northwest cloud bands (Theobald and McGowan, 2016; Theobald et al., 2016) that are found to be a significant factor in modern precipitation in this study. From this it can be hypothesised that, with the higher temperatures that have been modelled for the Pliocene, there likely would have been an increased frequency in the production of such cloud bands. This is likely to have been a significant factor in the increased precipitation over the Nullarbor during the Pliocene (Chan et al., 2011; Haywood et al., 2013; Willeit et al., 2013). Such suggestions are in keeping with both the overall climatic state of the Pliocene, and support the evidence of increased precipitation in the Nullarbor region. The isotopic signature of events sourced from Southern Ocean interactions with NCBs associated with strong Westerlies under modern conditions identifies such systems as having anomalously depleted $\delta^{18}\text{O}$ values in comparison to the mean local $\delta^{18}\text{O}$ values. An increase in the frequency of these cloud bands reaching the Nullarbor may theoretically be influenced by a number of factors (e.g. enhanced Westerlies and/or increased NW SSTs). However, it is difficult to disentangle these signals using modern precipitation alone. As such it cannot be concluded in this study which of these factors was causing the variations in NCB derived precipitation in the Pliocene. It is supposed that it is likely in response to a combination of these factors as it is unlikely that either elements could have had a strong enough influence

individually to have resulted in the degree of climate variation evident during the Pliocene in comparison to the present day (Haywood et al., 2010; Salzmann et al., 2011; Haywood et al., 2013). While differences in the synoptic systems may be present between the Pliocene and modern day, the principles resulting in temperature and moisture source driven $\delta^{18}\text{O}$ variation are likely to have remained the same. As such it is possible to argue that the $\delta^{18}\text{O}$ variations in both speleothems BT and M2 are representative of significant shifts in either moisture pathways to the Nullarbor region and/or temperature.

In order to assess the possible extent of moisture source and pathway on the $\delta^{18}\text{O}$ signals preserved in speleothems BT and M2, the following discussion reconsiders the evidence from the stable isotope and trace element profiles with specific reference to the understanding of modern precipitation and $\delta^{18}\text{O}$ signals. Based upon current systems (**Chapter 5**), it can be inferred that during periods of increasingly negative $\delta^{18}\text{O}$, it is likely that there was an increase in the occurrence of precipitation sourced from interactions between NCBs and Southern Ocean, and solely Southern Ocean air masses. In particular, increased frequencies of NCB sourced moisture has been found to result in increased rainfall over much of Australia (Ummenhofer et al., 2008). Regarding larger climate systems, under modern conditions, increases in NCB influenced moisture appears to closely correlate to negative IOD conditions (Ashok et al., 2003a), which are known to result in increased precipitation over much of Australia (see **Fig. 3.10**). Interestingly, negative IOD conditions have been shown to correlate to La Niña conditions, related to the increased SSTs in the waters north of Australia (see **Fig. 3.8** and **Fig 3.10**). This contradicts some modelled suggestions that El Niño-like conditions dominated during the Pliocene (Wara et al., 2005; Fedorov et al., 2006). However, negative IOD conditions have also been shown to persist independently of ENSO, (Ashok et al., 2003a); therefore, it is not necessarily the case that persistent negative IOD-like conditions are associated with a lack of El Niño-like conditions. Additionally, it has previously been ascertained that there is insufficient evidence for a permanent El Niño-like state during the Pliocene; therefore it is possible that La Niña-like conditions were prevalent alongside negative IOD-like conditions. This is an area of interest for future research to focus on, as it may provide significant insight into the likely rainfall patterns across Australia under the predicted increased intensity of El Niño events in the future (Pachauri and Meyer, 2014).

Based solely on the analyses of modern precipitation in this study, an increased prevalence of moisture sourced from the Southern Ocean and Southern Ocean / NCB interactions would be associated with cooler

temperatures (as precipitation from this source was most dominant in the winter months) and more frequent, higher rainfall amounts. In contrast, periods of particularly enriched $\delta^{18}\text{O}$ are inferred to represent an increase in the frequency of tropically sourced precipitation, which are associated with less frequent, low rainfall amount events. Under modern conditions, tropically sourced precipitation is most common in the spring and autumn months under comparatively warmer temperatures. These conclusions support the suggestion of the covariance of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ being precipitation driven, as the depletion/enrichment of $\delta^{18}\text{O}$ are associated with higher/lower precipitation amounts and frequencies, which would arguably result in increased/decreased biogenic activity and therefore the depletion/enrichment of $\delta^{13}\text{C}$. This is further supported by trace element profiles of Mg, Sr, Ba and U, which all indicate bedrock residence times to be a key driver of their variations. Where there are depleted/enriched $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values associated with increased/decreased rainfall, shorter/longer residence times would also be apparent, thus resulting in lower/higher Mg, Sr, Ba and U values. The evidence from the modern precipitation studies suggest that depleted $\delta^{18}\text{O}$ values are associated with events sourced from NCB and Southern Ocean interactions, with higher rainfall amounts and frequencies, and that enriched $\delta^{18}\text{O}$ values are associated with tropically sourced events with lower rainfall amounts and frequencies. This, alongside the agreement of $\delta^{18}\text{O}$ and multiple trace elements, greatly increases confidence in this conclusion and lends support to the notion that the Pliocene Nullarbor speleothems to be highly reflective of palaeoprecipitation. The fluid-inclusion $\delta^{18}\text{O}$ is in agreement with these conclusions, indicating a generally depleted $\delta^{18}\text{O}$ signature, which based on modern precipitation analyses would suggest an increase in Southern Ocean and Southern Ocean-NCB interactions, which are associated with higher rainfall amounts. However, such conditions are also associated with cooler temperatures under modern conditions, as these moisture sources were most prevalent in the winter months. This conflicts with the known warmer temperatures associated with the Pliocene. This apparent disparity suggests that while there is a relationship between moisture source and season/temperature, it is not causal, and that the annual variations in dominant moisture source is likely driven by factors other than temperature. As it has previously been determined that temperature is not the primary driver of $\delta^{18}\text{O}$ variation, and that it is closely related to changes in precipitation, it is reasonable to extrapolate this to suggest that under modern conditions, temperature is not a driver of precipitation $\delta^{18}\text{O}$, and that any relationship between them is a result of other influencing factors. This conclusion is further

supported by the evidence of this study, which indicates generally increased precipitation regimes through the growth of the speleothems, and also other evidence of Pliocene climates on the Nullarbor (Sniderman et al., 2016), and globally (Jansen et al., 2007), which consistently suggest both increased precipitation and temperature.

As it has previously been identified (**Chapter 5**) that temperature is closely correlated with modern precipitation $\delta^{18}\text{O}$, this relationship is further analysed here. The $\delta^{18}\text{O}$ profile of speleothem M2 is compared to the corresponding palaeotemperatures obtained from fluid-inclusion and clumped-isotope analyses (**Fig. 7.21**). Only one sample from speleothem M2 produced an accepted palaeotemperature from the combined fluid-inclusion and clumped-isotope analyses (M2 6); therefore the accepted palaeotemperatures from the individual analyses are also considered here with caution. While it has been deemed that the individual absolute temperatures from the fluid-inclusion and clumped-isotope analyses alone are not entirely reliable, within the scope of this multi-proxy discussion it is important to consider the overall trends of temperature variation suggested by them. It is also, however, important to note that due to the large overlap of stable isotope samples covered by each

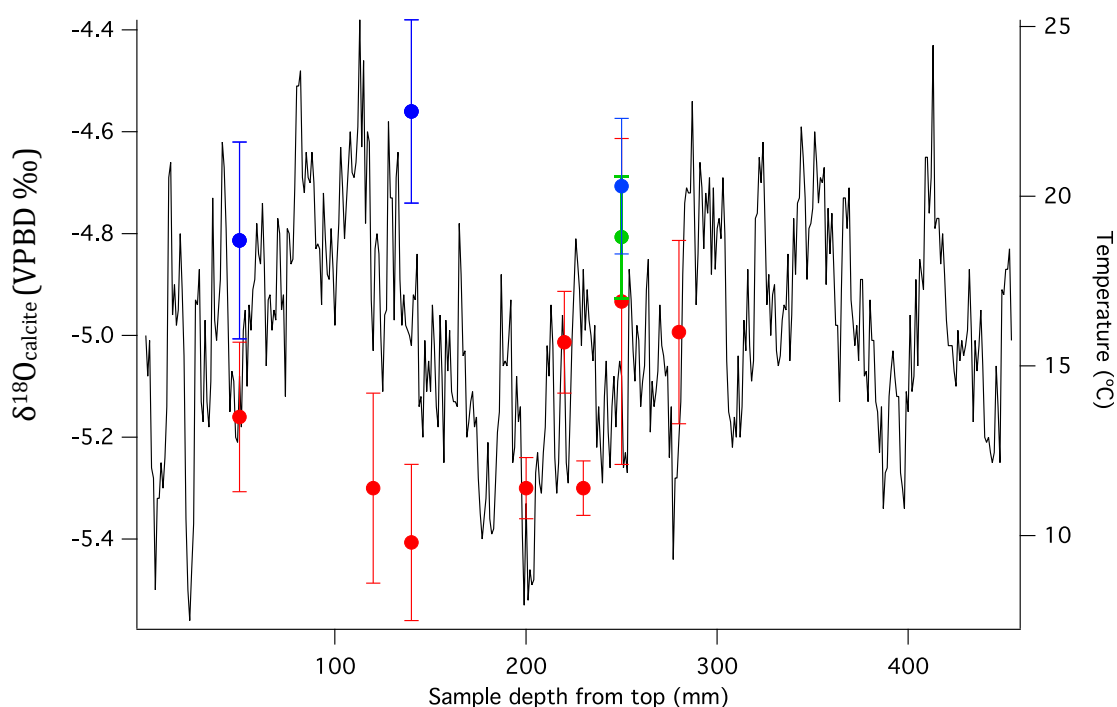


Fig. 7.21 – The stable isotope profile of speleothem M2 (black), with the corresponding temperatures obtained from individual fluid-inclusion (red) and clumped-isotope (blue) analyses. The single palaeotemperature estimate obtained for speleothem M2 from the combined fluid-inclusion and clumped-isotope analyses (M2 6) is shown in green.

palaeotemperature derived, accuracy is limited, however such analyses still provide a broad idea of the variability of temperature throughout the growth period of speleothem M2. With the clumped-isotope derived temperatures, there are uncertainties with the extent to which these analyses are affected by disequilibria during the speleothems growth. It is also understood that these disequilibrium conditions may not be consistent throughout the growth period of a speleothem, therefore the variability evident in the clumped-isotope temperatures may not be reflective of temperature variability during the Pliocene. The fluid-inclusion derived temperatures, however, while likely underestimating the actual temperature, are more likely to deviate systematically from actual temperatures. Therefore they are more likely to accurately represent the temperature variations throughout the speleothems growth period. This suggests that throughout the growth period of speleothem M2, there was significant temperature variability (with fluid-inclusion derived temperatures ranging from $9.8\text{ }^{\circ}\text{C} \pm 2.3\text{ }^{\circ}\text{C}$ to $16.9\text{ }^{\circ}\text{C} \pm 4.8\text{ }^{\circ}\text{C}$), which may correspond to the shifts in dominant moisture source, precipitation amount and vegetation cover suggested by the $\delta^{18}\text{O}$ profile. The range of values evident is suggested to reflect temperature variations throughout the Pliocene, conceivably reflecting the cool and warm maxima of MPWP climate cycles.

7.6.1. Explaining the Lag Between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in Speleothem BT

Previously, three “possibilities” were proposed to explain the apparent lag between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$; here they are revisited and reassessed in the context of the wider multi-proxy study. Firstly, possibility one, in which changes in precipitation amount from a single source followed by changes in moisture source, is used to explain the delayed response of $\delta^{18}\text{O}$. For this, an understanding of modern precipitation is important, as it relies upon each dominant moisture source having a wide variety of rainfall amounts associated with it, in order for shifts from low rainfall amounts to high rainfall amount and vice versa to be possible. As there do appear to be significant relationships between rainfall amount and moisture source, this possibility seems unlikely, however still possible. Possibility two, which suggests an increase in the frequency of low-rainfall amount events in order to increase vegetation above the cave but not immediately influence $\delta^{18}\text{O}$, also relies on modern precipitation studies to evaluate. For this possibility to be true, it would require rainfall frequency to be a more significant factor in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variations than rainfall amounts. As discussed above, $\delta^{18}\text{O}$ is primarily associated with moisture source, but then also correspondingly with rainfall amount and rainfall frequency. As such, it does not seem feasible, assuming similar conditions to modern day, that

rainfall frequency would alter either without rainfall amount also changing, or simply without imprinting on the $\delta^{18}\text{O}$ signal itself. Finally, possibility three, in which alternative limits to plant activity, namely temperature, alter prior to precipitation changes resulting in the lag. Unfortunately, the scale on which palaeotemperatures have been derived means it is not feasible to assess this possibility with a suitable level of reliability. However, the data do not disprove this, and it therefore remains a possible explanation for the apparent lag of $\delta^{18}\text{O}$ variations behind those of $\delta^{13}\text{C}$.

7.7. Conclusions

This chapter has highlighted the significance of utilising a multi-proxy approach in speleothem research. The multi-proxy approach allows for disentangling the signals of more complex systems where multiple factors are potentially involved, for example, with the apparent lag between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

The combined analyses of modern precipitation, speleothem calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, trace elements, fluid-inclusions, and clumped-isotopes has allowed for a robust interpretation of Pliocene climates in the Nullarbor region. While it has not been possible to apply an absolute timeframe, there are significant climatic variations noted within the speleothems, and thus the MPWP, identifying that while this was a period of maintained warmth, there were still significant changes in both temperature and precipitation. The key interpretations of this chapter are summarised as follows:

→ Due to the similar stable isotope values across all speleothems, and their similarity to the Nullarbor limestone at the time of their deposition, the low-frequency isotopic variations noted are considered to be reflective of regional, rather than local influences.

→ The covariation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles supports the conclusion that the apparent low-frequency variations reflect global or regional-scale climate variations

→ The larger $\delta^{13}\text{C}$ variations compared to those of $\delta^{18}\text{O}$ suggest a strong influence of overlying vegetation. This is supported by the apparent lag between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ shifts.

→ The covariation of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg, Sr, and Ba are suggested to reflect changes in rainfall, vegetation and residence times in the bedrock prior to speleothem deposition, by which increased/decreased $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg, Sr, and Ba reflects a decrease/increase in rainfall and vegetation cover, and an increase/decrease in residence time in the bedrock.

→ The general depletion of the $\delta^{18}\text{O}$ values in both the speleothem calcite and fluid-inclusion water is suggested to indicate an increased prevalence of moisture sourced from Southern Ocean and Southern Ocean- NCB interactions.

→ The conclusion from modern precipitation analyses that moisture sourced from Southern Ocean and Southern Ocean- NCB interactions is linked to more frequent, higher rainfall amounts supports the conclusion that these moisture sources were more prevalent in the Pliocene.

→ The range of temperatures produced from both fluid-inclusion and clumped-isotope analyses suggest notable temperature variability within the Pliocene in the Nullarbor region, perhaps reflecting cool and warm maxima of climate cycles in the MPWP.

8. Conclusion

This thesis has combined the use of traditional and novel speleothem proxies to provide insight into the climate of the Nullarbor Plain during the Pliocene, and more specifically, the MPWP. To assist in summarising the key findings of the thesis, the following discussion focuses on the four aims of the thesis set out in **Chapter 1**.

8.1. Aim 1 → To explore the potential for the U-Pb dating of long (>1 m) speleothems to allow applications of proxy data to precise timescales.

Two speleothems were identified for extensive U-Pb dating, BT and M2. Speleothem BT is almost 2 m, and M2 is the next longest sample from the same cave at almost 50 cm. Preliminary analyses of both speleothems identified that, even with extensive dating, it would not be possible to develop internal chronologies due to the large overlapping errors of the determined ages. As such, further dating focused solely on attempts to more precisely determine top and bottom dates, for the purpose of obtaining a maximum growth period for each speleothem. Through this strategy it was possible to obtain weighted-average ages of 3.17 ± 0.17 Ma for speleothem BT, and of 3.24 ± 0.10 Ma for speleothem M2. It was also possible to tentatively constrain the growth period of speleothem BT to between 3.28 and 3.08 Ma, and of speleothem M2 to between 3.35 and 2.75 Ma, thus placing both speleothems entirely within the Pliocene (5.33-2.58 Ma) and mostly within the MPWP (3.29-2.97 Ma). The concordant isochrons indicate that significant diagenetic alteration of the speleothems is unlikely to have occurred, therefore making them suitable for palaeoclimate interpretations.

It can be concluded that, with current U-Pb technologies it is not possible to develop internal climate time-series from Pliocene speleothems with relatively low U contents such as these (~ 1 ppm), although, it is certainly possible to adequately constrain the growth period of long speleothems to time periods within the Pliocene, and has thus allowed this study to provide unique insight into the climate of the Nullarbor Plain during this time period. However, at present the analytical uncertainties when applied to speleothems of such antiquity are large enough to exceed the likely growth period of the speleothem. As such, it is not possible to obtain precise enough ages to allow the development of internal chronologies. Despite this, the ability to anchor ancient speleothems to within approximate periods of time (i.e. the Pliocene), is a significant

advancement in speleothem research, and provides significant new opportunities for interpretations of palaeoclimate from terrestrial sources. Further advances are required to allow the development of climate time-series from ancient speleothems, however they can now be used to make interpretations of overall climatic states and variations from the more distant past.

8.2. Aim 2 → To evaluate isotopic patterns in modern precipitation and to investigate their use in informing interpretations of palaeoprecipitation.

Analyses of modern precipitation revealed significant trends in the drivers of isotopic composition of precipitation in the Nullarbor region, with the most significant driver being moisture source. Of the four moisture source classifications identified in this thesis, it was found that relatively depleted isotopic compositions were generally associated with moisture sourced from the Southern Ocean or NCB / Southern Ocean interactions, and relatively enriched isotopic compositions were generally associated with moisture sourced from the tropics or with Tasman influences. This is supported in modern precipitation dynamics by the seasonal nature of both isotopic compositions and dominant moisture sources in modern precipitation by which, moisture sourced from the Southern Ocean or NCB / Southern Ocean interactions is dominant in the winter months, where isotopic compositions are generally more depleted, and moisture sourced from tropics or with Tasman influences is dominant in the summer months, where isotopic compositions are generally more enriched.

It can be inferred that the isotopic variation of palaeoprecipitation would have been similarly driven by the dominant moisture source. Without the understanding of drivers of isotopic variation in modern precipitation, interpretations of palaeoprecipitation would have been significantly more limited. Even applying a multi-proxy approach of traditional speleothem proxies, interpretations of palaeoprecipitation are generally limited to variations in precipitation amount. However, with detailed analyses of modern precipitation, it is often possible to delve further into the causes of variations in precipitation amount, in turn often indicating changes in overall climate states. This thesis, for example, has identified that the increased precipitation in the Pliocene was likely a result of an increased prevalence of moisture sourced from the Southern Ocean and NCB / Southern Ocean interactions, associated with an increased prevalence of negative IOD-like conditions.

The key limitation found in the investigation of modern precipitation is the uncertainties surrounding which relationships are causal, and which are

coincidental. However, the application of multi-proxy analyses of the speleothems alongside the modern precipitation analyses allows a robust delineation of the multiple drivers of variation in palaeoprecipitation, during the Pliocene. This highlights the significant potential for studies of modern precipitation to have applications in speleothem research, to help provide robust interpretations of drivers of palaeoprecipitation variability and changes in overall climate states.

8.3. Aim 3 → To explore the potential of fluid-inclusion and carbonate clumped-isotope analyses to produce reliable palaeotemperature estimates in Pliocene speleothems.

From the exploration of both fluid-inclusion and clumped-isotope analyses, it is evident that there is great potential for the two methods, both individually and paired together, to produce robust and reliable palaeotemperature estimates. The final accepted fluid-inclusion analyses produced temperatures ranging from $9.8\text{ }^{\circ}\text{C} \pm 2.3\text{ }^{\circ}\text{C}$ to $25.0\text{ }^{\circ}\text{C} \pm 3.2\text{ }^{\circ}\text{C}$ across all speleothems, and $9.8\text{ }^{\circ}\text{C} \pm 2.3\text{ }^{\circ}\text{C}$ to $16.9\text{ }^{\circ}\text{C} \pm 4.8\text{ }^{\circ}\text{C}$ in speleothem M2. This is compared to the final accepted clumped-isotope analyses temperature range of $18.7\text{ }^{\circ}\text{C} \pm 2.9\text{ }^{\circ}\text{C}$ to $24.0\text{ }^{\circ}\text{C} \pm 3.8\text{ }^{\circ}\text{C}$ across all speleothems and $18.7\text{ }^{\circ}\text{C} \pm 2.9\text{ }^{\circ}\text{C}$ to $22.5\text{ }^{\circ}\text{C} \pm 2.7\text{ }^{\circ}\text{C}$ in speleothem M2. The variability between the two datasets is in keeping with the current understanding of the limitations of the two methods in speleothem studies in which fluid-inclusion analyses frequently produce temperatures too low and clumped-isotope analyses frequently produce temperatures that are too high.

The most significant limitation of the fluid-inclusion method for developing palaeotemperatures is the uncertainty surrounding the most applicable palaeotemperature equation to use. There are similar concerns with using the correct calibration equations within the clumped-isotope method, however it is also suggested that the suitability of individual speleothems is probably the over-riding consideration for these analyses – in particular the likelihood of disequilibrium conditions of speleothem deposition and the most accurate way to account for such disequilibria. Further research and in-situ studies will help to refine the calibration equations that address this, and therefore continue to improve the reliability of palaeotemperature estimates obtained from both fluid-inclusion and clumped-isotope methods individually.

In consideration of the current limits of the fluid-inclusion and clumped-isotope methods individually, it is recommended that the palaeotemperature methods derived from them alone, while somewhat reasonable, are considered

with caution. Using data derived from the two methods to derive error-weighted means and 95% error-weighted uncertainties produced three acceptable palaeotemperature estimates (with probability of fits >5%) ranging from $18.8\text{ }^{\circ}\text{C} \pm 1.8\text{ }^{\circ}\text{C}$ to $21.4\text{ }^{\circ}\text{C} \pm 1.3\text{ }^{\circ}\text{C}$. This suggests a temperature variability of approximately $2.5\text{ }^{\circ}\text{C}$, ranging from approximately $1\text{ }^{\circ}\text{C}$ to $3.5\text{ }^{\circ}\text{C}$ warmer than the present day average of the region of $18\text{ }^{\circ}\text{C}$. This is in agreement with models suggesting a temperature increase of $2\text{--}3\text{ }^{\circ}\text{C}$ in southwestern Australia, and a global average temperature increase of $3\text{--}4\text{ }^{\circ}\text{C}$ compared to modern temperatures. Therefore this thesis has succeeded in its aim of producing a reliable terrestrial palaeotemperature estimate for the Pliocene, providing promising insight for future research. While this is a resource intensive approach to obtaining palaeotemperatures, it is arguably the most robust approach available at present. Regarding the palaeotemperatures produced from the individual analyses, while the absolute temperatures must be considered with caution, they still provide significant information regarding the stability of Pliocene temperatures. It is well documented that the Pliocene temperatures were overall warmer than present, however, the findings of this thesis indicate significant variability in the temperature of the Nullarbor region, including periods where it may have been on average cooler than present.

8.4. Aim 4 → To apply a multi-proxy approach, using both traditional and novel speleothem proxies, to the study of Pliocene speleothems.

This thesis applied both traditional (stable isotope and trace element) and novel (fluid-inclusion and clumped-isotope) speleothem proxies, alongside further modern precipitation analyses, in a detailed multi-proxy approach. From these analyses, several robust interpretations of Pliocene climates in the Nullarbor region have been made. The stable isotope analyses of speleothems BT and M2 indicated significant variability in the climate over the lifespan of the speleothems, however, there are multiple possible drivers of these variations, which were not possible to delineate from these analyses alone. The addition of trace element analyses identified significant relationships between $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg, Sr, and Ba; relationships that together typically indicate that precipitation above the cave, and therefore residence times in the bedrock, are key drivers of isotopic variation. This multi-proxy approach using traditional speleothem proxies proved vital in explaining the variability evident in the geochemical signals of both speleothems. The addition of modern precipitation analyses allowed further interpretations of this apparent variability. From the relationships evident in modern precipitation it has been possible to determine

that during periods of depleted oxygen isotopes, it is likely that moisture sourced from the Southern Ocean or NCB / Southern Ocean interactions was more dominant, with on average more frequent, higher rainfall amounts. These periods are also associated with increased vegetation amounts above the cave, as supported by the decrease in Mg, Sr and Ba ratios to Ca, and the relative depletion of carbon isotopes. Conversely, during periods of enriched oxygen isotopes, it is likely that moisture sourced from the tropics or with Tasman influences dominated, with on average decreased rainfall. These periods are also associated with decreased vegetation amounts above the cave, as supported by the increase in Mg, Sr and Ba ratios to Ca, and the relative enrichment of carbon isotopes. Due to the lack of accepted palaeotemperatures obtained from speleothems BT and M2, it is not possible to determine whether or not these periods of $\delta^{18}\text{O}$ enrichment/depletion are directly associated with comparatively warmer/cooler temperatures. However, in the literature it is commonly accepted that enriched $\delta^{18}\text{O}$ is generally associated with warmer temperatures, and depleted $\delta^{18}\text{O}$ is generally associated with cooler temperatures. From the variability in temperatures evident from the individual fluid-inclusion and clumped-isotope analyses this is entirely plausible.

The application of a multi-proxy approach has allowed for a robust interpretation of climate variability during the Pliocene in the Nullarbor region. While the novel speleothem proxies used to obtain palaeotemperature estimates have had limited application in these multi-proxy discussions, the traditional proxies have been successfully applied to more ancient speleothems than those typically studied, and have produced reliable interpretations of palaeoprecipitation. While it has not been possible to apply these interpretations on an absolute time frame, the variability evident, and interpretations of the drivers of this variability, has provided invaluable insight into the Pliocene climate of the Nullarbor.

8.5. Gaps in the literature addressed

In addition to the four key aims of the thesis, several gaps in the literature were identified in **Chapter 2**, which this thesis has aimed to address:

- disproportionate palaeoclimate literature for the Southern Hemisphere in comparison to the Northern Hemisphere;
- a paucity of terrestrial sources of palaeoclimate information for the Pliocene period;
- the few applications of speleothem research beyond the previous ~500 kyr limit of U-Th dating;

- attempting to determine multiple ages (i.e. internal chronology) within a Pliocene speleothem;
- the use of novel techniques in obtaining palaeoclimate information from speleothems;
- obtaining reliable palaeotemperatures from speleothems; and
- developing an understanding of drivers of isotopic variation in precipitation in the Nullarbor region.

This thesis has focused on producing a Pliocene palaeoclimate record from a terrestrial source (i.e. speleothems) within the Southern Hemisphere, thus addressing the first two of these significant gaps in the literature. The thesis has successfully provided robust interpretations of the precipitation, vegetation, and temperature of the Nullarbor region within the Pliocene, and more specifically the MPWP. These interpretations are in general agreement with modelled data and from speleothem pollen records for the region. The main shortcoming of these interpretations has been the inability to apply them to a robust timescale. This has limited the interpretations to the overall climate variability within the MPWP, and restricted interpretations of the drivers of this variability. It has however, provided invaluable insight into the application of the U-Pb dating method to ancient speleothems. While advances in the precision of the dates obtained must be made to allow the development of internal chronologies for speleothems of this U content, this still provides significant new opportunities for speleothem research in the more distant past.

The multi-proxy use of traditional and novel techniques has allowed for robust interpretations of the climate signals preserved with the speleothems analysed in this thesis. The use of multiple speleothems allowed for a broader insight into the climate variations present within the MPWP, and the development of reliable palaeotemperature estimates for this time period. In addition, the use of modern precipitation analyses has assisted in the understanding of the drivers of the climate variations evident, in particular the drivers of palaeoprecipitation variations in the Nullarbor region. Overall, this thesis has provided unique and invaluable insight into the Pliocene climate of the Nullarbor region.

9. References

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10. Appendices

Appendix 1 – Eyre temperature data used for calculations of average surface temperature throughout the period of modern precipitation collection. Minimum and maximum temperatures sourced from Australian Bureau of Meteorology (www.bom.gov.au/climate/).

Date	Min Temp (°C)	Max Temp (°C)	Mean Temp (°C)
1/01/2014	19.7	22.5	N/A
2/01/2014	16.8	23.7	19.7
3/01/2014	9.8	23.3	16.8
4/01/2014	10.1	24.1	16.7
5/01/2014	11.0	24.2	17.6
6/01/2014	5.0	25.7	14.6
7/01/2014	13.6	33.2	19.7
8/01/2014	15.2	35.7	24.2
9/01/2014	8.4	26.2	22.1
10/01/2014	19.2	25.6	22.7
11/01/2014	18.9	27.0	22.3
12/01/2014	12.6	27.8	19.8
13/01/2014	15.2	37.0	21.5
14/01/2014	20.0	25.5	28.5
15/01/2014	19.7	27.7	22.6
16/01/2014	21.8	24.9	24.8
17/01/2014	18.3	25.5	21.6
18/01/2014	18.4	25.1	22.0
19/01/2014	18.6	25.4	21.9
20/01/2014	19.4	25.4	22.4
21/01/2014	19.5	24.4	22.5
22/01/2014	17.8	22.4	21.1
23/01/2014	18.4	22.6	20.4
24/01/2014	17.9	23.8	20.3
25/01/2014	19.0	29.5	21.4
26/01/2014	16.8	35.8	23.2
27/01/2014	19.0	43.5	27.4
28/01/2014	19.7	24.7	31.6
29/01/2014	18.8	24.6	21.8
30/01/2014	13.2	28.8	18.9
31/01/2014	12.8	29.2	20.8
1/02/2014	18.6	28.1	23.9

2/02/2014	21.2	26.2	24.7
3/02/2014	19.2	23.6	22.7
4/02/2014	19.0	24.5	21.3
5/02/2014	12.5	25.9	18.5
6/02/2014	12.5	26.3	19.2
7/02/2014	16.1	26.4	21.2
8/02/2014	19.8	23.9	23.1
9/02/2014	17.7	25.0	20.8
10/02/2014	13.7	26.3	19.4
11/02/2014	17.1	27.1	21.7
12/02/2014	21.0	23.3	24.1
13/02/2014	20.9	21.6	22.1
14/02/2014	19.3	22.2	20.5
15/02/2014	16.3	23.8	19.3
16/02/2014	9.6	28.9	16.7
17/02/2014	16.2	25.7	22.6
18/02/2014	18.3	25.0	22.0
19/02/2014	18.3	24.0	21.7
20/02/2014	13.0	24.0	18.5
21/02/2014	16.5	22.8	20.3
22/02/2014	16.4	24.1	19.6
23/02/2014	7.7	24.5	15.9
24/02/2014	10.6	25.0	17.6
25/02/2014	9.1	25.8	17.1
26/02/2014	15.7	22.7	20.8
27/02/2014	14.6	22.8	18.7
28/02/2014	7.3	24.3	15.1
1/03/2014	16.8	24.2	20.6
2/03/2014	8.7	24.9	16.5
3/03/2014	9.8	31.4	17.4
4/03/2014	6.9	26.0	19.2
5/03/2014	18.0	24.3	22.0
6/03/2014	11.1	23.7	17.7
7/03/2014	6.7	25.6	15.2
8/03/2014	12.7	34.2	19.2

9/03/2014	20.3	26.2	27.3
10/03/2014	17.9	24.1	22.1
11/03/2014	9.3	25.3	16.7
12/03/2014	8.3	25.0	16.8
13/03/2014	12.4	31.9	18.7
14/03/2014	13.1	24.6	22.5
15/03/2014	14.1	22.7	19.4
16/03/2014	13.3	24.7	18.0
17/03/2014	12.8	24.7	18.8
18/03/2014	17.5	25.1	21.1
19/03/2014	18.0	25.5	21.6
20/03/2014	20.2	21.3	22.9
21/03/2014	16.6	22.3	19.0
22/03/2014	7.4	23.7	14.9
23/03/2014	12.5	23.5	18.1
24/03/2014	10.1	23.3	16.8
25/03/2014	4.3	23.9	13.8
26/03/2014	6.1	24.2	15.0
27/03/2014	6.8	24.6	15.5
28/03/2014	8.4	26.4	16.5
29/03/2014	15.1	34.7	20.8
30/03/2014	17.3	31.3	26.0
31/03/2014	11.7	24.9	21.5
1/04/2014	16.5	22.8	20.7
2/04/2014	16.5	22.8	19.7
3/04/2014	13.8	22.2	18.3
4/04/2014	2.3	23.6	12.3
5/04/2014	10.7	26.4	17.2
6/04/2014	15.8	22.2	21.1
7/04/2014	12.2	24.1	17.2
8/04/2014	17.9	23.0	21.0
9/04/2014	18.6	23.1	20.8
10/04/2014	10.7	24.0	16.9
11/04/2014	6.2	22.8	15.1
12/04/2014	3.0	25.0	12.9
13/04/2014	6.2	23.7	15.6
14/04/2014	4.7	23.9	14.2
15/04/2014	7.9	27.5	15.9
16/04/2014	8.2	25.4	17.9
17/04/2014	8.4	32.8	16.9
18/04/2014	17.4	23.2	25.1
19/04/2014	8.8	30.1	16.0
20/04/2014	8.3	24.3	19.2
21/04/2014	16.6	23.9	20.5
22/04/2014	15.4	23.2	19.7
23/04/2014	2.4	25.6	12.8

24/04/2014	2.9	28.3	14.3
25/04/2014	14.7	23.0	21.5
26/04/2014	17.8	22.7	20.4
27/04/2014	15.8	27.5	19.3
28/04/2014	17.2	22.6	22.4
29/04/2014	10.0	20.4	16.3
30/04/2014	9.9	21.0	15.2
1/05/2014	9.9	22.0	15.5
2/05/2014	11.0	19.0	16.5
3/05/2014		20.0	N/A
4/05/2014	13.8	19.6	16.9
5/05/2014	11.1	19.0	15.4
6/05/2014	14.9	24.0	17.0
7/05/2014	16.0	30.0	20.0
8/05/2014	18.0	20.8	24.0
9/05/2014	10.0	22.0	15.4
10/05/2014	6.8	23.0	14.4
11/05/2014	5.5	25.0	14.3
12/05/2014	11.0	25.0	18.0
13/05/2014	5.2	22.0	15.1
14/05/2014	9.4	26.7	15.7
15/05/2014	7.0	22.8	16.9
16/05/2014	7.4	27.2	15.1
17/05/2014	15.4	25.2	21.3
18/05/2014	10.0	27.5	17.6
19/05/2014	12.5	24.0	20.0
20/05/2014	13.0	26.4	18.5
21/05/2014	14.0	22.7	20.2
22/05/2014	7.5	24.1	15.1
23/05/2014	10.5	29.5	17.3
24/05/2014	8.9	24.6	19.2
25/05/2014	14.0	22.0	19.3
26/05/2014	11.2	21.3	16.6
27/05/2014	12.0	20.3	16.7
28/05/2014	3.5	20.0	11.9
29/05/2014	4.5	19.0	12.3
30/05/2014	11.5	17.0	15.3
31/05/2014	13.5	19.0	15.3
1/06/2014	5.5	21.6	12.3
2/06/2014	4.0	23.2	12.8
3/06/2014	4.5	21.8	13.9
4/06/2014	4.5	22.2	13.2
5/06/2014	9.0	22.0	15.6
6/06/2014	1.0	20.0	11.5
7/06/2014	3.0	21.0	11.5
8/06/2014	6.9	19.5	14.0

9/06/2014	8.0	19.5	13.8
10/06/2014	10.9	24.0	15.2
11/06/2014	11.5	17.1	17.8
12/06/2014	12.0	18.0	14.6
13/06/2014	11.5	15.6	14.8
14/06/2014	5.1	17.0	10.4
15/06/2014	1.5	18.0	9.3
16/06/2014	-0.1	19.0	9.0
17/06/2014	-1.5	20.4	8.8
18/06/2014	4.5	23.3	12.5
19/06/2014	9.3	19.8	16.3
20/06/2014	2.7	20.3	11.3
21/06/2014	2.3	23.2	11.3
22/06/2014	10.3	16.0	16.8
23/06/2014	6.8	15.5	11.4
24/06/2014	6.8	16.0	11.2
25/06/2014	-1.2	18.4	7.4
26/06/2014	-2.2	23.4	8.1
27/06/2014	11.0	15.0	17.2
28/06/2014	10.7	16.0	12.9
29/06/2014	9.0	17.6	12.5
30/06/2014	-0.4	16.1	8.6
1/07/2014	4.0	21.6	10.1
2/07/2014	1.5	22.6	11.6
3/07/2014	10.5	16.1	16.6
4/07/2014	6.2	17.4	11.2
5/07/2014	-0.5	20.7	8.5
6/07/2014	1.5	25.7	11.1
7/07/2014	8.0	20.4	16.9
8/07/2014	7.5	14.8	14.0
9/07/2014	8.0	17.1	11.4
10/07/2014	4.0	15.1	10.6
11/07/2014	-0.5	18.0	7.3
12/07/2014	10.5	15.4	14.3
13/07/2014	4.1	20.0	9.8
14/07/2014	6.0	21.0	13.0
15/07/2014	7.0	17.0	14.0
16/07/2014	4.4	16.7	10.7
17/07/2014	5.4	17.0	11.1
18/07/2014	1.6	15.4	9.3
19/07/2014	7.0	20.1	11.2
20/07/2014	1.2	17.1	10.7
21/07/2014	7.6	17.0	12.4
22/07/2014	-1.5	22.6	7.8
23/07/2014	10.5	18.1	16.6
24/07/2014	9.3	17.4	13.7

25/07/2014	5.8	16.8	11.6
26/07/2014	1.8	22.5	9.3
27/07/2014	4.8	19.0	13.7
28/07/2014	0.5	21.2	9.8
29/07/2014	2.0	21.5	11.6
30/07/2014	0.0	22.0	10.8
31/07/2014	2.6	15.5	12.3
1/08/2014	10.0	17.0	12.8
2/08/2014	-0.5	19.0	8.3
3/08/2014	1.0	18.5	10.0
4/08/2014	8.5	18.0	13.5
5/08/2014	-3.0	20.0	7.5
6/08/2014	5.0	23.1	12.5
7/08/2014	0.5	26.5	11.8
8/08/2014	10.8	24.0	18.7
9/08/2014	12.8		18.4
10/08/2014		17.8	N/A
11/08/2014	-5.0	17.0	6.4
12/08/2014	-3.0	17.0	7.0
13/08/2014	-3.0	15.8	7.0
14/08/2014	-3.3	18.8	6.3
15/08/2014	-3.0	17.3	7.9
16/08/2014	9.0	19.3	13.2
17/08/2014	-2.5	18.0	8.4
18/08/2014	3.5	26.8	10.8
19/08/2014	8.0	24.0	17.4
20/08/2014	9.0	25.0	16.5
21/08/2014	8.8	28.0	16.9
22/08/2014	11.0	20.0	19.5
23/08/2014	7.0	18.3	13.5
24/08/2014	5.5	28.5	11.9
25/08/2014	13.5	33.5	21.0
26/08/2014	15.5	32.8	24.5
27/08/2014	15.0	23.0	23.9
28/08/2014	9.0	33.5	16.0
29/08/2014	6.0	35.0	19.8
30/08/2014	10.0	23.3	22.5
31/08/2014	13.5	19.5	18.4
1/09/2014	12.0	18.3	15.8
2/09/2014	-1.5	19.5	8.4
3/09/2014	9.5	20.8	14.5
4/09/2014	13.0	17.8	16.9
5/09/2014	1.5	22.0	9.7
6/09/2014	8.0	31.3	15.0
7/09/2014	17.5	25.5	24.4
8/09/2014	12.8	23.5	19.2

9/09/2014	11.3	20.5	17.4
10/09/2014	1.5	22.5	11.0
11/09/2014	0.8	21.3	11.7
12/09/2014	7.5	25.5	14.4
13/09/2014	11.0	35.0	18.3
14/09/2014	14.5	20.3	24.8
15/09/2014	4.5	21.0	12.4
16/09/2014	-0.5	20.0	10.3
17/09/2014	1.5	23.0	10.8
18/09/2014	12.0	24.5	17.5
19/09/2014	7.0	25.8	15.8
20/09/2014	14.0	25.5	19.9
21/09/2014	8.8	36.0	17.2
22/09/2014	16.5	20.5	26.3
23/09/2014	12.0	17.5	16.3
24/09/2014	12.5	21.0	15.0
25/09/2014	6.5	28.0	13.8
26/09/2014	17.0	35.0	22.5
27/09/2014	6.5	38.5	20.8
28/09/2014	11.5	22.5	25.0
29/09/2014	1.0	26.0	11.8
30/09/2014	4.0	21.5	15.0
1/10/2014	4.5	22.3	13.0
2/10/2014	9.0	25.5	15.7
3/10/2014	17.5	31.5	21.5
4/10/2014	15.0	21.5	23.3
5/10/2014	11.8	37.0	16.7
6/10/2014	14.5	21.5	25.8
7/10/2014	1.0	25.8	11.3
8/10/2014	11.0	31.0	18.4
9/10/2014	11.0	22.8	21.0
10/10/2014	15.3	22.0	19.1
11/10/2014	-1.5	24.5	10.3
12/10/2014	15.5	21.5	20.0
13/10/2014	12.5	19.0	17.0
14/10/2014	-3.0	24.0	8.0
15/10/2014	7.0	28.0	15.5
16/10/2014	9.0	33.8	18.5
17/10/2014	19.5	37.0	26.7
18/10/2014	15.5	27.5	26.3
19/10/2014	17.0	24.0	22.3
20/10/2014	16.0	26.0	20.0
21/10/2014	6.5	24.0	16.3
22/10/2014	15.0	23.0	19.5
23/10/2014	14.0	37.5	18.5
24/10/2014	5.0	26.0	21.3

25/10/2014	13.3	33.3	19.7
26/10/2014	17.0	24.5	25.2
27/10/2014	13.5	22.5	19.0
28/10/2014	-0.5	26.0	11.0
29/10/2014	13.0	35.0	19.5
30/10/2014	22.0	30.5	28.5
31/10/2014	15.0	22.5	22.8
1/11/2014	14.5	23.5	18.5
2/11/2014	5.5	28.8	14.5
3/11/2014	17.8	24.5	23.3
4/11/2014	9.0	26.0	16.8
5/11/2014	3.0	35.5	14.5
6/11/2014	20.0	43.5	27.8
7/11/2014	17.5	23.5	30.5
8/11/2014	16.0	27.0	19.8
9/11/2014		27.3	N/A
10/11/2014	14.5	30.5	20.9
11/11/2014		30.0	N/A
12/11/2014	18.5	25.5	24.3
13/11/2014	16.5	20.0	21.0
14/11/2014	13.5	19.5	16.8
15/11/2014	12.0	24.0	15.8
16/11/2014	7.0	26.5	15.5
17/11/2014	11.5	31.0	19.0
18/11/2014	16.0	39.0	23.5
19/11/2014	18.5	31.5	28.8
20/11/2014	11.5	30.2	21.5
21/11/2014	17.5	33.0	23.9
22/11/2014	11.7	25.2	22.4
23/11/2014	10.2	25.8	17.7
24/11/2014	15.7	23.0	20.8
25/11/2014		23.6	N/A
26/11/2014		26.8	N/A
27/11/2014		27.3	N/A
28/11/2014	16.0	29.5	21.7
29/11/2014	16.3	25.3	22.9
30/11/2014	17.4	25.5	21.4
1/12/2014	12.2	38.3	18.9
2/12/2014	16.8	23.3	27.6
3/12/2014	14.5	28.3	18.9
4/12/2014	10.8	33.8	19.6
5/12/2014	15.2	24.1	24.5
6/12/2014	17.8	24.2	21.0
7/12/2014	17.0	25.2	20.6
8/12/2014	10.3	26.0	17.8
9/12/2014	16.5	26.2	21.3

10/12/2014	18.3	24.5	22.3
11/12/2014	17.5	25.9	21.0
12/12/2014	14.0	29.8	20.0
13/12/2014	13.0	26.5	21.4
14/12/2014	16.3	26.8	21.4
15/12/2014	7.7	33.4	17.3
16/12/2014	16.5	25.0	25.0
17/12/2014	5.0	25.0	15.0
18/12/2014	16.0	25.5	20.5
19/12/2014	4.0	29.3	14.8
20/12/2014	13.0	36.9	21.2
21/12/2014	17.5	24.6	27.2
22/12/2014	17.8	25.3	21.2
23/12/2014	12.7	24.2	19.0
24/12/2014	15.3	25.3	19.8
25/12/2014	15.5	21.4	20.4
26/12/2014	16.5	23.4	19.0
27/12/2014	10.5	28.7	17.0
28/12/2014	11.0	31.0	19.9
29/12/2014	19.0	26.0	25.0
30/12/2014	6.8	31.7	16.4
31/12/2014	15.3	38.0	23.5
1/01/2015	20.2	25.6	29.1
2/01/2015	18.2	24.8	21.9
3/01/2015	18.2	24.8	21.5
4/01/2015	14.5	25.5	19.7
5/01/2015	12.0	25.2	18.8
6/01/2015	7.9	26.5	16.6
7/01/2015	14.0	27.1	20.3
8/01/2015	19.2	21.5	23.2
9/01/2015	15.5	22.5	18.5
10/01/2015	15.5	24.0	19.0
11/01/2015	14.5	22.7	19.3
12/01/2015	12.5	25.5	17.6
13/01/2015	7.5	25.5	16.5
14/01/2015	8.5	25.5	17.0
15/01/2015	14.0	34.2	19.8
16/01/2015	19.2	26.8	26.7
17/01/2015	19.2	26.2	23.0
18/01/2015	15.8	38.0	21.0
19/01/2015	17.5	28.4	27.8
20/01/2015	18.0	28.5	23.2
21/01/2015	12.2	28.2	20.4
22/01/2015	21.8	26.4	25.0
23/01/2015	18.3	26.8	22.4
24/01/2015	7.5	26.8	17.2

25/01/2015	17.4	25.5	22.1
26/01/2015	16.5	24.7	21.0
27/01/2015	7.0	25.6	15.9
28/01/2015	6.2	26.0	15.9
29/01/2015	6.0	27.8	16.0
30/01/2015	12.0	26.2	19.9
31/01/2015	19.4	26.5	22.8
1/02/2015	19.3	25.4	22.9
2/02/2015	18.5	26.2	22.0
3/02/2015	9.0	25.7	17.6
4/02/2015	15.1	25.7	20.4
5/02/2015	7.3	28.2	16.5
6/02/2015	12.7	26.5	20.5
7/02/2015	12.1	26.4	19.3
8/02/2015	18.5	31.2	22.5
9/02/2015	16.3	38.1	23.8
10/02/2015	21.0	38.7	29.6
11/02/2015	20.7	26.8	29.7
12/02/2015	20.0	33.6	23.4
13/02/2015	19.0	36.5	26.3
14/02/2015	21.7	31.8	29.1
15/02/2015	18.7	26.5	25.3
16/02/2015	17.3	25.6	21.9
17/02/2015	10.5	25.9	18.1
18/02/2015	10.7	26.5	18.3
19/02/2015	16.5	27.5	21.5
20/02/2015	14.2	26.7	20.9
21/02/2015	17.4	27.2	22.1
22/02/2015	11.9	27.7	19.6
23/02/2015	19.5	25.2	23.6
24/02/2015	13.8	32.6	19.5
25/02/2015	16.9	37.5	24.8
26/02/2015	19.5	39.8	28.5
27/02/2015	19.0	32.5	29.4
28/02/2015	20.6	26.2	26.6
1/03/2015	7.8	24.2	17.0
2/03/2015	15.6	23.6	19.9
3/03/2015	18.8	24.8	21.2
4/03/2015	14.3	25.1	19.6
5/03/2015	19.0	26.2	22.1
6/03/2015	17.2	24.5	21.7
7/03/2015	11.8	25.2	18.2
8/03/2015	5.2	25.7	15.2
9/03/2015	12.9	26.5	19.3
10/03/2015	8.2	27.8	17.4
11/03/2015	13.2	28.4	20.5

12/03/2015	12.7	27.6	20.6
13/03/2015	14.7	36.7	21.2
14/03/2015	17.0	39.3	26.9
15/03/2015	22.7	37.6	31.0
16/03/2015	14.9	27.7	26.3
17/03/2015	16.5	36.7	22.1
18/03/2015	18.5	36.8	27.6
19/03/2015	20.8	26.3	28.8
20/03/2015	10.3	25.4	18.3
21/03/2015	13.3	35.0	19.4
22/03/2015	19.3	24.1	27.2
23/03/2015	16.1	21.9	20.1
24/03/2015	1.5	22.7	11.7
25/03/2015	0.5	25.0	11.6
26/03/2015	5.7	23.0	15.4
27/03/2015	3.1	27.1	13.1
28/03/2015	13.5	24.2	20.3
29/03/2015	7.0	25.1	15.6
30/03/2015	7.1	28.3	16.1
31/03/2015	16.1	23.7	22.2
1/04/2015	19.5	24.9	21.6
2/04/2015	15.2	22.8	20.1
3/04/2015	7.2	25.0	15.0
4/04/2015	4.5	24.9	14.8
5/04/2015	4.9	25.8	14.9
6/04/2015	15.5	21.3	20.7
7/04/2015	10.2	22.5	15.8
8/04/2015	11.0	22.5	16.8
9/04/2015	14.8	28.5	18.7
10/04/2015	15.0	29.9	21.8
11/04/2015	18.2	32.4	24.1
12/04/2015	15.1	29.5	23.8
13/04/2015	8.9	24.6	19.2
14/04/2015	10.4	24.1	17.5
15/04/2015	5.9	23.5	15.0
16/04/2015	15.9	19.8	19.7
17/04/2015	13.3	22.4	16.6
18/04/2015	3.4	22.6	12.9
19/04/2015	6.8	22.6	14.7
20/04/2015	2.8	24.5	12.7
21/04/2015	0.2	22.2	12.4
22/04/2015	8.0	21.5	15.1
23/04/2015	5.4	24.2	13.5
24/04/2015	13.2	20.4	18.7
25/04/2015	13.1	21.2	16.8
26/04/2015	4.5	21.2	12.9

27/04/2015	2.0	20.6	11.6
28/04/2015	4.2	22.3	12.4
29/04/2015	5.0	24.2	13.7
30/04/2015	7.5	27.6	15.9
1/05/2015	11.2	22.8	19.4
2/05/2015	12.8	21.6	17.8
3/05/2015	15.2	31.5	18.4
4/05/2015	8.3	19.5	19.9
5/05/2015	10.1	18.5	14.8
6/05/2015	9.0	20.5	13.8
7/05/2015	6.8	19.2	13.7
8/05/2015	-0.7	21.1	9.3
9/05/2015	-0.9	23.2	10.1
10/05/2015	14.1	20.8	18.7
11/05/2015	15.0	21.2	17.9
12/05/2015	14.2	19.9	17.7
13/05/2015	12.5	20.5	16.2
14/05/2015	-2.5	21.8	9.0
15/05/2015	3.5	22.9	12.7
16/05/2015	3.1	24.0	13.0
17/05/2015	8.9	22.2	16.5
18/05/2015	11.3	24.9	16.8
19/05/2015	13.1	18.1	19.0
20/05/2015	11.6	18.4	14.9
21/05/2015	5.4	17.8	11.9
22/05/2015	-1.6	21.3	8.1
23/05/2015	8.8	24.4	15.1
24/05/2015	10.3	20.2	17.4
25/05/2015	9.5	21.2	14.9
26/05/2015	3.2	26.8	12.2
27/05/2015	6.1	20.5	16.5
28/05/2015	2.6	19.8	11.6
29/05/2015	4.2	19.2	12.0
30/05/2015	-1.2	19.0	9.0
31/05/2015	-1.6	19.9	8.7
1/06/2015	0.2	22.5	10.1
2/06/2015	6.7	21.7	14.6
3/06/2015	4.7	23.9	13.2
4/06/2015	4.5	24.2	14.2
5/06/2015	7.4	27.8	15.8
6/06/2015	6.3	28.8	17.1
7/06/2015	4.0	21.7	16.4
8/06/2015	-0.6	21.8	10.6
9/06/2015	15.1	19.5	18.5
10/06/2015	9.5	19.6	14.5
11/06/2015	2.8	20.6	11.2

12/06/2015	4.6	23.3	12.6
13/06/2015	4.0	20.0	13.7
14/06/2015	1.4	20.9	10.7
15/06/2015	10.0	18.9	15.5
16/06/2015	13.2	18.8	16.1
17/06/2015	10.8	18.1	14.8
18/06/2015	5.9	16.3	12.0
19/06/2015	8.5	21.7	12.4
20/06/2015	10.4	25.9	16.1
21/06/2015	10.6	20.3	18.3
22/06/2015	10.4	16.8	15.4
23/06/2015	12.1	15.3	14.5
24/06/2015	5.1	16.6	10.2
25/06/2015	-1.3	19.5	7.7
26/06/2015	-0.3	22.0	9.6
27/06/2015	0.2	19.4	11.1
28/06/2015	1.5	19.4	10.5
29/06/2015	0.4	20.0	9.9
30/06/2015	-0.5	21.1	9.8
1/07/2015	5.4	22.8	13.3
2/07/2015	3.3	24.1	13.1
3/07/2015	6.8	18.4	15.5
4/07/2015	-1.2	23.7	8.6
5/07/2015	0.4	21.8	12.1
6/07/2015	-0.3	19.2	10.8
7/07/2015	-0.5	22.1	9.4
8/07/2015	1.6	23.7	11.9
9/07/2015	11.8	17.4	17.8
10/07/2015	5.4	16.4	11.4
11/07/2015	10.6	16.2	13.5
12/07/2015	7.1	16.8	11.7
13/07/2015	3.9	16.3	10.4
14/07/2015	11.2	16.5	13.8
15/07/2015	10.0	16.1	13.3
16/07/2015	2.8	16.3	9.5
17/07/2015	0.3	18.3	8.3
18/07/2015	2.8	19.3	10.6
19/07/2015	3.2	21.7	11.3
20/07/2015	0.4	24.7	11.1
21/07/2015	10.6	16.8	17.7
22/07/2015	-2.8	18.7	7.0
23/07/2015	8.4	20.1	13.6
24/07/2015	7.8	17.7	14.0
25/07/2015	1.2	18.0	9.5
26/07/2015	6.8	16.4	12.4
27/07/2015	-0.9	15.8	7.8

28/07/2015	0.4	19.4	8.1
29/07/2015		21.7	N/A
30/07/2015	5.7	19.2	13.7
31/07/2015	12.5	16.9	15.9
1/08/2015	10.8	15.8	13.9
2/08/2015	10.2	15.9	13.0
3/08/2015	8.9	18.0	12.4
4/08/2015	1.1	17.3	9.6
5/08/2015	2.8	17.3	10.1
6/08/2015	-3.4	17.5	7.0
7/08/2015	3.7	22.5	10.6
8/08/2015	11.0	25.5	16.8
9/08/2015	3.6	16.4	14.6
10/08/2015	3.9	17.9	10.2
11/08/2015	10.7	15.2	14.3
12/08/2015	10.1	17.2	12.7
13/08/2015	8.0	19.4	12.6
14/08/2015	0.8	21.5	10.1
15/08/2015	7.5	25.2	14.5
16/08/2015	4.0	25.1	14.6
17/08/2015	4.2	23.8	14.7
18/08/2015	13.2	22.4	18.5
19/08/2015	3.4	23.6	12.9
20/08/2015	8.7	19.6	16.2
21/08/2015	10.7	18.6	15.2
22/08/2015	4.1	18.7	11.4
23/08/2015	0.8	17.2	9.8
24/08/2015	4.9	17.2	11.1
25/08/2015	6.1	17.1	11.7
26/08/2015	1.4	18.1	9.3
27/08/2015	6.7	19.4	12.4
28/08/2015	5.8	22.8	12.6
29/08/2015	7.1	27.6	15.0
30/08/2015	10.2	26.6	18.9
31/08/2015	10.5	19.1	18.6
1/09/2015	5.6	15.2	12.4
2/09/2015	10.6	17.6	12.9
3/09/2015	7.5	17.0	12.6
4/09/2015	4.5	24.6	10.8
5/09/2015	11.6	19.0	18.1
6/09/2015	11.6	18.5	15.3
7/09/2015	-0.1	19.1	9.2
8/09/2015	-2.7	20.7	8.2
9/09/2015	7.1	26.9	13.9
10/09/2015	9.9	34.7	18.4
11/09/2015	15.7	21.7	25.2

12/09/2015	11.5	24.2	16.6
13/09/2015	12.4	21.2	18.3
14/09/2015	6.5	19.0	13.9
15/09/2015	1.5	18.2	10.3
16/09/2015	11.1	18.8	14.7
17/09/2015	4.5	19.5	11.7
18/09/2015	4.5	24.6	12.0
19/09/2015	11.1	27.2	17.9
20/09/2015	11.8	18.7	19.5
21/09/2015	11.6	19.1	15.2
22/09/2015	3.4	19.0	11.3
23/09/2015	-1.4	20.9	8.8
24/09/2015	-0.3	26.4	10.3
25/09/2015	7.7	29.0	17.1
26/09/2015	9.2	31.0	19.1
27/09/2015	14.6	20.2	22.8
28/09/2015	7.2	21.9	13.7
29/09/2015	10.0	34.0	16.0
30/09/2015	14.5	21.0	24.3
1/10/2015	2.9	30.8	12.0
2/10/2015	14.4	41.0	22.6
3/10/2015	16.1		28.6
4/10/2015	3.6	33.6	N/A
5/10/2015	7.3	24.0	20.5
6/10/2015	14.4	20.8	19.2
7/10/2015	6.5	21.2	13.7
8/10/2015	-0.6	21.5	10.3
9/10/2015	2.1	21.0	11.8
10/10/2015	1.0	21.2	11.0
11/10/2015	7.9	21.1	14.6
12/10/2015	14.9	20.9	18.0
13/10/2015	12.8	31.6	16.9
14/10/2015	9.9	31.8	20.8
15/10/2015	15.5	22.0	23.7
16/10/2015	5.9	23.0	14.0
17/10/2015	5.5	24.6	14.3
18/10/2015	13.4	39.1	19.0
19/10/2015	16.9	21.1	28.0
20/10/2015	15.7	22.0	18.4
21/10/2015	10.3	24.9	16.2
22/10/2015	5.5	28.1	15.2
23/10/2015	13.1	37.4	20.6
24/10/2015	10.9	23.9	24.2
25/10/2015	16.7	22.9	20.3
26/10/2015	14.6	24.7	18.8
27/10/2015	14.2	27.6	19.5

28/10/2015	10.0	22.5	18.8
29/10/2015	14.0	22.1	18.3
30/10/2015	13.0	27.3	17.6
31/10/2015	10.0	28.8	18.7
1/11/2015	15.9	23.2	22.4
2/11/2015	15.5	21.1	19.4
3/11/2015	15.6	19.2	18.4
4/11/2015	14.7	22.5	17.0
5/11/2015	2.9	28.6	12.7
6/11/2015	13.9	38.2	21.3
7/11/2015	18.0	33.5	28.1
8/11/2015	14.2	33.2	23.9
9/11/2015	17.1	20.4	25.2
10/11/2015	16.8	23.0	18.6
11/11/2015	16.5	24.2	19.8
12/11/2015	12.9	24.6	18.6
13/11/2015	14.6	22.5	19.6
14/11/2015	4.2	23.6	13.4
15/11/2015	10.2	31.8	16.9
16/11/2015	17.2	26.4	24.5
17/11/2015	17.6	35.1	22.0
18/11/2015	19.6	23.2	27.4
19/11/2015	15.9	23.0	19.6
20/11/2015	15.9	22.8	19.5
21/11/2015	15.0	22.1	18.9
22/11/2015	4.1	24.9	13.1
23/11/2015	7.4	33.7	16.2
24/11/2015	15.9	30.5	24.8
25/11/2015	17.4	23.0	24.0
26/11/2015	14.5	22.6	18.8
27/11/2015	4.8	24.7	13.7
28/11/2015	12.7	35.3	18.7
29/11/2015	12.1	23.8	23.7
30/11/2015	15.6	23.8	19.7
1/12/2015	15.7	22.5	19.8
2/12/2015	8.4	25.3	15.5
3/12/2015	12.7	38.4	19.0
4/12/2015	17.8	34.3	28.1
5/12/2015	18.5	29.4	26.4
6/12/2015	17.6	31.6	23.5
7/12/2015	9.1	27.0	20.4
8/12/2015	13.9	24.6	20.5
9/12/2015	8.4	25.0	16.5
10/12/2015	17.2	24.7	21.1
11/12/2015	16.2	24.9	20.5
12/12/2015		30.0	N/A

13/12/2015	17.8	34.6	23.9
14/12/2015	18.3	25.4	26.5
15/12/2015	16.5	28.0	21.0
16/12/2015	7.6	28.1	17.8
17/12/2015	11.4	27.4	19.8
18/12/2015	15.0	28.4	21.2
19/12/2015	19.6	25.7	24.0
20/12/2015	16.9	23.9	21.3
21/12/2015	15.0	24.8	19.5
22/12/2015	12.0	24.2	18.4
23/12/2015	18.6	32.9	21.4
24/12/2015	14.3	37.0	23.6
25/12/2015	17.9	24.0	27.5
26/12/2015	15.2	25.1	19.6
27/12/2015	7.8	29.8	16.5
28/12/2015	7.8	33.1	18.8
29/12/2015	12.8	39.1	23.0
30/12/2015	19.4	44.4	29.3
31/12/2015	19.4	22.5	31.9
1/01/2016	18.5	24.1	20.5
2/01/2016	18.4	25.2	21.3
3/01/2016	15.9	25.1	20.6
4/01/2016	16.6	26.5	20.9
5/01/2016	12.2	25.7	19.4
6/01/2016	18.5	25.7	22.1
7/01/2016	18.5	25.7	22.1
8/01/2016	18.1	26.3	21.9
9/01/2016	7.4	26.3	16.9
10/01/2016	13.4	29.7	19.9
11/01/2016	10.6	30.1	20.2
12/01/2016	12.6	29.6	21.4
13/01/2016	19.4	27.0	24.5
14/01/2016	18.1	25.2	22.6
15/01/2016	9.4	27.7	17.3
16/01/2016	9.6	30.1	18.7
17/01/2016	9.9	30.8	20.0
18/01/2016	13.4	32.8	22.1
19/01/2016	21.2	31.3	27.0
20/01/2016	20.2	39.0	25.8
21/01/2016	18.9	28.5	29.0
22/01/2016	19.0	26.9	23.8
23/01/2016	8.5	26.8	17.7
24/01/2016	7.7	27.3	17.3
25/01/2016	10.6	27.0	19.0
26/01/2016	17.8	26.6	22.4
27/01/2016	14.8	29.1	20.7

28/01/2016	18.6	26.9	23.9
29/01/2016	18.0	25.6	22.5
30/01/2016	17.8	28.8	21.7
31/01/2016	15.5	39.0	22.2
1/02/2016	19.5	21.7	29.3
2/02/2016	15.2	23.7	18.5
3/02/2016	18.0	26.0	20.9
4/02/2016	16.5	25.5	21.3
5/02/2016	17.8	26.2	21.7
6/02/2016	6.7	25.8	16.5
7/02/2016	10.1	25.5	18.0
8/02/2016	15.6	25.5	20.6
9/02/2016	5.9	26.5	15.7
10/02/2016	7.8	26.7	17.2
11/02/2016	13.3	35.8	20.0
12/02/2016	18.8	38.0	27.3
13/02/2016	19.9	27.1	29.0
14/02/2016	18.8	26.0	23.0
15/02/2016	17.3	26.0	21.7
16/02/2016	17.9	26.1	22.0
17/02/2016	10.0	28.0	18.1
18/02/2016	7.1	26.1	17.6
19/02/2016	18.9	26.2	22.5
20/02/2016	16.6	28.0	21.4
21/02/2016	16.8	33.8	22.4
22/02/2016	20.6	38.0	27.2
23/02/2016	19.2	26.2	28.6
24/02/2016	18.2	24.9	22.2
25/02/2016	17.3	24.8	21.1
26/02/2016	5.6	25.3	15.2
27/02/2016	9.4	28.5	17.4
28/02/2016	14.0	33.7	21.3
29/02/2016	19.0	41.4	26.4
1/03/2016	21.3	26.9	31.4
2/03/2016	18.6	25.5	22.8
3/03/2016	8.2	27.9	16.9
4/03/2016	16.9	21.0	22.4
5/03/2016	16.9	23.7	19.0
6/03/2016	17.0	25.2	20.4
7/03/2016	18.6	24.2	21.9
8/03/2016	17.8	25.4	21.0
9/03/2016	19.2	25.6	22.3
10/03/2016	11.5	29.3	18.6
11/03/2016	17.0	29.4	23.2
12/03/2016	15.8	26.8	22.6
13/03/2016	13.9	23.5	20.4

14/03/2016	19.5	26.0	21.5
15/03/2016	18.7	26.3	22.4
16/03/2016	16.8	35.4	21.6
17/03/2016	20.5	24.9	28.0
18/03/2016	17.2	22.9	21.1
19/03/2016	5.7	24.6	14.3
20/03/2016	13.0	25.4	18.8
21/03/2016	13.9	27.5	19.7
22/03/2016	16.5	23.9	22.0
23/03/2016	20.0	23.7	22.0
24/03/2016	17.8	24.4	20.8
25/03/2016	17.5	23.8	21.0
26/03/2016	6.2	23.6	15.0
27/03/2016	11.8	21.3	17.7
28/03/2016	15.0	23.2	18.2
29/03/2016	7.3	23.9	15.3
30/03/2016	7.3	25.2	15.6
31/03/2016	14.0	31.8	19.6
1/04/2016	11.8	25.8	21.8
2/04/2016	16.9	24.9	21.4
3/04/2016	5.3	25.4	15.1
4/04/2016	11.0	35.8	18.2
5/04/2016	17.9	20.9	26.9
6/04/2016	15.2	22.1	18.1
7/04/2016	12.8	22.2	17.5
8/04/2016	3.4	24.0	12.8
9/04/2016	9.9	25.6	17.0
10/04/2016	4.5	24.3	15.1
11/04/2016	3.0	23.9	13.7
12/04/2016	5.1	25.8	14.5
13/04/2016	9.8	25.6	17.8
14/04/2016	14.8	30.4	20.2
15/04/2016	8.2	25.8	19.3
16/04/2016	16.6	23.6	21.2
17/04/2016	13.5	29.8	18.6
18/04/2016	18.1	32.8	24.0
19/04/2016	15.7	24.5	24.3
20/04/2016	18.2	24.9	21.4
21/04/2016	16.5	23.7	20.7
22/04/2016	8.3	20.5	16.0
23/04/2016	8.0	24.9	14.3
24/04/2016	8.9	30.4	16.9
25/04/2016	14.5	36.6	22.5
26/04/2016	17.7	28.0	27.2
27/04/2016	11.5	21.3	19.8
28/04/2016		24.5	N/A

29/04/2016	4.4	24.8	14.5
30/04/2016	8.5	19.4	16.7
1/05/2016	6.6	21.4	13.0
2/05/2016	0.4	23.9	10.9
3/05/2016	12.3	22.5	18.1
4/05/2016	6.6	27.7	14.6
5/05/2016	7.3	23.4	17.5
6/05/2016	10.6	21.5	17.0
7/05/2016	13.5	24.9	17.5
8/05/2016	11.2	18.0	18.1
9/05/2016	13.9	18.7	16.0
10/05/2016	14.3	21.0	16.5
11/05/2016	-0.4	22.7	10.3
12/05/2016	3.1	28.2	12.9
13/05/2016	5.0	31.4	16.6
14/05/2016	10.2	24.0	20.8
15/05/2016	4.1	28.7	14.1
16/05/2016	7.0	22.2	17.9
17/05/2016	-0.6	25.3	10.8
18/05/2016	5.0	22.1	15.2
19/05/2016	1.8	21.6	12.0
20/05/2016	8.5	29.3	15.1
21/05/2016	14.9	28.9	22.1
22/05/2016	10.1	19.8	19.5
23/05/2016	-1.6	22.3	9.1
24/05/2016	4.6	27.0	13.5
25/05/2016	11.5	20.1	19.3
26/05/2016	5.1	21.5	12.6
27/05/2016	9.9	19.7	15.7
28/05/2016	-1.1	19.8	9.3
29/05/2016	8.5	19.7	14.2
30/05/2016	8.2	17.4	14.0
31/05/2016	-0.9	19.3	8.3
1/06/2016	2.8	18.7	11.1
2/06/2016	-0.3	19.3	9.2
3/06/2016	-3.5	22.0	7.9
4/06/2016	6.2	21.3	14.1
5/06/2016	10.8	16.8	16.1
6/06/2016	3.5	19.8	10.2
7/06/2016	12.0	15.7	15.9
8/06/2016	9.6	17.3	12.7
9/06/2016	9.9	17.3	13.6
10/06/2016	1.4	17.7	9.4
11/06/2016	5.3	19.7	11.5
12/06/2016	6.7	20.3	13.2
13/06/2016	9.8	20.7	15.1

14/06/2016	10.6	15.2	15.7
15/06/2016	8.9	17.2	12.1
16/06/2016	9.4	17.8	13.3
17/06/2016	12.4	16.0	15.1
18/06/2016	8.5	17.1	12.3
19/06/2016	-2.5	18.2	7.3
20/06/2016	8.3	19.8	13.3
21/06/2016	10.7	17.1	15.3
22/06/2016	0.2	18.2	8.7
23/06/2016	4.9	15.4	11.6
24/06/2016	5.3	15.7	10.4
25/06/2016	5.6	17.9	10.7
26/06/2016	1.9	17.9	9.9
27/06/2016	-1.2	18.6	8.4
28/06/2016	-2.3		8.2
29/06/2016		20.3	N/A
30/06/2016	4.3	17.3	12.3
1/07/2016	0.2	18.1	8.8
2/07/2016	-0.3	20.4	8.9
3/07/2016	-0.3		10.1
4/07/2016		15.9	N/A
5/07/2016	8.6	16.2	12.3
6/07/2016	2.6	15.2	9.4
7/07/2016	5.5	17.2	10.4
8/07/2016	4.8	15.9	11.0
9/07/2016	7.8	18.9	11.9
10/07/2016	8.1	15.6	13.5
11/07/2016	8.6	16.1	12.1
12/07/2016	5.9	15.5	11.0
13/07/2016	6.2	15.3	10.9
14/07/2016	-1.8	17.4	6.8
15/07/2016	4.7	20.0	11.1
16/07/2016	1.5	21.9	10.8
17/07/2016	10.8	15.8	16.4
18/07/2016	11.1	17.3	13.5
19/07/2016	10.8	16.7	14.1
20/07/2016	7.6	17.2	12.2
21/07/2016	10.5	16.9	13.9
22/07/2016	10.2	14.5	13.6
23/07/2016	3.8	14.2	9.2
24/07/2016	3.6	14.7	8.9
25/07/2016	3.5	16.4	9.1

26/07/2016	2.6	17.4	9.5
27/07/2016	10.0	17.0	13.7
28/07/2016	4.5	22.2	10.8
29/07/2016	5.5	23.5	13.9
30/07/2016	16.3	20.3	19.9
31/07/2016	8.3	21.0	14.3
1/08/2016	8.8	16.7	14.9
2/08/2016	0.0	16.2	8.4
3/08/2016	0.2	18.8	8.2
4/08/2016	2.6	22.5	10.7
5/08/2016	9.4	17.3	16.0
6/08/2016	8.8	23.4	13.1
7/08/2016	3.5	21.5	13.5
8/08/2016	0.4	21.5	11.0
9/08/2016	7.3	16.8	14.4
10/08/2016	7.0	17.0	11.9
11/08/2016	-2.2	21.6	7.4
12/08/2016	3.8	19.0	12.7
13/08/2016	-4.0	19.5	7.5
14/08/2016	2.9	23.8	11.2
15/08/2016	3.0	30.8	13.4
16/08/2016	6.6	19.5	18.7
17/08/2016	9.8	32.5	14.7
18/08/2016	11.6	16.4	22.1
19/08/2016	5.7	16.8	11.1
20/08/2016	-2.8	22.5	7.0
21/08/2016	2.8	17.2	12.7
22/08/2016	-1.1	17.8	8.1
23/08/2016	-1.0	18.0	8.4
24/08/2016	10.4	15.3	14.2
25/08/2016	10.1	18.1	12.7
26/08/2016	-2.7	21.7	7.7
27/08/2016	8.5	29.1	15.1
28/08/2016	12.5	19.8	20.8
29/08/2016	8.5	21.0	14.2
30/08/2016	9.5	18.2	15.3
31/08/2016	-0.7	25.8	8.8

Appendix 2 – Stable isotope, rainfall amount, and temperature data for all rainfall events, organised by site, then date of collection.

Site	Date of Event	Rainfall Amount (mm)	$\delta^{18}\text{O}$ (VSMOW)	δD (VSMOW)	d excess	Average Temp (°C)
ARU	9/07/2014	0.5	-1.38	12.84	23.86	11.4
ARU	14/07/2014	3.0	-7.47	-37.90	21.83	13.0
ARU	22/07/2014	18.5	-6.73	-29.85	23.97	7.8
ARU	23/07/2014	1.0	-5.12	-23.22	17.74	16.6
ARU	24/07/2014	2.0	-2.52	-1.67	18.46	13.7
ARU	30/08/2014	2.5	-2.26	-11.56	6.49	22.5
ARU	8/09/2014	4.0	-0.91	1.71	8.98	19.2
ARU	11/01/2015	2.0	-2.02	-11.81	4.35	19.3
ARU	21/02/2015	2.0	-1.87	-10.97	3.99	22.1
ARU	26/02/2015	10.0	-1.90	-9.87	5.30	28.5
ARU	27/02/2015	8.0	-1.80	-9.80	4.58	29.4
ARU	31/03/2015	3.0	-1.11	4.75	13.61	16.1
ARU	1/04/2015	1.0	-1.01	4.27	12.33	21.6
ARU	11/04/2015	6.0	-1.24	4.26	14.18	24.1
ARU	15/04/2015	17.0	-1.05	4.44	12.85	15.0
ARU	16/04/2015	1.5	-1.74	-9.51	4.42	19.7
ARU	25/04/2015	2.0	-1.26	4.76	14.87	16.8
ARU	1/05/2015	4.5	-1.65	-9.58	3.61	19.4
ARU	2/05/2015	1.0	-2.07	-11.07	5.47	17.8
ARU	19/06/2015	2.0	-2.23	-12.00	5.87	12.4
ARU	23/06/2015	3.0	-6.99	-40.77	15.16	14.5
ARU	9/07/2015	4.0	-1.59	-6.63	6.09	17.8
ARU	21/07/2015	8.5	-1.16	-9.98	-0.67	17.7
ARU	31/07/2015	2.0	-1.24	-10.07	-0.13	15.9
ARU	1/08/2015	52.0	-2.32	-14.58	3.98	13.9
ARU	6/08/2015	5.0	-6.05	-34.10	14.31	7.0
ARU	18/08/2015	9.0	-1.19	-10.16	-0.63	18.5
ARU	1/09/2015	7.5	-6.04	-34.28	14.02	12.4
ARU	2/09/2015	2.5	-6.04	-34.37	13.98	12.9
ARU	29/10/2015	4.0	-1.66	-7.06	6.25	18.3
ARU	1/11/2015	6.0	-1.60	-5.99	6.79	22.4
ARU	2/11/2015	6.0	-4.96	-33.60	6.07	19.4
ARU	3/11/2015	14.0	-5.03	-33.90	6.38	18.4
EUC	2/05/2014	13.8	-3.84	-8.30	22.40	16.5
EUC	3/05/2014	1.8	-1.55	4.50	16.90	19.0
EUC	4/05/2014	1.0	-2.22	-3.98	13.76	16.9
EUC	5/05/2014	0.2	-1.78	-3.56	10.65	15.4
EUC	8/05/2014	7.4	-2.57	-16.93	3.60	24.0

EUC	9/05/2014	14.0	-6.63	-43.27	9.78	15.4
EUC	16/05/2014	6.6	-2.71	-13.33	8.37	15.1
EUC	17/05/2014	0.8	1.74	14.33	0.41	21.3
EUC	18/05/2014	0.8	0.34	8.55	5.86	17.6
EUC	22/05/2014	15.0	-3.97	-17.18	14.59	15.1
EUC	29/05/2014	1.0	-2.70	-7.85	13.74	12.3
EUC	30/05/2014	2.0	-5.24	-30.65	11.27	15.3
EUC	31/05/2014	10.8	-6.00	-27.82	20.19	15.3
EUC	16/06/2014	17.6	-5.51	-28.08	15.99	9.0
EUC	23/06/2014	1.2	-2.48	3.53	23.35	11.4
EUC	25/06/2014	0.4	-1.48	5.97	17.83	7.4
EUC	28/06/2014	8.8	-3.42	-6.58	20.77	12.9
EUC	29/06/2014	3.6	-1.88	4.60	19.65	12.5
EUC	30/06/2014	0.2	-0.77	4.79	10.92	8.6
EUC	9/07/2014	5.4	-3.79	-5.62	24.68	11.4
EUC	10/07/2014	0.6	0.31	15.52	13.05	10.6
EUC	12/07/2014	4.0	-2.15	-0.46	16.73	14.3
EUC	13/07/2014	0.4	-0.92	8.29	15.66	9.8
EUC	15/07/2014	0.8	-6.08	-34.11	14.52	14.0
EUC	21/07/2014	0.2	0.23	-0.65	-2.46	12.4
EUC	24/07/2014	15.0	-10.25	-61.26	20.74	13.7
EUC	25/07/2014	2.0	-4.34	-19.59	15.14	11.6
EUC	1/08/2014	0.8	-0.73	13.37	19.18	12.8
EUC	11/08/2014	3.0	-0.74	7.81	13.72	6.4
EUC	14/08/2014	5.8	-3.11	-3.19	21.71	6.3
EUC	1/09/2014	2.6	-2.85	-14.93	7.86	15.8
EUC	5/09/2014	0.4	-3.21	-12.49	13.19	9.7
EUC	23/09/2014	2.2	-2.50	-5.07	14.93	16.3
EUC	24/09/2014	6.0	-2.20	-1.39	16.21	15.0
EUC	13/10/2014	0.2	1.28	11.46	1.23	17.0
EUC	18/10/2014	0.6	3.44	26.09	-1.43	26.3
EUC	20/10/2014	0.1	5.56	29.37	-15.15	20.0
EUC	21/10/2014	8.6	0.43	10.14	6.69	16.3
EUC	31/10/2014	6.6	-0.58	-2.00	2.63	22.8
EUC	14/11/2014	4.0	0.37	10.91	7.98	16.8
EUC	15/11/2014	30.4	-2.27	-0.59	17.59	15.8
EUC	20/11/2014	5.8	1.77	21.50	7.34	21.5
EUC	29/11/2014	8.6	-1.02	3.35	11.50	22.9
EUC	2/12/2014	7.6	1.77	16.00	1.87	27.6
EUC	14/12/2014	0.4	1.69	6.34	-7.15	21.4
EUC	26/12/2014	0.8	-0.93	4.63	12.07	19.0
EUC	3/01/2015	2.4	0.57	4.76	0.16	21.5
EUC	8/01/2015	0.6	2.09	12.37	-4.35	23.2
EUC	11/01/2015	4.2	-1.59	2.58	15.31	19.3
EUC	12/01/2015	1.8	-2.73	-8.46	13.38	17.6
EUC	13/01/2015	9.8	-4.34	-20.40	14.35	16.5

EUC	27/02/2015	0.8	6.07	11.22	-37.30	29.4
EUC	2/03/2015	3.2	-0.86	1.04	7.93	19.9
EUC	3/03/2015	6.8	-2.66	-11.72	9.57	21.2
EUC	4/03/2015	1.4	-1.07	2.05	10.65	19.6
EUC	5/03/2015	0.6	-1.91	-7.86	7.45	22.1
EUC	23/03/2015	0.8	-1.56	1.42	13.88	20.1
EUC	24/03/2015	1.6	-1.00	10.82	18.84	11.7
EUC	28/03/2015	4.4	-3.82	-20.63	9.96	20.3
EUC	29/03/2015	2.2	-1.94	-2.48	13.04	15.6
EUC	1/04/2015	0.4	3.94	19.24	-12.29	21.6
EUC	6/04/2015	0.4	-0.66	5.10	10.40	20.7
EUC	7/04/2015	0.4	-0.12	15.80	16.76	15.8
EUC	12/04/2015	0.2	6.68	14.29	-39.19	23.8
EUC	16/04/2015	12.0	-4.30	-22.40	11.97	19.7
EUC	17/04/2015	20.0	-3.43	-11.98	15.46	16.6
EUC	19/04/2015	1.6	-1.36	5.59	16.51	14.7
EUC	26/04/2015	7.4	-2.46	-2.95	16.72	12.9
EUC	27/04/2015	6.0	-4.08	-11.20	21.44	11.6
EUC	24/05/2015	0.4	-1.68	-8.36	5.12	17.4
EUC	29/05/2015	0.2	-2.57	-1.45	19.12	12.0
EUC	30/05/2015	4.4	-2.52	1.55	21.70	9.0
EUC	31/05/2015	0.2	-3.57	-6.18	22.39	8.7
EUC	9/06/2015	1.8	-1.00	4.74	12.75	18.5
EUC	10/06/2015	0.6	0.05	9.81	9.43	14.5
EUC	15/06/2015	0.4	-1.59	-0.97	11.73	15.5
EUC	18/06/2015	3.4	-2.65	-12.83	8.35	12.0
EUC	20/06/2015	0.2	-1.27	-10.39	-0.20	16.1
EUC	22/06/2015	8.8	-4.00	-15.84	16.16	15.4
EUC	23/06/2015	8.6	-7.68	-47.16	14.29	14.5
EUC	24/06/2015	1.6	-1.12	7.95	16.91	10.2
EUC	10/07/2015	1.2	-5.28	-27.22	14.98	11.4
EUC	11/07/2015	5.0	-2.72	0.88	22.66	13.5
EUC	12/07/2015	0.4	-1.61	9.88	22.74	11.7
EUC	13/07/2015	0.4	-2.16	6.18	23.46	10.4
EUC	14/07/2015	2.0	-2.19	0.30	17.84	13.8
EUC	15/07/2015	2.4	-2.20	-3.92	13.66	13.3
EUC	16/07/2015	3.4	-2.51	-3.49	16.56	9.5
EUC	17/07/2015	1.6	-2.73	-3.50	18.35	8.3
EUC	23/07/2015	2.2	-3.73	-15.29	14.55	13.6
EUC	26/07/2015	2.6	-2.22	-0.20	17.59	12.4
EUC	27/07/2015	0.4	-1.21	8.98	18.64	7.8
EUC	31/07/2015	1.0	-2.81	-19.14	3.34	15.9
EUC	1/08/2015	9.4	-7.55	-43.22	17.19	13.9
EUC	2/08/2015	5.0	-6.90	-38.45	16.72	13.0
EUC	4/08/2015	0.2	-3.56	-7.86	20.65	9.6
EUC	13/08/2015	0.8	-1.37	-1.12	9.84	12.6

EUC	23/08/2015	42.0	-6.10	-33.88	14.96	9.8
EUC	24/08/2015	0.4	-2.12	-6.90	10.03	11.1
EUC	25/08/2015	7.4	-4.05	-12.63	19.76	11.7
EUC	26/08/2015	0.6	-2.68	-3.72	17.75	9.3
EUC	31/08/2015	5.4	-1.65	-3.82	9.41	18.6
EUC	1/09/2015	5.8	-2.06	-8.02	8.43	12.4
EUC	2/09/2015	3.6	-7.25	-39.14	18.84	12.9
EUC	3/09/2015	1.6	-1.86	-2.95	11.95	12.6
EUC	7/09/2015	0.6	-1.36	6.43	17.32	9.2
EUC	20/09/2015	0.6	-1.56	-5.33	7.15	19.5
EUC	21/09/2015	0.6	-0.76	8.18	14.26	15.2
EUC	26/09/2015	0.6	1.08	11.14	2.50	19.1
EUC	15/10/2015	1.4	5.50	36.71	-7.30	23.7
EUC	19/10/2015	2.0	8.41	47.48	-19.80	28.0
EUC	27/10/2015	1.2	3.30	19.59	-6.81	19.5
EUC	29/10/2015	4.6	3.24	17.70	-8.22	18.3
EUC	1/11/2015	4.0	-1.50	-14.22	-2.21	22.4
EUC	2/11/2015	3.2	-1.82	-13.68	0.86	19.4
EUC	3/11/2015	13.2	-2.57	-8.82	11.75	18.4
EUC	4/11/2015	4.6	-1.96	-9.08	6.60	17.0
EUC	5/11/2015	0.4	-0.99	1.39	9.33	12.7
EUC	18/11/2015	0.2	13.38	60.46	-46.58	27.4
EUC	26/11/2015	0.4	-0.38	6.71	9.78	18.8
EUC	5/12/2015	1.6	-0.65	-3.42	1.75	26.4
EUC	6/12/2015	6.2	0.61	8.43	3.53	23.5
EUC	22/12/2015	1.2	2.61	20.32	-0.54	18.4
EUC	23/12/2015	8.0	-1.30	-4.16	6.21	21.4
EUC	24/12/2015	7.6	-3.54	-16.58	11.70	23.6
EUC	25/12/2015	2.0	-1.46	-0.36	11.33	27.5
EUC	11/01/2016	0.4	3.47	17.97	-9.75	20.2
EUC	22/01/2016	0.2	-0.21	8.03	9.69	23.8
EUC	26/01/2016	0.8	-0.84	-2.70	3.98	22.4
EUC	1/02/2016	4.2	0.13	-1.39	-2.46	29.3
EUC	2/02/2016	34.0	-7.58	-47.81	12.86	18.5
EUC	4/02/2016	0.6	-1.77	-2.65	11.51	21.3
EUC	21/02/2016	0.6	1.00	9.96	1.93	22.4
EUC	22/02/2016	0.6	1.91	12.44	-2.88	27.2
EUC	23/02/2016	0.6	3.97	20.17	-11.55	28.6
EUC	24/02/2016	17.2	-3.37	-11.06	15.89	22.2
EUC	25/02/2016	2.6	-1.87	1.14	16.11	21.1
EUC	5/03/2016	7.8	-0.74	6.51	12.45	19.0
EUC	6/03/2016	8.6	-1.68	4.17	17.61	20.4
EUC	7/03/2016	5.0	-1.89	1.34	16.46	21.9
EUC	8/03/2016	1.0	-0.99	1.72	9.65	21.0
EUC	14/03/2016	0.6	-0.07	4.54	5.06	21.5
EUC	15/03/2016	0.2	1.11	10.51	1.62	22.4

EUC	23/03/2016	4.4	-1.17	-3.29	6.10	22.0
EUC	28/03/2016	4.4	-2.79	-10.90	11.43	18.2
EUC	29/03/2016	1.8	-1.25	4.56	14.55	15.3
EUC	5/04/2016	2.8	-0.44	6.77	10.30	26.9
EUC	20/04/2016	0.6	0.26	0.05	-2.05	21.4
EUC	23/04/2016	0.4	-0.75	6.64	12.62	14.3
EUC	7/05/2016	9.0	-1.67	-1.86	11.53	17.5
EUC	8/05/2016	12.6	-7.90	-45.49	17.71	18.1
EUC	9/05/2016	10.4	-7.13	-42.61	14.45	16.0
EUC	10/05/2016	0.6	-2.94	-7.03	16.49	16.5
EUC	16/05/2016	0.2	6.93	17.97	-37.46	17.9
EUC	22/05/2016	0.2	4.23	12.10	-21.71	19.5
EUC	25/05/2016	4.0	-2.06	-9.13	7.32	19.3
EUC	26/05/2016	1.4	0.00	9.31	9.30	12.6
EUC	29/05/2016	0.6	4.50	23.62	-12.36	14.2
EYR	28/04/2014	0.8	-0.42	-6.07	-2.75	22.4
EYR	30/04/2014	2.2	-1.97	-0.64	15.15	15.2
EYR	3/05/2014	15.2	-2.59	-1.28	19.47	19.0
EYR	4/05/2014	6.4	-2.04	-4.10	12.21	16.9
EYR	5/05/2014	0.2	-0.38	4.53	7.54	15.4
EYR	6/05/2014	3.0	-4.32	-31.48	3.10	17.0
EYR	8/05/2014	5.0	-5.45	-35.09	8.49	24.0
EYR	9/05/2014	21.0	-8.88	-59.30	11.71	15.4
EYR	17/05/2014	2.2	-1.38	-7.88	3.17	21.3
EYR	22/05/2014	0.4	-2.35	-14.97	3.85	15.1
EYR	28/05/2014	0.8	-0.97	-0.16	7.63	11.9
EYR	30/05/2014	14.4	-5.42	-26.98	16.37	15.3
EYR	31/05/2014	9.2	-2.73	-6.49	15.37	15.3
EYR	1/06/2014	0.4	-1.94	-2.74	12.79	12.3
EYR	12/06/2014	7.2	-4.97	-24.10	15.62	14.6
EYR	13/06/2014	2.2	-1.52	2.97	15.11	14.8
EYR	14/06/2014	2.2	-1.05	9.05	17.41	10.4
EYR	15/06/2014	0.8	-1.63	4.47	17.53	9.3
EYR	23/06/2014	6.2	-2.64	4.59	25.71	11.4
EYR	24/06/2014	2.8	-2.06	5.63	22.13	11.2
EYR	27/06/2014	3.0	-4.21	-19.28	14.42	17.2
EYR	28/06/2014	14.2	-3.62	-7.60	21.38	12.9
EYR	29/06/2014	5.0	-1.71	5.35	19.06	12.5
EYR	30/06/2014	0.4	-1.15	2.66	11.84	8.6
EYR	4/07/2014	0.4	-0.88	13.38	20.38	11.2
EYR	9/07/2014	19.6	-4.59	-18.92	17.81	11.4
EYR	10/07/2014	1.0	-1.60	11.27	24.05	10.6
EYR	12/07/2014	1.4	-1.08	6.97	15.63	14.3
EYR	15/07/2014	4.4	-7.49	-41.32	18.58	14.0
EYR	21/07/2014	1.4	-1.81	-9.91	4.56	12.4
EYR	23/07/2014	11.6	-7.35	-38.20	20.61	16.6

EYR	24/07/2014	0.2	-5.20	-25.79	15.78	13.7
EYR	25/07/2014	1.8	-2.50	-5.13	14.84	11.6
EYR	31/07/2014	0.2	0.60	15.53	10.73	12.3
EYR	13/08/2014	1.8	-2.23	-4.45	13.39	7.0
EYR	22/08/2014	2.1	-0.78	5.81	12.02	19.5
EYR	31/08/2014	5.3	-3.02	-16.04	8.09	18.4
EYR	1/09/2014	10.0	-3.58	-16.77	11.89	15.8
EYR	7/09/2014	1.0	0.13	6.26	5.23	24.4
EYR	9/09/2014	1.4	-3.28	-5.66	20.55	17.4
EYR	11/09/2014	0.2	-0.57	2.17	6.73	11.7
EYR	18/09/2014	1.1	0.66	8.24	2.96	17.5
EYR	23/09/2014	31.5	-2.96	-8.16	15.50	16.3
EYR	24/09/2014	0.6	-0.72	3.81	9.57	15.0
EYR	5/10/2014	1.5	0.82	6.90	0.37	16.7
EYR	18/10/2014	0.4	3.47	18.53	-9.21	26.3
EYR	19/10/2014	0.3	3.07	19.98	-4.54	22.3
EYR	20/10/2014	2.4	2.47	19.57	-0.19	20.0
EYR	31/10/2014	2.8	-1.26	-1.78	8.29	22.8
EYR	13/11/2014	5.0	-0.39	3.92	7.04	21.0
EYR	14/11/2014	26.2	-2.01	-1.37	14.73	16.8
EYR	15/11/2014	6.8	-2.20	-3.88	13.73	15.8
EYR	19/11/2014	0.4	4.71	38.13	0.45	28.8
EYR	29/11/2014	5.2	0.17	8.20	6.87	22.9
EYR	2/12/2014	10.2	-1.98	-4.64	11.20	27.6
EYR	14/12/2014	0.6	1.63	11.32	-1.71	21.4
EYR	21/12/2014	13.2	-1.06	-6.21	2.28	27.2
EYR	23/12/2014	2.4	-1.55	1.37	13.79	19.0
EYR	25/12/2014	1.0	-2.31	-3.31	15.15	20.4
EYR	3/01/2015	0.6	-0.14	1.47	2.60	21.5
EYR	4/01/2015	0.1	4.35	22.31	-12.49	19.7
EYR	9/01/2015	0.6	-1.27	4.92	15.10	18.5
EYR	10/01/2015	1.8	-1.97	-0.25	15.51	19.0
EYR	11/01/2015	6.6	-2.05	0.29	16.69	19.3
EYR	12/01/2015	5.0	-1.12	4.12	13.09	17.6
EYR	17/01/2015	1.6	-0.69	6.40	11.92	23.0
EYR	27/02/2015	9.2	-0.69	-7.53	-2.03	29.4
EYR	28/02/2015	1.8	-2.35	-17.43	1.34	26.6
EYR	2/03/2015	1.0	-2.46	-12.71	6.97	19.9
EYR	5/03/2015	0.5	0.19	6.05	4.51	22.1
EYR	21/03/2015	0.2	2.75	19.09	-2.88	19.4
EYR	23/03/2015	0.6	0.03	11.66	11.44	20.1
EYR	24/03/2015	1.0	0.43	16.05	12.62	11.7
EYR	28/03/2015	7.6	-1.10	-2.94	5.87	20.3
EYR	1/04/2015	0.8	-2.42	-9.37	9.99	21.6
EYR	2/04/2015	0.3	0.95	12.19	4.56	20.1
EYR	6/04/2015	0.1	0.11	8.71	7.86	20.7

EYR	7/04/2015	0.4	-1.42	12.58	23.91	15.8
EYR	11/04/2015	0.4	5.32	12.77	-29.83	24.1
EYR	12/04/2015	4.6	-1.56	-4.81	7.70	23.8
EYR	16/04/2015	4.8	-1.95	0.09	15.65	19.7
EYR	19/04/2015	0.4	-0.12	11.44	12.38	14.7
EYR	24/04/2015	1.2	-1.74	6.42	20.32	18.7
EYR	25/04/2015	1.8	-3.17	-5.85	19.53	16.8
EYR	26/04/2015	0.1	1.54	10.63	-1.70	12.9
EYR	1/05/2015	5.6	-6.48	-54.48	-2.61	19.4
EYR	5/05/2015	0.6	-0.50	10.92	14.90	14.8
EYR	6/05/2015	4.0	-3.02	-8.16	15.99	13.8
EYR	7/05/2015	0.4	-1.40	0.71	11.93	13.7
EYR	9/05/2015	0.8	-0.49	5.28	9.17	10.1
EYR	10/05/2015	0.6	-1.24	-0.31	9.61	18.7
EYR	11/05/2015	1.2	-1.19	3.45	12.99	17.9
EYR	13/05/2015	0.4	0.48	6.10	2.28	16.2
EYR	16/05/2015	0.2	-0.92	0.62	7.96	13.0
EYR	17/05/2015	1.0	2.65	12.55	-8.68	16.5
EYR	18/05/2015	1.4	-2.98	-9.72	14.11	16.8
EYR	19/05/2015	1.8	-2.21	-6.56	11.15	19.0
EYR	20/05/2015	0.8	-1.57	1.30	13.85	14.9
EYR	22/05/2015	1.0	1.91	6.40	-8.85	8.1
EYR	26/05/2015	0.2	0.44	8.35	4.81	12.2
EYR	10/06/2015	0.4	0.54	7.30	2.99	14.5
EYR	14/06/2015	7.0	-3.80	-18.59	11.80	10.7
EYR	16/06/2015	4.4	-4.62	-21.45	15.53	16.1
EYR	21/06/2015	11.4	-4.24	-20.87	13.05	18.3
EYR	22/06/2015	4.2	-6.17	-36.94	12.46	15.4
EYR	24/06/2015	0.2	-1.82	-0.74	13.82	10.2
EYR	8/07/2015	22.0	-7.57	-41.58	18.99	11.9
EYR	12/07/2015	1.2	-1.46	10.21	21.89	11.7
EYR	13/07/2015	2.2	-1.50	9.24	21.21	10.4
EYR	14/07/2015	2.4	-1.93	4.63	20.06	13.8
EYR	15/07/2015	2.2	-1.10	4.06	12.86	13.3
EYR	16/07/2015	7.8	-1.77	2.95	17.12	9.5
EYR	21/07/2015	4.0	-7.86	-47.45	15.44	17.7
EYR	26/07/2015	5.6	-4.33	-15.63	19.02	12.4
EYR	31/07/2015	6.7	-5.22	-38.89	2.89	15.9
EYR	1/08/2015	34.4	-10.00	-66.89	13.11	13.9
EYR	3/08/2015	0.4	-1.68	1.88	15.30	12.4
EYR	5/08/2015	1.0	-3.49	-12.59	15.35	10.0
EYR	10/08/2015	0.6	-4.47	-21.10	14.65	10.2
EYR	11/08/2015	3.4	-3.51	-9.05	19.05	14.3
EYR	12/08/2015	3.8	-1.99	-0.24	15.65	12.7
EYR	13/08/2015	0.4	-2.62	-11.59	9.40	12.6
EYR	18/08/2015	7.0	-4.36	-22.64	12.28	18.5

EYR	19/08/2015	0.4	-2.96	-11.81	11.85	12.9
EYR	20/08/2015	2.2	-0.83	-1.82	4.85	16.2
EYR	23/08/2015	7.0	-6.07	-36.98	11.56	9.8
EYR	24/08/2015	1.4	-3.49	-20.15	7.77	11.1
EYR	25/08/2015	3.2	-3.26	-11.74	14.31	11.7
EYR	1/09/2015	5.2	-1.54	-3.93	8.35	12.4
EYR	2/09/2015	6.4	-3.61	-12.67	16.18	12.9
EYR	3/09/2015	1.4	-1.61	0.78	13.69	12.6
EYR	14/09/2015	1.8	-1.59	1.68	14.36	13.9
EYR	16/09/2015	1.5	-1.68	-5.35	8.06	14.7
EYR	15/10/2015	0.6	3.95	24.74	-6.89	23.7
EYR	18/10/2015	2.6	3.10	25.61	0.81	19.0
EYR	27/10/2015	0.5	1.98	15.14	-0.73	19.5
EYR	29/10/2015	2.4	1.05	2.30	-6.09	18.3
EYR	2/11/2015	2.0	-3.10	-13.40	11.40	19.4
EYR	3/11/2015	40.6	-4.60	-22.90	13.90	18.4
EYR	4/11/2015	2.8	-1.70	-7.30	6.30	17.0
EYR	7/11/2015	0.7	4.40	19.90	-15.30	28.1
EYR	9/11/2015	13.8	-0.20	8.20	9.80	25.2
EYR	19/11/2015	3.6	1.10	14.80	6.00	19.6
EYR	25/11/2015	0.2	5.20	32.40	-9.20	24.0
EYR	26/11/2015	0.4	-0.20	11.50	13.10	18.8
EYR	4/12/2015	7.4	-1.20	-2.00	7.60	28.1
EYR	5/12/2015	12.2	-0.60	3.50	8.30	26.4
EYR	18/12/2015	0.2	3.80	11.10	-19.30	21.2
EYR	11/01/2016	0.8	-1.00	-9.50	-1.50	20.2
EYR	26/01/2016	4.2	-1.80	-7.20	7.20	22.4
EYR	1/02/2016	26.0	-5.10	-28.30	12.50	29.3
EYR	22/02/2016	7.2	-0.70	-6.40	-0.80	27.2
EYR	23/02/2016	1.6	1.90	5.40	-9.80	28.6
EYR	24/02/2016	28.2	-1.70	1.10	14.70	22.2
EYR	4/03/2016	3.0	3.00	17.80	-6.20	22.4
EYR	5/03/2016	9.6	0.90	12.80	5.60	19.0
EYR	6/03/2016	14.0	-2.10	0.70	17.50	20.4
EYR	7/03/2016	0.4	0.20	8.10	6.50	21.9
EYR	8/03/2016	2.4	-1.30	-1.50	8.90	21.0
EYR	9/03/2016	1.4	-1.70	-3.70	9.90	22.3
EYR	23/03/2016	2.8	-1.00	1.40	9.40	22.0
EYR	24/03/2016	0.4	-0.10	6.50	7.30	20.8
EYR	25/03/2016	1.2	-0.90	1.90	9.10	21.0
EYR	27/03/2016	0.4	-0.40	-3.20	0.00	17.7
EYR	28/03/2016	6.2	-1.70	0.90	14.50	18.2
EYR	5/04/2016	4.0	-1.50	-7.50	4.50	26.9
EYR	6/04/2016	2.0	-1.90	-2.50	12.70	18.1
EYR	14/04/2016	0.2	-0.10	1.20	2.00	20.2
EYR	19/04/2016	1.2	2.50	1.20	-18.80	24.3

EYR	20/04/2016	1.4	-2.00	-9.00	7.00	21.4
EYR	22/04/2016	0.8	-0.60	1.80	6.60	16.0
EYR	24/04/2016	0.6	-0.30	5.90	8.30	16.9
EYR	26/04/2016	2.0	5.40	25.70	-17.50	27.2
EYR	27/04/2016	0.6	1.00	14.30	6.30	19.8
EYR	30/04/2016	5.8	-5.60	-23.90	20.90	16.7
MUN	2/05/2014	2.4	-2.38	2.56	21.60	16.5
MUN	9/05/2014	8.2	-8.77	-59.21	10.94	15.4
MUN	22/05/2014	4.8	-0.94	-1.12	6.41	15.1
MUN	26/05/2014	0.8	-0.67	-0.09	5.26	16.6
MUN	29/05/2014	0.6	-0.30	7.21	9.62	12.3
MUN	30/05/2014	3.8	-4.96	-25.32	14.36	15.3
MUN	31/05/2014	11.2	-5.80	-31.56	14.84	15.3
MUN	11/06/2014	2.4	-8.44	-68.71	-1.16	17.8
MUN	12/06/2014	11.8	-7.31	-41.82	16.67	14.6
MUN	13/06/2014	1.6	-1.91	5.67	20.95	14.8
MUN	23/06/2014	0.8	-2.11	4.70	21.56	11.4
MUN	29/06/2014	2.8	-2.19	-1.59	15.92	12.5
MUN	9/07/2014	6.4	-4.72	-8.58	29.15	11.4
MUN	16/07/2014	2.8	-6.56	-35.56	16.92	10.7
MUN	21/07/2014	1.6	0.69	6.35	0.86	12.4
MUN	23/07/2014	31.0	-9.66	-56.84	20.41	16.6
MUN	25/07/2014	3.8	-4.17	-17.42	15.94	11.6
MUN	31/08/2014	0.8	0.27	1.52	-0.66	18.4
MUN	23/09/2014	3.4	-2.79	-5.60	16.74	16.3
MUN	14/11/2014	17.2	-1.38	5.23	16.25	16.8
MUN	8/06/2015	0.4	-2.72	-15.03	6.77	10.6
MUN	9/06/2015	1.0	-1.10	4.85	13.66	18.5
MUN	10/06/2015	0.2	0.87	12.93	5.94	14.5
MUN	15/06/2015	0.6	-2.93	-10.82	12.60	15.5
MUN	16/06/2015	4.0	-4.66	-21.67	15.63	16.1
MUN	17/06/2015	1.0	-1.99	0.43	16.39	14.8
MUN	20/06/2015	1.0	0.42	-1.99	-5.31	16.1
MUN	21/06/2015	1.8	-1.12	-6.24	2.73	18.3
MUN	22/06/2015	8.5	-4.83	-27.93	10.73	15.4
MUN	23/06/2015	2.2	-5.94	-35.83	11.72	14.5
MUN	24/06/2015	1.4	-1.07	9.27	17.87	10.2
MUN	12/07/2015	2.4	-1.80	3.12	17.50	11.7
MUN	14/07/2015	1.6	-1.52	6.28	18.44	13.8
MUN	15/07/2015	1.0	-1.74	1.98	15.91	13.3
MUN	16/07/2015	5.4	-2.57	-3.06	17.48	9.5
MUN	17/07/2015	3.0	-2.52	-2.28	17.84	8.3
MUN	1/08/2015	22.4	-8.54	-51.41	16.92	13.9
MUN	4/08/2015	0.6	-1.35	-2.82	7.99	9.6
MUN	11/08/2015	1.2	-3.60	-9.18	19.60	14.3
MUN	13/08/2015	0.8	-1.88	-2.94	12.09	12.6

MUN	19/08/2015	3.0	-3.67	-15.75	13.62	12.9
MUN	19/08/2015	4.0	-4.10	-20.88	11.89	12.9
MUN	20/08/2015	1.8	-1.22	0.63	10.39	16.2
MUN	23/08/2015	1.6	-3.00	-13.58	10.39	9.8
MUN	25/08/2015	7.6	-4.29	-15.02	19.27	11.7
MUN	26/08/2015	5.6	-4.64	-14.40	22.71	9.3
MUN	10/11/2015	3.0	-0.89	4.28	11.37	18.6
MUN	8/03/2016	5.0	-2.07	-3.78	12.81	21.0
MUN	9/03/2016	2.2	-1.84	-1.99	12.76	22.3
MUN	25/03/2016	1.0	-1.29	-0.06	10.27	21.0
MUN	28/03/2016	9.6	-3.04	-8.50	15.81	18.2
MUN	5/04/2016	6.0	-3.05	-14.79	9.61	26.9
MUN	6/04/2016	7.0	-2.48	-4.96	14.89	18.1
MUN	19/04/2016	2.0	3.90	11.41	-19.79	24.3
MUN	25/05/2016	8.2	-1.43	-12.73	-1.25	19.3
MUN	2/07/2016	1.2	-0.66	5.86	11.17	8.9
MUN	4/07/2016	6.3	-3.27	-11.43	14.77	7.8
MUN	5/07/2016	1.6	-1.94	0.28	15.81	12.3
MUN	6/07/2016	1.2	-0.62	4.53	9.49	9.4
MUN	9/07/2016	12.8	-10.30	-68.90	13.50	11.9
MUN	10/07/2016	1.8	-2.05	-10.93	5.45	13.5
MUN	12/07/2016	1.0	-2.44	-5.98	13.57	11.0
MUN	13/07/2016	1.8	-0.61	10.18	15.03	10.9
MUN	18/07/2016	4.4	-2.89	-10.82	12.29	13.5
MUN	19/07/2016	29.0	-4.71	-18.34	19.35	14.1
MUN	8/08/2016	6.0	-5.11	-24.16	16.68	11.0
MUN	16/08/2016	0.8	2.83	23.78	1.14	18.7
RAW	12/07/2014	0.4	-1.50	1.90	13.87	14.3
RAW	13/07/2014	0.8	-1.22	7.01	16.74	9.8
RAW	15/07/2014	0.8	-4.28	-21.63	12.64	14.0
RAW	21/07/2014	0.8	-3.77	-24.38	5.78	12.4
RAW	23/07/2014	10.4	-5.33	-20.07	22.60	16.6
RAW	24/07/2014	0.2	-5.02	-20.94	19.21	13.7
RAW	16/08/2014	2.0	2.91	9.34	-13.90	13.2
RAW	20/08/2014	0.4	2.68	15.11	-6.29	16.5
RAW	22/08/2014	0.2	1.15	3.38	-5.86	19.5
RAW	18/09/2014	3.0	2.66	18.79	-2.50	17.5
RAW	23/09/2014	9.0	-3.98	-14.21	17.64	16.3
RAW	20/10/2014	3.2	-0.47	0.50	4.24	20.0
RAW	7/11/2014	1.8	10.56	59.80	-24.66	30.5
RAW	13/11/2014	35.4	-1.54	1.26	13.58	21.0
RAW	14/11/2014	4.6	-4.47	-16.53	19.20	16.8
RAW	15/11/2014	25.8	-6.50	-34.63	17.37	15.8
RAW	18/11/2014	2.0	5.48	31.04	-12.84	23.5
RAW	19/11/2014	3.2	5.51	39.16	-4.92	28.8
RAW	29/11/2014	1.2	0.04	7.21	6.91	22.9

RAW	21/12/2014	20.0	-8.93	-59.38	12.05	27.2
RAW	22/12/2014	1.8	-2.82	-15.36	7.16	21.2
RAW	2/01/2015	0.4	-1.02	-11.30	-3.14	21.9
RAW	3/01/2015	3.0	3.15	10.05	-15.14	21.5
RAW	27/02/2015	10.4	-4.91	-26.21	13.07	29.4
RAW	28/02/2015	10.2	-6.02	-34.54	13.59	26.6
RAW	2/03/2015	19.2	-7.97	-52.55	11.25	19.9
RAW	3/03/2015	1.2	-7.83	-50.96	11.66	21.2
RAW	5/03/2015	2.0	-2.09	-10.58	6.14	22.1
RAW	21/03/2015	1.2	-0.44	1.18	4.73	19.4
RAW	28/03/2015	11.0	-1.81	4.42	18.88	20.3
RAW	1/04/2015	2.0	0.37	7.31	4.33	21.6
RAW	9/04/2015	0.4	-0.56	-30.09	-25.59	18.7
RAW	12/04/2015	8.2	-0.93	-1.79	5.65	23.8
RAW	16/04/2015	15.0	-4.14	-19.46	13.66	19.7
RAW	17/04/2015	5.0	-2.22	-2.12	15.63	16.6
RAW	1/05/2015	2.8	-1.67	-31.61	-18.25	19.4
RAW	2/05/2015	1.2	-4.54	-43.36	-7.05	17.8
RAW	22/06/2015	3.0	-6.76	-42.97	11.14	15.4
RAW	23/06/2015	1.8	-9.52	-66.90	9.28	14.5
RAW	24/06/2015	0.4	-5.92	-29.31	18.05	10.2
RAW	9/07/2015	9.6	-9.05	-59.12	13.28	17.8
RAW	10/07/2015	3.0	-5.70	-26.50	19.07	11.4
RAW	15/07/2015	1.2	-2.83	-5.91	16.70	13.3
RAW	16/07/2015	0.4	-1.32	8.11	18.65	9.5
RAW	23/07/2015	0.2	1.32	13.33	2.74	13.6
RAW	24/07/2015	1.4	-0.50	2.20	6.20	14.0
RAW	29/07/2015	1.8	3.31	8.86	-17.59	19.4
RAW	1/08/2015	25.8	-10.04	-64.92	15.40	13.9
RAW	2/08/2015	2.8	-10.72	-70.53	15.27	13.0
RAW	18/08/2015	4.4	-3.36	-24.37	2.51	18.5
RAW	19/08/2015	2.4	-2.70	-8.14	13.44	12.9
RAW	23/08/2015	2.0	-3.86	-21.26	9.61	9.8
RAW	25/08/2015	0.2	-3.07	-15.56	8.97	11.7
RAW	14/09/2015	0.8	-2.89	-9.46	13.66	13.9
RAW	19/10/2015	0.4	10.61	67.00	-17.90	28.0
RAW	29/10/2015	5.8	-0.98	2.97	10.84	18.8
RAW	1/11/2015	1.0	-1.53	-18.81	-6.57	22.4
RAW	2/11/2015	1.6	-0.54	0.22	4.55	19.4
RAW	3/11/2015	4.6	-4.15	-14.74	18.50	18.4
RAW	4/11/2015	2.0	-4.62	-28.25	8.71	17.0
RAW	7/11/2015	4.4	3.46	21.83	-5.83	28.1
RAW	8/11/2015	1.0	3.69	22.00	-7.50	23.9
RAW	9/11/2015	9.0	0.97	14.67	6.91	25.2
RAW	19/11/2015	6.0	1.55	19.07	6.67	19.6
RAW	19/01/2016	2.2	-5.95	-35.85	11.76	27.0

RAW	20/01/2016	8.0	-4.25	-16.23	17.77	25.8
RAW	21/01/2016	3.8	-2.20	-0.17	17.43	29.0
RAW	26/01/2016	1.4	-1.21	-1.17	8.54	22.4
RAW	27/01/2016	1.0	-0.66	4.35	9.66	20.7
RAW	1/02/2016	10.2	-3.22	-13.80	11.97	29.3
RAW	2/02/2016	7.0	-6.20	-35.30	14.31	18.5
RAW	21/02/2016	2.4	-0.39	-3.83	-0.74	22.4
RAW	24/02/2016	16.2	-1.40	3.65	14.89	22.2
RAW	4/03/2016	1.4	4.60	20.01	-16.76	22.4
RAW	5/03/2016	9.8	-0.26	-0.52	1.56	19.0
RAW	6/03/2016	17.4	-2.40	-3.80	15.40	20.4
RAW	7/03/2016	0.4	-0.51	8.01	12.09	21.9
RAW	8/03/2016	0.6	-1.70	-2.33	11.29	21.0
RAW	23/03/2016	7.6	-1.93	-2.54	12.92	22.0
RAW	24/03/2016	1.4	0.84	10.04	3.28	20.8
RAW	28/03/2016	13.2	-5.89	-29.10	17.99	18.2
RAW	5/04/2016	1.4	-2.39	-10.26	8.85	26.9
RAW	6/04/2016	1.6	-1.70	-2.86	10.77	18.1
RAW	26/04/2016	0.6	6.74	27.40	-26.50	27.2
RAW	7/05/2016	6.4	-2.12	-3.45	13.51	17.5
RAW	8/05/2016	0.4	-1.06	-13.67	-5.20	18.1
RAW	9/05/2016	4.4	-4.30	-19.47	14.96	16.0
RAW	22/05/2016	0.2	-0.91	-19.87	-12.59	19.5
RAW	25/05/2016	7.2	-1.27	-5.10	5.09	19.3
RAW	29/05/2016	1.0	-0.03	4.28	4.48	14.2
RAW	15/06/2016	2.8	-0.62	2.04	7.02	12.1
RAW	16/06/2016	5.4	-2.69	-10.07	11.48	13.3
RAW	18/06/2016	0.8	-2.76	-3.20	18.86	12.3
RAW	21/06/2016	2.0	-2.08	-3.39	13.24	15.3
RAW	3/07/2016	1.4	0.51	3.85	-0.20	10.1
RAW	4/07/2016	1.0	-0.68	1.86	7.26	7.8
RAW	7/07/2016	2.2	-2.79	-9.73	12.58	10.4
RAW	9/07/2016	3.4	-2.25	-1.21	16.81	11.9
RAW	10/07/2016	3.8	-4.26	-20.05	14.04	13.5
RAW	18/07/2016	9.6	-5.35	-32.00	10.78	13.5
RAW	19/07/2016	4.6	-2.90	-6.13	17.10	14.1
RAW	20/07/2016	0.4	-2.41	-0.58	18.67	12.2
SED	13/07/2014	1.0	-1.63	-1.56	11.44	9.8
SED	15/07/2014	1.6	-4.26	-23.01	11.08	14.0
SED	21/07/2014	0.8	-2.66	-15.75	5.52	12.4
SED	23/07/2014	15.0	-4.96	-15.97	23.74	16.6
SED	18/09/2014	3.0	3.43	18.84	-8.57	17.5
SED	20/10/2014	6.0	1.17	9.91	0.57	20.0
SED	13/11/2014	6.4	-0.13	7.65	8.65	21.0
SED	14/11/2014	12.0	-2.54	-0.91	19.39	16.8
SED	15/11/2014	1.2	-4.82	-23.72	14.84	15.8

SED	17/11/2014	3.8	6.43	50.36	-1.08	19.0
SED	29/11/2014	3.2	-3.33	-11.25	15.36	22.9
SED	2/12/2014	2.4	4.06	24.75	-7.73	27.6
SED	21/12/2014	13.8	1.16	6.47	-2.83	27.2
SED	3/01/2015	6.0	1.50	7.83	-4.16	21.5
SED	26/02/2015	1.4	-7.07	-41.98	14.55	28.5
SED	27/02/2015	22.6	-7.00	-42.59	13.44	29.4
SED	28/02/2015	4.2	-6.07	-34.35	14.18	26.6
SED	2/03/2015	47.0	-9.83	-62.90	15.76	19.9
SED	4/03/2015	0.8	-3.09	-13.47	11.28	19.6
SED	5/03/2015	4.0	-3.01	-12.80	11.30	22.1
SED	6/03/2015	2.4	-1.42	-1.75	9.64	21.7
SED	21/03/2015	10.0	0.53	6.61	2.38	19.4
SED	22/03/2015	1.8	2.18	17.83	0.40	27.2
SED	28/03/2015	7.4	-0.37	16.84	19.79	20.3
SED	1/04/2015	4.0	-4.31	-21.54	12.97	21.6
SED	11/04/2015	0.8	4.47	0.21	-35.55	24.1
SED	12/04/2015	4.4	-1.29	-4.29	6.03	23.8
SED	16/04/2015	17.0	-4.55	-25.36	11.00	19.7
SED	17/04/2015	1.2	-1.07	3.45	12.02	16.6
SED	1/05/2015	3.0	-1.94	-35.48	-19.98	19.4
SED	28/05/2015	3.0	-1.64	-2.62	10.49	11.6
SED	21/06/2015	4.0	-1.84	-10.40	4.34	18.3
SED	22/06/2015	5.2	-4.04	-20.63	11.70	15.4

Appendix 3 – All fluid inclusion data obtained, including all subsample replicates. Successful analyses in black and unsuccessful analyses in red. Unsuccessful analyses were due to unreadable peaks in the IsodatAcquisition programme – most often due to insufficient water contents of < 0.2 µL/g, however also occasionally due to too high water contents of approximately > 1.1 µL/g.

Sample	Wgt (g)	δ ² H (VSMOW)	δ ¹⁸ O (VSMOW)	Wtr Amt (µL/g)
132-2_a	1.63	-122.74	-11.70	0.02
1411-11_a	0.33	-36.77	-4.66	0.74
1411-11_b	1.87	-42.17	61.87	1.57
1411-11_c	0.82	-41.41	6.04	1.09
1411-11_d	0.47	-35.62	-6.40	1.00
1411-11_e	0.43	-40.04	-6.03	0.81
1411-6_a	1.59	-127.85	-2.95	0.02
1536-11_b	0.74	-131.57	12.83	0.04
1536-4_b	1.00	-59.57	2.28	0.19
1536-8_a	1.07	-48.45	-2.80	0.46
1536-8_b	0.79	-65.04	-2.83	0.25
2200-4_a	1.13	-39.57	-2.64	0.53
2200-4_b	0.98	-44.06	-1.83	0.41
22M9 1_a	1.39	-42.47	-6.55	0.69
22M9 1_b	1.04	-41.64	-6.44	0.57
22M9 1_c	1.01	-49.33	-4.74	0.64
22M9 2_a	1.49	-67.63	-6.63	0.10
22M9 3_a	1.10	-115.94	-5.93	0.03
360-1_a	1.91	-108.21	-8.54	0.07
370-3_a	1.12	-49.84	-1.64	0.38
370-3_b	1.38	-75.47	-4.62	0.17
370-3_c	0.82	-57.52	-2.10	0.36
370-7.1_b	1.44	35.82	11.94	0.06
370-7.2_b	1.29	-99.99	-7.85	0.08
483-6.1_a	1.75	-74.06	-3.47	0.14
483-6.2_a	1.30	-69.79	-9.83	0.14
483-6.2_b	1.32	-51.11	-1.13	0.24
BTF 21.1	1.90	-53.58	-0.37	0.14
BTF 3.2	1.60	-82.43	2.37	0.03
BTF 37.1	1.90	-68.56	-2.38	0.11

FIA 1_a	0.55	-106.71	-5.27	0.07
FIA 2_a	0.56	-62.48	-3.12	0.30
FIA 2_b	0.58	-57.83	-2.87	0.29
FIA 3_a	0.53	-74.74	1.77	0.15
FIA 4_a	0.53	-94.77	-1.47	0.07
FIA 5_a	0.65	-96.29	0.27	0.08
FIB 1_a	0.51	-144.56	10.94	0.04
FIB 2_a	0.46	-146.69	-6.05	0.03
FIB 3_a	0.83	-97.35	-1.51	0.05
FIB 4_a	0.45	-145.15	-8.42	0.03
FIB 5_a	0.46	-122.16	0.01	0.03
FIB 6_a	0.67	-124.61	-1.01	0.04
FIB 7_a	0.85	-131.27	-1.56	0.04
FIB 8_a	1.00	-112.71	-3.92	0.07
FIB 9_a	0.86	-122.61	-0.49	0.03
FIC 1_a	0.73	-111.31	0.33	0.06
FIC 2_a	0.87	-140.54	-6.73	0.07
FIC 3_a	1.06	-77.12	-1.50	0.14
FIC 4_a	1.15	-74.91	-4.64	0.18
FIC 4_b	1.17	-63.59	-2.74	0.25
FIC 5_a	0.59	-75.41	-2.08	0.18
FIC 5_b	0.87	-88.45	-5.84	0.19
FID 1_a	0.82	-55.35	119.03	0.00
FID 1_b	0.23	-66.60	-2.13	0.22
FID 1_c	0.34	-67.40	-5.12	0.37
FID 2_a	0.93	-85.48	85.48	0.15
FID 3_a	0.43	-80.56	0.25	0.13
FID 4_a	0.55	-66.68	-0.09	0.19
FID 4_b	0.69	-79.01	-6.46	0.25
FID 5_a	0.79	-56.37	-4.64	0.00
FID 5_b	0.38	-67.94	-5.26	0.32
FID 5_c	0.39	-51.28	-0.31	0.53
FID 6_a	1.35	-46.88	73.57	0.00
FID 6_b	0.52	-61.72	-3.60	0.40
FID 6_c	0.64	-55.26	-3.16	0.57
FID 7_a	0.74	-55.37	-3.91	0.48

FID 7_b	0.27	-61.28	-5.86	0.43
FID 7_c	0.27	-53.57	-4.33	0.51
FID 7_d	0.31	-56.91	-1.95	0.44
FIE 1_a	0.93	-73.45	0.11	0.11
FIE 2_a	1.05	-69.02	-2.90	0.22
FIE 2_b	1.42	-60.54	-4.14	0.35
FIE 3_a	1.05	-72.63	-0.84	0.13
FIE 4_a	0.93	-75.85	-0.14	0.12
FIE 5_a	0.81	-69.89	-6.15	0.27
FIE 5_b	1.01	-55.30	-4.11	0.31
FIE 6_a	0.96	-46.10	-2.65	0.51
FIE 6_c	0.51	-94.31	-8.96	0.10
FIE 7_a	1.20	-40.93	2.13	0.00
FIE 7_b	0.58	-72.36	-4.03	0.21
FIE 7_c	0.59	-56.11	-1.97	0.30
FIE 8_a	0.62	-57.28	-1.35	0.19
FIE 8_b	0.26	-78.72	-6.34	0.18
FIE 8_b	0.97	-57.92	-2.01	0.31
FIF 1_a	0.20	-146.93	-21.19	0.02
FIF 10_a	0.44	-64.96	-1.92	0.27
FIF 10_b	0.27	-75.27	-3.29	0.20
FIF 11_a	0.20	-73.66	-7.39	0.26
FIF 11_b	0.21	-76.28	-3.74	0.16
FIF 12_a	0.63	-91.82	-8.25	0.01
FIF 13_a	0.39	-57.47	-6.63	0.51
FIF 13_b	0.33	-65.28	-4.75	0.31
FIF 14_a	0.38	-71.41	-1.42	0.20
FIF 14_b	0.37	-83.13	-2.76	0.13
FIF 15_a	0.60	-85.85	-6.30	0.14
FIF 2_a	0.28	-92.46	-7.53	0.09
FIF 3_a	0.29	-85.34	-4.89	0.14
FIF 4_a	0.41	-67.41	-5.82	0.16
FIF 5_a	0.20	-130.08	16.25	0.01
FIF 6_a	0.20	-96.93	-3.79	0.09
FIF 7_a	0.56	-81.46	-0.76	0.11
FIF 8_a	0.28	-59.74	-1.21	0.23
FIF 9_a	0.47	-61.70	-4.90	0.26
FIF 9_b	0.38	-48.90	-3.20	0.33
FIM 1_a	1.40	-87.31	-3.15	0.10
FIM 10_a	1.53	-53.35	-0.25	0.26
FIM 10_b	1.57	-66.20	-5.57	0.31
FIM 11_a	1.23	-76.98	-3.02	0.13
FIM 12_a	1.00	-53.59	-4.06	0.00
FIM 12_c	0.28	-66.67	-7.70	0.18
FIM 13_a	0.51	-57.21	-6.57	0.34
FIM 13_b	0.63	-51.62	-6.80	0.44
FIM 14_a	0.64	-57.60	-7.27	0.32
FIM 14_b	0.51	-74.55	-6.49	0.18
FIM 15_a	0.80	-82.88	-7.70	0.08
FIM 16_a	0.97	-47.32	-4.62	0.00
FIM 16_c	0.37	-67.79	-4.53	0.17
FIM 17_a	0.92	-61.13	-5.89	0.31
FIM 17_b	0.74	-59.49	-5.48	0.41
FIM 18_a	1.22	-51.21	-6.43	0.45
FIM 18_b	1.15	-50.13	-6.20	0.51
FIM 18_c	0.51	-78.52	-5.20	0.21
FIM 19_a	1.72	-41.83	71.77	0.00
FIM 19_b	0.79	-66.94	-3.34	0.24
FIM 19_c	0.74	-49.70	-6.63	0.00
FIM 19_d	0.33	-59.41	-3.54	0.24
FIM 2_a	0.91	-43.73	-0.92	0.00
FIM 2_b	0.41	-61.33	-3.80	0.33
FIM 2_c	0.42	-69.66	-7.10	0.20
FIM 20_a	1.75	-57.24	-4.52	0.44
FIM 20_b	1.35	-58.07	-6.37	0.34
FIM 21_a	0.99	-51.39	-4.83	0.42
FIM 21_b	0.92	-67.28	-4.50	0.27
FIM 22_a	1.01	-77.45	-3.80	0.13
FIM 23_a	1.32	-82.36	-4.02	0.18
FIM 24_a	0.73	-157.57	-0.83	0.02
FIM 25_a	0.98	-115.32	5.19	0.06
FIM 3_a	1.08	-46.11	-3.36	0.41
FIM 3_b	0.68	-90.52	-6.67	0.15
FIM 4_a	1.25	-44.22	32.36	0.00
FIM 4_b	0.43	-75.61	-4.52	0.23
FIM 4_c	0.48	-44.24	5.30	0.00
FIM 4_d	0.30	-72.90	-7.96	0.27
FIM 5_a	1.30	-46.81	-1.42	0.36
FIM 5_b	1.07	-44.77	95.00	0.00
FIM 6_a	0.78	-47.68	-2.32	0.50
FIM 6_b	0.73	-45.71	15.39	0.00
FIM 7_a	1.59	-45.53	-1.41	0.46
FIM 7_b	1.71	-35.90	121.11	0.00
FIM 8_a	1.73	-91.32	-1.42	0.17
FIM 9_a	1.04	-71.62	0.35	0.14
M2F 10.1	1.00	-39.60	-3.67	0.25
M2F 10.2	1.29	-71.41	-1.33	0.09
M2F 10.2	1.29	-71.41	-1.33	0.09
M2F 10.3	1.33	-77.08	4.97	0.09
M2F 10.3	1.33	-77.08	4.97	0.09

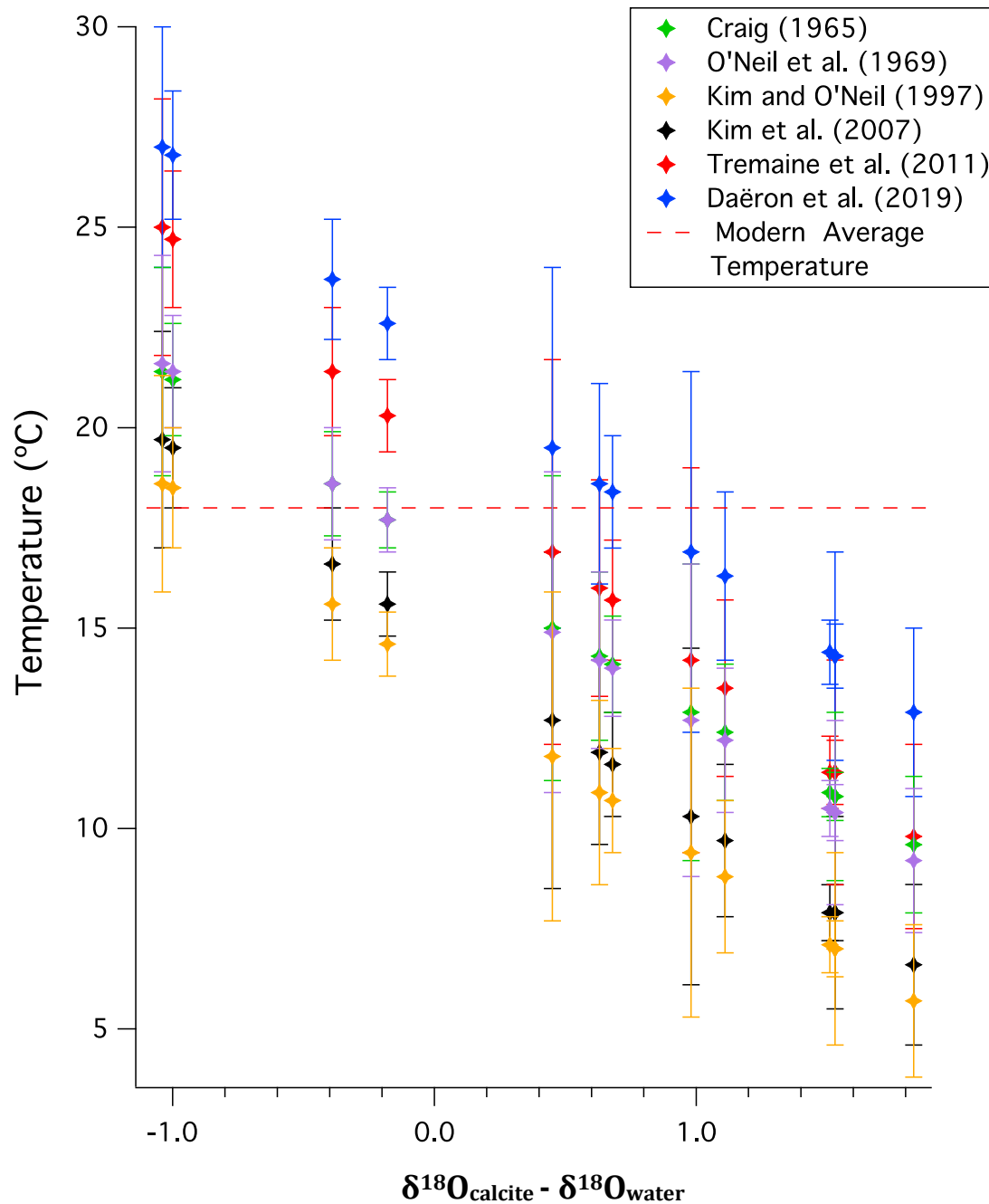
M2F 11.1	0.86	-97.86	-8.02	0.04
M2F 13.1	0.96	-77.01	-4.18	0.07
M2F 13.1	0.96	-77.01	-4.18	0.07
M2F 17.1	1.60	-86.59	-1.01	0.05
M2F 18.1	1.69	-46.18	-4.88	0.50
M2F 18.1	1.69	-46.18	-4.88	0.50
M2F 18.2	1.60	-42.70	-3.82	0.37
M2F 18.2	1.60	-42.70	-3.82	0.37
M2F 19.1	1.46	-37.36	-4.10	0.53
M2F 19.1	1.46	-37.36	-4.10	0.53
M2F 19.2	1.53	-44.74	-4.52	0.49
M2F 19.2	1.53	-44.74	-4.52	0.49
M2F 19.3	1.37	-37.82	-1.06	0.42
M2F 20.1	1.65	-54.27	-2.05	0.13
M2F 20.1	1.65	-54.27	-2.05	0.13
M2F 20.2	2.01	-45.55	-0.68	0.27
M2F 2R.1	1.30	-40.45	-6.57	1.05
M2F 2R.2	0.50	-39.32	-5.96	0.51
M2F 2R.3	0.44	-50.74	-8.54	0.35
M2F 3.1	1.80	-36.09	-7.11	1.13
M2F 3.2	0.81	-51.18	-7.06	0.38
M2F 3.3	0.96	-39.22	-6.35	0.55
M2F 31.1	1.16	-76.85	-7.07	0.07
M2F 33.1	1.56	-83.36	3.73	0.05
M2F 3R.1	1.30	-37.34	-6.59	0.50
M2F 3R.2	1.60	-36.46	-5.95	0.88
M2F 5.2	1.00	-41.66	-5.33	0.33
M2F 5s_a	1.20	-48.81	-7.20	0.39
M2F 5s_a	1.20	-48.81	-7.20	0.39
M2F 5s_b	1.10	-51.06	-1.94	0.21
M2F 5s_b	1.10	-51.06	-1.94	0.21
M2F 6.1	1.00	-39.38	-5.99	0.42
M2F 6.2	1.30	-40.20	-4.71	0.49
M2F 6.2	1.30	-40.20	-4.71	0.49
M2F 7.1	1.10	-43.81	-6.00	0.48

M2F 7.2	1.60	-49.46	-5.29	0.38
M2F 7.2	1.60	-49.46	-5.29	0.38
M2F 8.1	0.90	-44.35	-3.00	0.23
M2F 8.2	1.90	-52.07	-4.54	0.20
M2F 8.2	1.90	-52.07	-4.54	0.20
M2F 9.1	0.90	-78.29	-4.44	0.05
M2F 9.2	1.70	-59.10	-4.73	0.13
M2F 9.2	1.70	-59.10	-4.73	0.13
N180-5_a	1.57	-46.67	-1.38	0.33
N180-5_b	1.75	-44.54	-3.67	0.50
N180-5_c	0.67	-96.21	-11.79	0.07
W6B 1_a	1.00	5.21	-6.55	>1.73
W6B 1_b	0.17	-45.31	-5.80	0.47
W6B 1_c	0.14	-49.18	-5.19	0.28
W6B 2_a	0.88	-35.20	-5.96	0.72
W6B 2_b	0.59	-27.62	-4.99	1.10
W6B 2_c	0.49	-38.38	-7.14	0.89
W6B 2_c	0.49	-38.28	-7.19	0.89
W6B 3_a	0.63	-91.09	-4.54	0.06
W7G 1_a	0.59	-112.15	-4.51	0.03
W7G 2_a	2.00	-70.81	-2.25	0.12
W7G 3_a	0.81	-128.17	11.23	0.03
W7G 3_a	0.81	-128.17	11.24	0.03
WS 1_a	1.42	-51.85	-5.00	0.21
WS 1_b	2.60	-48.97	-5.22	0.28
WS 1_b	2.60	-48.64	-5.21	0.28
WS 1_c	0.50	-87.47	-7.55	0.10
WS 1_c	0.50	-87.47	-7.57	0.10
WS 2_a	0.96	-71.79	-3.78	0.07
WS 2_a	0.96	-71.14	-3.77	0.07

Appendix 4 – The temperature estimates produced by the fluid-inclusion and calcite data using different palaeotemperature equations.

Sample	Craig (1965)		O'Neil et al. (1969)		Kim and O'Neil (1997)		Kim et al. (2007)		Tremaine et al. (2011)		Daëron et al. (2019)	
	T (°C)	+/- T (°C)	T (°C)	+/- T (°C)	T (°C)	+/- T (°C)	T (°C)	+/- T (°C)	T (°C)	+/- T (°C)	T (°C)	+/- T (°C)
FIM 13	10.9	0.6	10.5	0.7	7.1	0.7	7.9	0.7	11.4	0.9	14.4	0.8
FIM 17	14.1	1.2	14.0	1.2	10.7	1.3	11.6	1.3	15.7	1.5	18.4	1.4
FIM 18	10.8	0.6	10.4	0.7	7.0	0.7	7.9	0.7	11.4	0.8	14.3	0.8
M2 2R	12.4	1.7	12.2	1.8	8.8	1.9	9.7	1.9	13.5	2.2	16.3	2.1
M2 3	10.8	2.1	10.4	2.3	7.0	2.4	7.9	2.4	11.4	2.8	14.3	2.6
M2 3R	9.6	1.7	9.2	1.8	5.7	1.9	6.6	2.0	9.8	2.3	12.9	2.1
M2 6	15.0	3.8	14.9	4.0	11.8	4.1	12.7	4.2	16.9	4.8	19.5	4.5
M2 7	14.3	2.1	14.2	2.2	10.9	2.3	11.9	2.3	16.0	2.7	18.6	2.5
1411-11	12.9	3.7	12.7	3.9	9.4	4.1	10.3	4.2	14.2	4.8	16.9	4.5
2200-4	21.4	2.6	21.6	2.7	18.6	2.7	19.7	2.7	25.0	3.2	27.0	3.0
FIA 2	17.7	0.7	17.7	0.8	14.6	0.8	15.6	0.8	20.3	0.9	22.6	0.9
FID 6	21.2	1.4	21.4	1.4	18.5	1.5	19.5	1.5	24.7	1.7	26.8	1.6
FID 7	18.6	1.3	18.6	1.4	15.6	1.4	16.6	1.4	21.4	1.6	23.7	1.5

Appendix 5 – Comparisons of the temperature estimates produced by the fluid-inclusion and calcite data using different palaeotemperature equations.



Appendix 6 – All stable isotope data obtained from the central growth axes (1-1944) and Hendy Test profiles (H1.1 – H19.10) of speleothem BT.

Sample	$\delta^{13}\text{C}$ (VPDB)	$\delta^{18}\text{O}$ (VPDB)						
1	-8.80	-4.15	37	-8.60	-4.30	74	-9.87	-4.03
2	-9.03	-4.15	38	-9.11	-4.21	75	-9.89	-3.89
3	-9.29	-4.28	39	-9.62	-4.36	76	-9.70	-4.01
4	-9.32	-4.21	40	-9.62	-4.81	77	-9.94	-3.92
5	-8.98	-4.19	41	-9.89	-4.52	78	-10.48	-4.08
6	-9.39	-4.35	42	-9.87	-4.24	79	-10.30	-4.10
7	-9.11	-4.12	43	-9.68	-4.48	80	-10.34	-4.13
8	-9.09	-4.06	44	-9.55	-4.74	81	-10.08	-4.12
9	-9.55	-4.19	45	-9.86	-4.41	82	-10.12	-4.16
10	-9.77	-4.12	46	-9.73	-4.51	83	-9.87	-4.10
11	-9.76	-4.16	47	-9.59	-3.84	84	-9.44	-4.11
12	-9.85	-4.28	48	-9.63	-3.80	85	-9.01	-4.39
13	-9.77	-4.20	49	-9.28	-4.19	86	-8.53	-4.02
14	-9.54	-4.38	50	-9.33	-4.07	87	-9.14	-4.35
15	-9.59	-4.34	51	-9.24	-4.15	88	-10.72	-4.55
16	-9.61	-4.26	52	-9.17	-4.09	89	-10.71	-4.42
17	-9.69	-4.24	53	-9.01	-4.28	90	-10.71	-4.47
18	-9.60	-4.27	54	-8.99	-4.18	91	-10.69	-4.56
19	-9.73	-4.28	55	-9.52	-4.17	92	-10.67	-4.49
20	-9.55	-4.33	56	-9.51	-4.20	93	-10.64	-4.49
21	-9.36	-4.30	57	-9.31	-4.36	94	-10.53	-4.28
22	-8.72	-4.34	58	-9.51	-4.34	95	-10.68	-4.23
23	-9.18	-4.53	59	-9.70	-4.35	96	-10.71	-4.02
24	-8.63	-4.05	60	-9.31	-4.24	97	-10.67	-4.22
25	-8.35	-4.00	61	-9.50	-4.43	98	-10.63	-4.26
26	-8.52	-3.91	62	-9.58	-4.21	99	-10.72	-4.14
27	-8.71	-4.02	63	-9.72	-4.18	100	-10.73	-4.35
28	-8.91	-4.13	64	-10.21	-4.27	101	-10.90	-4.39
29	-9.13	-4.11	65	-9.75	-4.18	102	-10.78	-4.31
30	-9.09	-4.16	66	-9.81	-4.28	103	-10.82	-4.54
31	-9.37	-4.23	67	-9.51	-4.21	104	-10.85	-4.29
32	-9.35	-4.20	68	-9.13	-4.14	105	-10.66	-4.35
33	-9.29	-4.21	69	-9.71	-4.21	106	-10.54	-4.22
34	-9.18	-4.16	70	-10.04	-4.05	107	-10.73	-4.40
35	-8.86	-3.64	71	-10.18	-4.26	108	-10.60	-4.56
36	-8.83	-4.57	72	-10.09	-4.24	109	-10.81	-4.39
			73	-10.22	-4.10	110	-10.90	-4.55

111	-10.55	-4.60
112	-10.54	-4.57
113	-10.80	-4.46
114	-10.93	-4.55
115	-10.65	-4.74
116	-10.49	-4.71
117	-10.88	-4.66
118	-10.83	-4.79
119	-10.90	-4.72
120	-10.81	-4.86
121	-10.77	-4.61
122	-10.67	-4.69
123	-10.60	-4.71
124	-10.63	-4.71
125	-10.73	-4.53
126	-10.65	-4.56
127	-10.63	-4.37
128	-10.52	-4.48
129	-10.59	-4.52
130	-10.64	-4.49
131	-10.74	-4.53
132	-10.71	-4.59
133	-10.78	-4.46
134	-10.76	-4.55
135	-10.70	-4.51
136	-10.87	-4.40
137	-10.82	-4.34
138	-10.55	-4.26
139	-10.54	-4.22
140	-10.61	-4.55
141	-10.75	-4.40
142	-10.74	-4.48
143	-10.67	-4.50
144	-10.67	-4.41
145	-10.55	-4.38
146	-10.67	-4.48
147	-10.55	-4.56
148	-10.69	-4.54
149	-10.48	-4.43
150	-10.48	-4.38
151	-10.70	-4.45

152	-10.58	-4.47
153	-10.47	-4.20
154	-10.47	-4.15
155	-10.53	-4.37
156	-10.34	-4.24
157	-10.33	-4.16
158	-10.52	-4.38
159	-10.50	-4.36
160	-10.49	-4.42
161	-10.60	-4.53
162	-10.54	-4.54
163	-10.54	-4.42
164	-10.67	-4.56
165	-10.54	-4.62
166	-10.48	-4.57
167	-10.36	-4.42
168	-10.66	-4.53
169	-10.66	-4.50
170	-10.69	-4.54
171	-10.60	-4.51
172	-10.75	-4.58
173	-10.87	-4.58
174	-10.57	-4.47
175	-10.72	-4.36
176	-10.45	-4.53
177	-10.62	-4.49
178	-10.87	-4.45
179	-10.78	-4.40
180	-10.67	-4.24
181	-10.77	-4.27
182	-10.64	-4.35
183	-10.57	-4.17
184	-10.60	-4.24
185	-10.64	-4.17
186	-10.59	-4.04
187	-10.50	-4.07
188	-10.66	-4.11
189	-10.53	-4.05
190	-10.62	-4.16
191	-10.61	-4.26
192	-10.65	-4.38

193	-10.59	-4.60
194	-10.78	-4.31
195	-10.28	-4.55
196	-10.67	-4.64
197	-11.06	-4.44
198	-10.92	-4.35
199	-10.80	-4.36
200	-10.90	-4.64
201	-10.83	-4.73
202	-10.71	-4.78
203	-10.93	-4.73
204	-10.76	-4.77
205	-10.84	-4.94
206	-10.85	-4.88
207	-10.91	-4.72
208	-10.98	-4.77
209	-10.84	-4.91
210	-10.81	-4.94
211	-10.87	-4.91
212	-10.71	-4.91
213	-10.89	-4.91
214	-10.79	-4.96
215	-10.98	-5.03
216	-11.09	-4.74
217	-11.06	-4.64
218	-10.75	-4.50
219	-10.58	-4.47
220	-10.25	-4.39
221	-10.37	-4.44
222	-10.72	-4.32
223	-9.09	-3.70
224	-10.40	-4.15
225	-10.53	-4.49
226	-10.44	-4.42
227	-10.59	-4.28
228	-10.63	-4.34
229	-10.47	-4.39
230	-10.58	-4.34
231	-10.39	-4.21
232	-10.79	-4.18
233	-10.43	-4.15

234	-10.45	-4.12
235	-10.44	-4.13
236	-10.51	-4.06
237	-10.41	-4.11
238	-10.46	-4.04
239	-10.75	-4.15
240	-10.59	-4.08
241	-10.58	-4.14
242	-10.59	-4.17
243	-10.75	-4.15
244	-10.69	-4.17
245	-10.70	-3.91
246	-10.76	-4.26
247	-10.74	-4.23
248	-10.78	-4.47
249	-10.84	-4.48
250	-10.88	-4.51
251	-10.73	-4.46
252	-10.67	-4.28
253	-10.78	-4.30
254	-10.85	-4.45
255	-10.76	-4.38
256	-10.78	-4.25
257	-10.69	-4.24
258	-10.48	-4.33
259	-10.50	-4.37
260	-10.70	-4.60
261	-10.80	-4.41
262	-10.69	-4.45
263	-10.74	-4.45
264	-10.82	-4.50
265	-10.99	-4.68
266	-11.04	-4.40
267	-11.18	-4.40
268	-11.12	-4.52
269	-10.74	-4.47
270	-10.57	-4.38
271	-10.68	-4.54
272	-10.51	-4.78
273	-10.73	-4.91
274	-10.92	-4.92

275	-10.54	-4.87
276	-10.16	-4.61
277	-10.66	-4.52
278	-10.82	-4.48
279	-10.45	-4.47
280	-10.38	-4.47
281	-10.61	-4.46
282	-10.88	-4.42
283	-10.53	-4.38
284	-10.47	-4.28
285	-10.46	-4.42
286	-10.66	-4.36
287	-10.78	-4.64
288	-10.43	-4.61
289	-10.13	-4.42
290	-10.23	-4.42
291	-10.39	-4.34
292	-10.28	-4.02
293	-10.49	-4.24
294	-10.61	-4.08
295	-10.36	-4.12
296	-10.52	-4.22
297	-10.49	-4.35
298	-10.37	-4.20
299	-10.62	-4.24
300	-10.49	-4.17
301	-10.56	-4.36
302	-10.59	-4.38
303	-10.79	-4.35
304	-10.52	-4.53
305	-10.32	-4.58
306	-9.62	-4.43
307	-9.16	-4.38
308	-9.78	-4.33
309	-10.37	-4.25
310	-10.56	-4.45
311	-10.67	-4.47
312	-10.40	-4.37
313	-10.71	-4.30
314	-10.88	-4.33
315	-11.02	-4.55

316	-10.37	-4.27
317	-10.62	-4.39
318	-10.78	-4.45
319	-10.51	-4.31
320	-10.42	-4.43
321	-10.40	-4.40
322	-10.61	-4.54
323	-10.33	-4.46
324	-10.61	-4.49
325	-10.49	-4.58
326	-10.54	-4.43
327	-10.56	-4.48
328	-10.81	-4.47
329	-10.85	-4.45
330	-10.91	-4.52
331	-10.82	-4.58
332	-10.64	-4.47
333	-10.89	-4.49
334	-10.85	-4.53
335	-10.83	-4.57
336	-10.61	-4.49
337	-10.55	-4.54
338	-10.61	-4.51
339	-10.60	-4.55
340	-10.31	-4.29
341	-10.19	-4.40
342	-10.80	-4.52
343	-10.33	-4.51
344	-10.28	-4.42
345	-10.68	-4.55
346	-10.49	-4.67
347	-10.56	-4.56
348	-10.66	-4.63
349	-10.63	-4.62
350	-10.77	-4.73
351	-11.04	-4.68
352	-10.93	-4.56
353	-10.73	-4.55
354	-10.53	-4.64
355	-10.59	-4.58
356	-10.62	-4.49

357	-10.17	-4.40
358	-10.74	-4.42
359	-10.50	-4.29
360	-9.95	-4.05
361	-10.42	-4.00
362	-11.21	-4.30
363	-11.16	-4.32
364	-11.04	-4.35
365	-10.90	-4.22
366	-10.74	-4.55
367	-10.92	-4.46
368	-10.73	-4.61
369	-10.69	-4.51
370	-11.05	-4.32
371	-10.98	-4.39
372	-11.00	-4.15
373	-10.86	-4.27
374	-10.93	-4.24
375	-10.84	-4.17
376	-10.53	-4.20
377	-10.19	-4.18
378	-10.11	-4.24
379	-10.38	-4.22
380	-10.61	-4.19
381	-10.64	-4.16
382	-11.05	-4.33
383	-10.89	-4.27
384	-10.93	-4.22
385	-10.91	-4.31
386	-10.92	-4.18
387	-11.07	-4.39
388	-10.95	-4.36
389	-10.73	-4.20
390	-10.79	-4.33
391	-10.71	-4.28
392	-10.75	-4.21
393	-10.77	-4.35
394	-10.36	-4.22
395	-10.27	-4.27
396	-10.82	-4.48
397	-10.83	-4.64

398	-10.91	-4.55
399	-10.83	-4.38
400	-10.83	-4.38
401	-10.78	-4.31
402	-10.77	-4.39
403	-10.61	-4.24
404	-10.72	-4.46
405	-10.81	-4.44
406	-10.89	-4.59
407	-10.73	-4.62
408	-10.67	-4.51
409	-10.53	-4.43
410	-10.64	-4.42
411	-10.67	-4.36
412	-10.78	-4.38
413	-10.65	-4.45
414	-10.76	-4.38
415	-10.80	-4.34
416	-10.74	-4.37
417	-10.88	-4.53
418	-10.51	-4.45
419	-10.71	-4.60
420	-10.56	-4.61
421	-11.00	-4.58
422	-10.67	-4.33
423	-10.47	-4.35
424	-10.84	-4.32
425	-10.80	-4.37
426	-10.91	-4.71
427	-11.07	-4.74
428	-11.09	-4.70
429	-10.61	-4.60
430	-10.36	-4.49
431	-10.40	-4.49
432	-10.40	-4.29
433	-10.37	-4.44
434	-10.45	-4.36
435	-10.39	-4.23
436	-10.56	-4.33
437	-10.67	-4.37
438	-10.56	-4.54

439	-10.29	-4.35
440	-10.89	-4.35
441	-10.95	-4.45
442	-10.16	-4.44
443	-9.63	-4.39
444	-9.62	-4.17
445	-9.97	-4.19
446	-10.44	-4.23
447	-10.03	-4.28
448	-9.51	-4.34
449	-9.22	-4.38
450	-9.69	-4.26
451	-10.40	-4.25
452	-10.52	-4.43
453	-10.42	-4.54
454	-9.26	-4.29
455	-8.70	-4.05
456	-8.95	-3.96
457	-8.90	-3.88
458	-8.28	-4.04
459	-8.06	-3.84
460	-8.43	-3.91
461	-9.55	-4.20
462	-10.01	-4.17
463	-10.11	-4.31
464	-10.28	-4.38
465	-9.68	-4.01
466	-9.98	-4.01
467	-10.07	-4.20
468	-9.85	-4.46
469	-9.84	-4.32
470	-9.98	-4.33
471	-9.90	-4.20
472	-9.81	-4.24
473	-9.50	-4.18
474	-9.83	-4.04
475	-9.64	-4.15
476	-9.82	-4.05
477	-9.76	-4.06
478	-10.12	-4.23
479	-9.72	-3.98

480	-9.80	-4.15
481	-9.75	-4.06
482	-9.92	-4.35
483	-9.79	-4.44
484	-9.79	-4.14
485	-9.84	-4.20
486	-9.83	-4.11
487	-9.54	-4.10
488	-9.54	-4.02
489	-9.49	-3.89
490	-9.71	-3.88
491	-9.77	-4.12
492	-9.61	-4.11
493	-9.66	-4.27
494	-9.82	-4.28
495	-10.29	-4.22
496	-9.92	-4.10
497	-10.22	-4.12
498	-9.47	-4.20
499	-9.17	-4.10
500	-9.35	-4.22
501	-8.87	-4.00
502	-8.80	-3.79
503	-9.26	-3.90
504	-9.26	-4.20
505	-9.47	-4.47
506	-9.16	-4.51
507	-9.54	-4.80
508	-9.69	-4.42
509	-8.96	-4.09
510	-9.14	-4.37
511	-9.07	-4.30
512	-9.01	-4.17
513	-8.67	-4.22
514	-9.32	-4.19
515	-9.02	-4.25
516	-8.77	-4.21
517	-8.42	-4.08
518	-8.73	-4.18
519	-9.09	-4.25
520	-9.76	-4.34

521	-9.54	-4.54
522	-8.64	-4.35
523	-8.42	-4.48
524	-9.28	-4.48
525	-9.69	-4.35
526	-9.60	-4.17
527	-9.64	-4.17
528	-9.54	-4.26
529	-8.81	-4.32
530	-9.18	-4.17
531	-8.91	-4.10
532	-8.75	-4.26
533	-8.93	-4.19
534	-9.42	-4.31
535	-9.31	-4.39
536	-9.35	-4.28
537	-9.23	-4.24
538	-9.48	-4.44
539	-10.06	-4.24
540	-9.68	-4.44
541	-9.30	-4.34
542	-9.85	-4.28
543	-9.92	-4.45
544	-9.42	-4.47
545	-9.07	-4.47
546	-9.09	-4.51
547	-9.22	-4.65
548	-9.56	-4.72
549	-9.25	-4.91
550	-9.20	-4.81
551	-9.30	-4.24
552	-9.37	-4.33
553	-9.25	-4.34
554	-9.29	-4.36
555	-9.54	-4.23
556	-9.77	-4.16
557	-9.23	-4.00
558	-9.55	-4.13
559	-9.20	-4.39
560	-9.35	-4.13
561	-9.16	-4.24

562	-8.72	-3.94
563	-8.65	-3.92
564	-9.20	-3.96
565	-8.92	-3.89
566	-8.56	-3.95
567	-8.63	-3.90
568	-8.63	-3.88
569	-9.62	-4.04
570	-9.76	-4.13
571	-9.19	-3.96
572	-9.14	-4.10
573	-8.97	-3.88
574	-9.17	-3.90
575	-9.13	-3.97
576	-9.12	-3.84
577	-9.18	-3.92
578	-9.26	-4.08
579	-8.76	-4.00
580	-9.06	-4.28
581	-9.64	-4.33
582	-10.04	-4.59
583	-10.32	-4.70
584	-10.27	-4.56
585	-10.07	-4.51
586	-9.80	-4.23
587	-9.76	-4.35
588	-9.94	-4.54
589	-10.08	-4.21
590	-9.90	-4.29
591	-10.20	-4.32
592	-10.03	-4.21
593	-10.25	-4.22
594	-10.10	-4.30
595	-9.65	-4.06
596	-10.55	-4.22
597	-9.27	-3.83
598	-8.98	-4.02
599	-8.80	-4.06
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601	-9.08	-4.22
602	-9.06	-4.34

603	-10.09	-4.58
604	-10.34	-4.44
605	-10.24	-4.57
606	-9.17	-4.43
607	-9.74	-4.30
608	-9.94	-4.33
609	-9.55	-4.13
610	-9.90	-4.17
611	-8.89	-4.21
612	-9.56	-4.03
613	-9.88	-4.39
614	-9.90	-4.55
615	-8.99	-4.68
616	-8.58	-4.43
617	-8.50	-4.16
618	-9.25	-4.09
619	-10.11	-4.00
620	-9.04	-3.90
621	-8.06	-3.83
622	-8.11	-3.78
623	-8.54	-3.76
624	-8.54	-3.83
625	-8.96	-4.11
626	-9.05	-3.91
627	-9.26	-3.96
628	-9.51	-4.15
629	-9.29	-4.23
630	-9.29	-4.31
631	-9.30	-4.23
632	-9.70	-4.29
633	-10.00	-4.18
634	-9.66	-4.14
635	-9.44	-4.04
636	-8.45	-3.65
637	-7.90	-3.78
638	-8.51	-3.71
639	-8.48	-3.85
640	-8.56	-3.95
641	-8.51	-3.81
642	-8.74	-3.91
643	-8.71	-3.90

644	-9.10	-3.85
645	-9.70	-4.15
646	-9.35	-4.39
647	-9.14	-4.12
648	-9.22	-4.08
649	-9.09	-4.04
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651	-9.55	-4.32
652	-9.59	-4.40
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654	-9.33	-4.38
655	-9.36	-4.04
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657	-9.04	-4.05
658	-9.18	-4.16
659	-8.85	-4.16
660	-9.42	-4.40
661	-9.51	-4.56
662	-9.85	-4.71
663	-9.87	-4.39
664	-9.57	-4.32
665	-9.17	-4.36
666	-9.36	-4.21
667	-9.23	-4.14
668	-9.39	-4.29
669	-9.46	-4.47
670	-9.70	-4.83
671	-9.88	-4.78
672	-9.56	-4.60
673	-9.82	-4.55
674	-9.61	-4.37
675	-9.47	-4.63
676	-9.71	-4.50
677	-9.77	-4.34
678	-9.60	-4.45
679	-9.39	-4.26
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681	-9.48	-4.26
682	-9.69	-4.31
683	-9.43	-4.28
684	-9.47	-4.37

685	-9.53	-4.39
686	-10.10	-4.36
687	-9.70	-4.49
688	-9.77	-4.41
689	-10.14	-4.44
690	-9.58	-4.66
691	-8.75	-4.50
692	-9.13	-4.45
693	-9.17	-4.17
694	-8.62	-4.26
695	-9.65	-4.32
696	-9.84	-4.49
697	-9.51	-4.72
698	-9.33	-4.73
699	-9.05	-4.37
700	-9.03	-4.33
701	-9.63	-4.47
702	-9.31	-4.52
703	-9.43	-4.23
704	-9.11	-4.28
705	-8.90	-4.17
706	-8.87	-4.38
707	-8.85	-4.60
708	-8.97	-4.52
709	-9.00	-4.39
710	-8.85	-4.13
711	-9.44	-4.25
712	-9.56	-4.26
713	-9.87	-4.38
714	-9.36	-4.40
715	-9.45	-4.66
716	-9.66	-4.75
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718	-9.53	-4.66
719	-9.37	-4.39
720	-9.60	-4.39
721	-9.29	-4.30
722	-8.74	-4.25
723	-8.84	-3.91
724	-8.99	-3.80
725	-9.45	-4.13

726	-9.29	-4.12
727	-9.44	-4.30
728	-9.58	-4.33
729	-8.90	-4.30
730	-8.99	-4.31
731	-8.99	-4.07
732	-8.98	-3.80
733	-9.43	-4.03
734	-9.51	-4.33
735	-9.61	-4.06
736	-9.65	-4.21
737	-9.24	-4.32
738	-8.99	-4.20
739	-9.13	-4.17
740	-9.46	-4.46
741	-9.86	-4.48
742	-9.49	-4.37
743	-9.70	-4.25
744	-9.41	-4.40
745	-9.31	-4.47
746	-9.14	-4.30
747	-9.30	-4.53
748	-8.81	-4.44
749	-9.52	-4.30
750	-9.11	-4.20
751	-9.11	-4.28
752	-8.93	-4.07
753	-9.45	-4.37
754	-9.41	-4.37
755	-9.34	-4.30
756	-9.25	-4.39
757	-9.27	-4.39
758	-9.02	-4.14
759	-9.02	-4.19
760	-9.10	-4.07
761	-8.76	-4.16
762	-9.10	-4.34
763	-10.01	-4.51
764	-8.74	-4.52
765	-8.90	-4.29
766	-9.34	-4.39

767	-9.58	-4.33
768	-9.03	-4.20
769	-9.33	-4.54
770	-9.58	-4.33
771	-9.48	-4.27
772	-9.71	-4.56
773	-9.70	-4.39
774	-9.41	-4.47
775	-9.37	-4.58
776	-9.30	-4.25
777	-8.90	-4.23
778	-8.78	-4.03
779	-8.86	-4.28
780	-8.80	-4.35
781	-8.92	-4.18
782	-8.77	-4.15
783	-8.80	-3.68
784	-8.76	-3.94
785	-8.79	-4.15
786	-8.36	-4.25
787	-9.71	-4.18
788	-9.85	-4.27
789	-9.35	-4.34
790	-9.51	-4.28
791	-10.17	-4.43
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795	-9.82	-4.01
796	-9.73	-4.06
797	-9.34	-4.02
798	-9.19	-4.08
799	-9.23	-3.93
800	-9.21	-3.97
801	-9.55	-3.95
802	-10.16	-4.39
803	-9.99	-4.10
804	-9.62	-4.29
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807	-9.50	-4.15

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812	-9.38	-4.46
813	-9.50	-4.25
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816	-9.49	-4.47
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861	-8.91	-4.86
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1393	-9.14	-4.13
1394	-9.02	-4.42
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H3.2	-10.65	-3.99
H3.3	-10.63	-4.04
H3.4	-10.53	-3.92
H3.5	-10.59	-4.04
H3.6	-10.78	-3.66
H3.7	-10.57	-4.18
H3.8	-10.49	-4.12
H3.9	-10.51	-4.19
H3.10	-10.47	-4.04
H4.1	-11.13	-4.65
H4.2	-11.09	-4.55
H4.3	-10.82	-4.44
H4.4	-10.80	-4.52
H4.5	-10.58	-4.61
H4.6	-10.82	-4.42
H4.7	-11.00	-4.55
H4.8	-10.79	-4.44
H4.9	-10.76	-4.41
H4.10	-10.83	-4.44
H5.1	-10.28	-4.05
H5.2	-10.08	-3.88
H5.3	-10.02	-3.94
H5.4	-9.92	-3.98
H5.5	-9.87	-3.78
H5.6	-10.16	-3.87
H5.7	-10.32	-4.03
H5.8	-10.23	-3.89
H5.9	-10.32	-4.02
H5.10	-10.09	-3.79
H6.1	-9.13	-4.17
H6.2	-9.12	-3.89

H6.3	-8.99	-4.21
H6.4	-9.10	-4.28
H6.5	-9.21	-4.34
H6.6	-9.11	-4.24
H6.7	-9.33	-4.30
H6.8	-9.35	-4.24
H6.9	-9.43	-4.15
H6.10	-9.46	-4.08
H7.1	-9.67	-4.63
H7.2	-9.46	-4.47
H7.3	-9.56	-4.58
H7.4	-9.44	-4.62
H7.5	-9.52	-4.67
H7.6	-9.36	-4.43
H7.7	-9.38	-4.52
H7.8	-9.26	-4.34
H7.9	-9.26	-4.28
H7.10	-9.31	-4.37
H8.1	-9.90	-4.43
H8.2	-9.61	-4.36
H8.3	-9.32	-4.38
H8.4	-9.35	-4.30
H8.5	-9.44	-4.41
H8.6	-9.71	-4.30
H8.7	-9.83	-4.26
H8.8	-9.95	-4.46
H8.9	-9.98	-4.48
H8.10	-10.05	-4.56
H9.1	-10.31	-4.51
H9.2	-10.28	-4.87
H9.3	-10.40	-4.69
H9.4	-10.40	-4.76
H9.5	-10.41	-4.74
H9.6	-10.41	-4.67
H9.7	-10.38	-4.82
H9.8	-10.43	-4.61
H9.9	-10.41	-4.74
H9.10	-10.37	-4.80
H10.1	-10.74	-4.75
H10.2	-10.70	-4.79
H10.3	-10.75	-4.98

H10.4	-10.49	-4.66
H10.5	-10.42	-4.79
H10.6	-10.52	-4.51
H10.7	-10.83	-4.85
H10.8	-10.80	-5.04
H10.9	-10.77	-4.71
H10.10	-9.96	-4.73
H11.1	-10.89	-4.53
H11.2	-10.82	-4.68
H11.3	-10.61	-4.54
H11.4	-10.55	-4.73
H11.5	-10.49	-4.59
H11.6	-10.93	-4.74
H11.7	-10.98	-4.56
H11.8	-10.75	-4.63
H11.9	-10.77	-4.51
H11.10	-10.55	-4.50
H12.1	-10.31	-4.26
H12.2	-10.56	-4.77
H12.3	-11.04	-4.85
H12.4	-10.89	-4.54
H12.5	-10.76	-4.71
H12.6	-10.80	-4.59
H12.7	-10.89	-4.69
H12.8	-10.81	-4.83
H12.9	-11.07	-4.84
H12.10	-10.79	-4.64
H13.1	-9.22	-4.30
H13.2	-9.17	-4.43
H13.3	-9.31	-4.63
H13.4	-9.15	-4.46
H13.5	-9.12	-4.58
H13.6	-9.50	-4.60
H13.7	-9.36	-4.69
H13.8	-9.30	-4.76
H13.9	-9.28	-4.82
H13.10	-9.31	-4.81
H14.1	-8.35	-4.53
H14.2	-8.30	-4.25
H14.3	-8.31	-4.38
H14.4	-8.33	-4.48

H14.5	-8.48	-4.41
H14.6	-8.64	-4.15
H14.7	-8.68	-4.26
H14.8	-8.68	-4.17
H14.9	-8.57	-4.26
H14.10	-8.61	-4.48
H15.1	-8.20	-3.96
H15.2	-8.33	-3.85
H15.3	-8.33	-4.08
H15.4	-8.41	-4.01
H15.5	-8.47	-3.93
H15.6	-8.59	-3.94
H15.7	-8.46	-4.03
H15.8	-8.36	-3.96
H15.9	-8.30	-3.79
H15.10	-8.08	-3.77
H16.1	-9.38	-3.74
H16.2	-9.33	-3.84
H16.3	-9.58	-3.45

H16.4	-9.61	-4.10
H16.5	-9.62	-4.25
H16.6	-9.64	-4.22
H16.7	-9.58	-3.97
H16.8	-9.63	-4.17
H16.9	-9.50	-3.83
H16.10	-9.64	-4.29
H17.1	-9.42	-4.50
H17.2	-9.42	-4.46
H17.3	-9.47	-4.34
H17.4	-9.46	-4.35
H17.5	-9.45	-4.55
H17.6	-9.41	-4.43
H17.7	-9.38	-4.27
H17.8	-9.41	-4.44
H17.9	-9.36	-4.52
H17.10	-9.34	-4.33
H18.1	-8.89	-5.18
H18.2	-8.93	-5.20

H18.3	-8.95	-5.24
H18.4	-8.98	-5.24
H18.5	-9.12	-5.29
H18.6	-9.17	-5.20
H18.7	-9.15	-5.25
H18.8	-9.22	-5.29
H18.9	-9.25	-5.20
H18.10	-9.15	-5.00
H19.1	-8.97	-4.25
H19.2	-9.06	-4.45
H19.3	-9.04	-4.25
H19.4	-9.00	-4.26
H19.5	-9.00	-4.34
H19.6	-9.13	-4.25
H19.7	-9.05	-4.30
H19.8	-8.93	-4.22
H19.9	-8.75	-3.56
H19.10	-8.85	-4.38

Appendix 7 – All stable isotope data obtained from the central growth axes (1-454) and Hendy Test profiles (H1.1 – H5.10) of speleothem M2.

Sample	$\delta^{13}\text{C}$ (VPDB)	$\delta^{18}\text{O}$ (VPDB)						
1	-9.55	-5.00	41	-9.39	-4.62	83	-9.24	-4.69
2	-9.62	-5.08	42	-9.24	-4.67	84	-9.26	-4.72
3	-9.64	-2.86	43	-10.29	-4.79	85	-9.45	-4.64
4	-10.60	-5.28	44	-10.26	-4.97	86	-9.39	-4.69
5	-10.36	-5.28	45	-9.83	-5.15	87	-9.59	-4.70
6	-10.51	-5.50	46	-10.08	-5.07	88	-9.73	-4.64
7	-10.10	-5.32	47	-10.01	-5.09	89	-9.64	-4.70
8	-9.33	-5.32	48	-10.20	-5.20	90	-9.28	-4.83
9	-9.78	-5.25	49	-10.29	-5.21	91	-8.95	-4.82
10	-9.95	-5.30	50	-10.13	-5.08	92	-8.98	-4.83
11	-9.96	-5.24	51	-10.14	-5.18	93	-9.23	-4.94
12	-9.63	-5.14	52	-10.11	-4.99	94	-8.55	0.37
13	-9.04	-4.71	53	-9.60	-4.95	95	-9.17	-4.81
14	-8.65	-4.66	54	-9.93	-5.10	96	-9.28	-4.88
15	-8.78	-5.07	55	-9.70	-4.94	97	-9.20	-4.89
16	-9.05	-4.90	56	-9.61	-4.99	98	-8.98	-4.79
17	-9.17	-4.98	57	-9.03	-4.91	99	-9.27	-4.87
18	-9.27	-4.95	58	-8.82	-4.89	100	-9.07	-4.98
19	-9.71	-4.89	59	-8.61	-4.78	101	-9.12	-4.86
20	-9.93	-4.91	60	-8.70	-4.84	102	-9.11	-4.78
21	-10.62	-5.04	61	-8.69	-4.86	103	-8.83	-4.63
22	-11.45	-5.36	62	-8.79	-4.74	104	-9.04	-4.71
23	-11.45	-5.50	63	-9.01	-4.86	105	-9.30	-4.81
24	-11.48	-5.56	64	-9.11	-5.06	106	-9.22	-4.74
25	-11.43	-5.46	65	-9.19	-4.93	107	-9.34	-4.67
26	-11.08	-5.37	66	-8.89	-4.92	108	-9.40	-4.60
27	-9.49	-4.89	67	-8.91	-4.99	109	-9.89	-4.70
28	-10.29	-4.94	68	-9.03	-4.95	110	-9.96	-4.69
29	-11.06	-5.03	69	-9.08	-4.97	111	-9.34	-4.66
30	-11.10	-5.13	70	-8.87	-4.77	112	-9.03	-4.59
31	-10.98	-5.17	71	-8.91	-4.80	113	-8.90	-4.38
32	-10.60	-4.97	72	-9.14	-4.95	114	-9.60	-4.63
33	-10.53	-5.13	73	-9.24	-4.92	115	-9.49	-4.46
34	-10.54	-5.18	74	-9.52	-5.12	116	-9.79	-4.78
35	-10.45	-5.09	75	-9.30	-4.79	117	-10.35	-4.60
36	-10.34	-4.73	76	-9.13	-4.80	118	-10.61	-4.62
37	-10.19	-4.97	77	-9.24	-4.86	119	-10.75	-4.93
38	-9.67	-5.01	78	-9.04	-2.70	120	-10.86	-5.03
39	-9.65	-4.95	79	-7.82	0.03	121	-10.90	-4.83
40	-9.65	-4.89	80	-8.60	-2.76	122	-8.38	3.84
			81	-8.73	-4.60	123	-10.74	-4.84
			82	-9.16	-4.82	124	-11.02	-5.00

125	-11.04	-5.11
126	-10.97	-4.96
127	-10.76	-4.06
128	-10.78	-4.80
129	-10.53	-4.73
130	-10.63	-4.73
131	-11.00	-4.97
132	-6.80	6.97
133	-10.32	-4.64
134	-10.81	-4.87
135	-7.57	5.34
136	-10.65	-5.16
137	-10.66	-4.98
138	-10.51	-4.99
139	-10.27	-5.00
140	-10.19	-5.02
141	-10.11	-4.92
142	-10.07	-4.93
143	-10.67	-4.84
144	-10.86	-5.14
145	-10.94	-5.12
146	-10.92	-5.20
147	-10.69	-5.01
148	-10.75	-5.11
149	-10.91	-5.05
150	-10.70	-5.11
151	-10.75	-4.94
152	-10.83	-5.02
153	-10.86	-5.14
154	-10.97	-5.18
155	-11.00	-4.96
156	-10.86	-5.08
157	-10.93	-5.25
158	-10.84	-4.97
159	-10.70	-5.07
160	-10.93	-4.99
161	-11.08	-5.11
162	-11.02	-5.13
163	-11.09	-5.13
164	-11.18	-5.14
165	-10.40	-4.78
166	-10.70	-4.88
167	-11.18	-5.04
168	-10.97	-5.03
169	-10.97	-5.20
170	-10.99	-5.17

171	-10.89	-5.13
172	-10.91	-5.11
173	-10.88	-5.18
174	-11.00	-5.16
175	-11.16	-5.28
176	-11.17	-5.35
177	-11.18	-5.40
178	-11.38	-5.36
179	-11.36	-5.32
180	-11.26	-5.21
181	-11.23	-5.36
182	-11.43	-5.39
183	-11.33	-5.38
184	-11.21	-5.29
185	-11.19	-5.19
186	-11.31	-5.15
187	-11.08	-4.88
188	-10.73	-5.06
189	-10.70	-5.05
190	-10.90	-5.06
191	-11.03	-5.00
192	-10.54	-4.93
193	-11.16	-5.25
194	-11.15	-5.22
195	-10.97	-5.08
196	-10.97	-5.17
197	-11.08	-5.14
198	-11.31	-5.39
199	-11.40	-5.53
200	-11.34	-5.33
201	-11.27	-5.52
202	-11.25	-5.46
203	-10.84	-5.63
204	-11.05	-5.48
205	-10.77	-5.27
206	-10.66	-5.23
207	-10.65	-5.29
208	-10.23	-5.31
209	-10.47	-5.23
210	-10.43	-5.18
211	-10.37	-5.02
212	-10.39	-5.08
213	-10.43	-4.94
214	-10.57	-5.02
215	-10.44	-5.24
216	-10.88	-5.40

217	-10.92	-5.25
218	-10.43	-5.09
219	-10.23	-4.38
220	-10.48	-4.95
221	-10.66	-5.25
222	-10.81	-5.29
223	-10.81	-5.16
224	-10.74	-5.01
225	-10.85	-4.91
226	-10.84	-4.81
227	-10.96	-4.86
228	-11.07	-4.91
229	-10.89	-5.02
230	-10.69	-4.87
231	-9.98	-4.96
232	-11.15	-4.91
233	-9.84	-4.89
234	-10.65	-4.96
235	-10.43	-5.05
236	-10.49	-4.98
237	-10.74	-5.22
238	-11.11	-5.14
239	-11.17	-5.22
240	-11.11	-5.29
241	-11.08	-5.12
242	-10.98	-5.05
243	-10.96	-5.19
244	-10.80	-5.26
245	-10.66	-5.14
246	-10.63	-5.08
247	-10.64	-5.18
248	-10.59	-5.09
249	-10.16	-5.05
250	-10.12	-5.08
251	-10.46	-5.26
252	-10.28	-5.23
253	-10.11	-5.27
254	-10.29	-4.87
255	-10.73	-4.93
256	-11.00	-5.03
257	-11.14	-5.09
258	-10.93	-4.98
259	-10.83	-5.01
260	-10.79	-5.14
261	-10.75	-5.09
262	-10.91	-5.06

263	-10.64	-4.91
264	-10.58	-4.85
265	-10.75	-5.19
266	-10.67	-5.09
267	-10.83	-5.14
268	-10.49	-5.11
269	-10.21	-5.07
270	-10.21	-4.66
271	-11.00	-5.02
272	-10.91	-5.04
273	-10.22	-5.08
274	-10.06	-5.06
275	-10.27	-5.24
276	-10.14	-5.14
277	-10.08	-5.44
278	-10.04	-5.28
279	-10.60	-5.28
280	-10.28	-5.20
281	-10.25	-5.13
282	-10.08	-4.88
283	-9.85	-4.74
284	-10.01	-4.71
285	-10.24	-4.72
286	-10.19	-4.72
287	-10.18	-4.54
288	-10.22	-4.74
289	-10.46	-4.94
290	-10.68	-4.84
291	-10.81	-4.66
292	-10.95	-4.71
293	-10.82	-4.83
294	-10.50	-4.72
295	-10.69	-4.76
296	-10.69	-4.69
297	-10.88	-4.88
298	-11.00	-4.71
299	-11.29	-4.87
300	-11.04	-4.79
301	-10.99	-4.77
302	-10.70	-4.81
303	-10.80	-4.69
304	-10.69	-4.80
305	-10.49	-5.05
306	-10.57	-5.15
307	-10.41	-5.17
308	-10.41	-5.22

309	-10.54	-5.16
310	-10.80	-5.20
311	-10.52	-5.04
312	-10.47	-5.20
313	-10.30	-5.14
314	-10.35	-4.97
315	-10.57	-5.03
316	-10.75	-4.87
317	-10.59	-5.02
318	-10.64	-5.09
319	-10.64	-5.05
320	-10.47	-4.77
321	-10.25	-4.76
322	-10.36	-4.65
323	-10.09	-3.69
324	-10.63	-4.62
325	-10.85	-4.78
326	-10.75	-4.94
327	-10.63	-4.88
328	-10.86	-5.00
329	-10.71	-4.92
330	-10.77	-4.90
331	-10.67	-5.03
332	-10.83	-5.06
333	-10.81	-5.04
334	-10.73	-4.97
335	-10.73	-4.94
336	-10.81	-4.95
337	-10.57	-4.84
338	-10.55	-5.05
339	-10.65	-4.96
340	-9.98	-4.77
341	-10.08	-4.88
342	-10.42	-4.74
343	-10.33	-4.73
344	-10.36	-4.59
345	-10.10	-4.65
346	-10.18	-4.73
347	-10.07	-4.89
348	-10.29	-4.79
349	-10.71	-4.71
350	-10.98	-4.75
351	-10.64	-4.60
352	-10.40	-4.66
353	-10.72	-4.74
354	-10.81	-4.69

355	-10.89	-4.70
356	-10.89	-4.67
357	-11.11	-4.90
358	-9.92	-4.57
359	-10.86	-4.84
360	-10.68	-4.76
361	-10.66	-4.87
362	-10.79	-4.98
363	-10.84	-4.98
364	-10.90	-5.13
365	-10.79	-4.91
366	-10.74	-4.73
367	-10.67	-4.73
368	-10.54	-4.79
369	-10.71	-4.71
370	-10.64	-4.93
371	-10.69	-4.97
372	-10.75	-5.02
373	-10.52	-4.98
374	-10.44	-5.05
375	-10.55	-4.89
376	-9.97	-4.89
377	-11.04	-5.08
378	-11.06	-5.07
379	-11.20	-5.13
380	-10.90	-4.93
381	-10.97	-5.01
382	-10.82	-5.01
383	-10.97	-5.13
384	-11.08	-5.15
385	-11.25	-5.23
386	-11.36	-5.14
387	-11.22	-5.34
388	-11.19	-5.27
389	-11.09	-5.26
390	-10.91	-5.12
391	-11.22	-5.07
392	-11.10	-5.03
393	-11.00	-5.08
394	-10.99	-5.12
395	-10.80	-5.12
396	-10.88	-5.27
397	-11.12	-5.30
398	-11.02	-5.34
399	-10.63	-5.11
400	-10.56	-5.15

401	-10.61	-4.96
402	-10.86	-5.11
403	-11.01	-5.08
404	-10.90	-4.89
405	-11.09	-5.06
406	-10.71	-4.85
407	-10.60	-4.88
408	-10.57	-4.91
409	-10.50	-4.65
410	-10.45	-4.65
411	-10.65	-4.76
412	-10.52	-4.69
413	-10.33	-4.43
414	-10.41	-4.79
415	-10.25	-4.77
416	-10.26	-4.77
417	-10.57	-4.86
418	-10.51	-4.80
419	-10.42	-4.88
420	-10.47	-4.97
421	-10.67	-5.02
422	-10.67	-5.02
423	-10.74	-5.02
424	-10.71	-5.07
425	-10.89	-5.10
426	-10.83	-4.99
427	-10.94	-5.05
428	-10.85	-5.01
429	-10.92	-5.04
430	-10.94	-5.02
431	-10.88	-4.99
432	-10.79	-4.87
433	-11.00	-4.99
434	-10.96	-5.17
435	-11.01	-5.01
436	-10.95	-5.07

437	-10.79	-5.02
438	-10.57	-4.95
439	-10.67	-5.06
440	-10.49	-5.20
441	-10.49	-5.21
442	-10.80	-5.20
443	-10.85	-5.23
444	-11.17	-5.25
445	-11.03	-5.23
446	-11.18	-5.06
447	-11.07	-5.14
448	-11.13	-5.25
449	-10.52	-4.91
450	-10.34	-4.92
451	-10.50	-4.87
452	-10.61	-4.87
453	-10.73	-4.83
454	-10.88	-5.01
H1.1	-9.42	-4.80
H1.2	-9.58	-4.82
H1.3	-9.39	-4.92
H1.4	-9.52	-4.93
H1.5	-9.45	-4.85
H1.6	-9.43	-4.87
H1.7	-9.18	-4.87
H1.8	-9.33	-4.82
H1.9	-9.85	-4.87
H1.10	-9.66	-4.99
H2.1	-9.66	-4.87
H2.2	-9.95	-4.84
H2.3	-10.78	-4.98
H2.4	-10.54	-4.96
H2.5	-10.72	-4.97
H2.6	-10.85	-5.03
H2.7	-10.44	-4.99
H2.8	-9.94	-4.83

H2.9	-9.86	-4.95
H2.10	-10.12	-4.69
H3.1	-10.26	-5.22
H3.2	-10.32	-5.21
H3.3	-10.27	-5.19
H3.4	-10.14	-5.27
H3.5	-10.36	-5.18
H3.6	-10.61	-5.29
H3.7	-10.42	-5.26
H3.8	-10.19	-5.25
H3.9	-9.43	-3.02
H3.10	-10.12	-5.32
H4.1	-10.07	-4.85
H4.2	-10.25	-4.92
H4.3	-10.55	-4.78
H4.4	-10.83	-4.97
H4.5	-10.96	-5.28
H4.6	-10.56	-5.00
H4.7	-10.24	-5.03
H4.8	-10.11	-5.04
H4.9	-10.17	-5.14
H4.10	-10.20	-4.84
H5.1	-11.41	-5.38
H5.2	-11.53	-5.42
H5.3	-11.48	-5.45
H5.4	-11.22	-5.49
H5.5	-10.78	-5.40
H5.6	-11.01	-5.48
H5.7	-11.43	-5.55
H5.8	-11.53	-5.47
H5.9	-11.42	-5.43
H5.10	-11.50	-5.15

Appendix 8 – All stable isotope data obtained from the central growth axes of all additional speleothems.

Sample Number	$\delta^{13}\text{C}$ (VPDB)	$\delta^{18}\text{O}$ (VPDB)	Average $\delta^{13}\text{C}$	StDev	Average $\delta^{18}\text{O}$	StDev
A2-1	-5.93	-3.32				
A2-2	-5.96	-3.40				
A2-3	-6.00	-3.40				
A2-4	-6.15	-3.43				
A2-5	-6.19	-3.49	-6.05	0.12	-3.41	0.06
C4-1	-6.33	-4.46				
C4-2	-4.68	-4.19				
C4-3	-6.49	-4.70				
C4-4	-4.75	-4.27				
C4-5	-5.03	-3.80	-5.46	0.88	-4.29	0.34
C5-1	-7.05	-4.44				
C5-2	-6.23	-4.73				
C5-3	-6.67	-4.99				
C5-5	-6.09	-4.83	-6.51	0.44	-4.75	0.23
D1-1	-11.25	-4.49				
D1-2	-11.00	-4.45				
D1-3	-11.06	-4.08				
D1-4	-11.01	-4.18				
D1-5	-10.99	-4.26				
D1-6	-11.11	-4.84	-11.07	0.10	-4.38	0.27
D4-1	-9.53	-4.47				
D4-2	-9.88	-4.06				
D4-3	-10.71	-4.20				
D4-4	-10.08	-4.18				
D4-5	-10.26	-4.47				
D4-6	-10.74	-4.26	-10.20	0.47	-4.27	0.17
D5-1	-11.11	-4.20				
D5-2	-11.24	-3.98				
D5-3	-11.27	-3.93				
D5-4	-11.35	-3.95				
D5-5	-11.51	-4.17	-11.29	0.15	-4.05	0.13
D6-1	-11.23	-4.16				
D6-2	-11.28	-3.98				
D6-3	-11.59	-4.35				
D6-4	-11.47	-4.50				

D6-5	-11.68	-4.41				
D6-6	-11.79	-4.31	-11.51	0.22	-4.28	0.19
D7-1	-11.19	-4.51				
D7-2	-11.84	-4.37				
D7-3	-11.55	-4.58				
D7-4	-11.80	-4.58	-11.60	0.30	-4.51	0.10
E2-1	-10.19	-5.43				
E2-2	-10.25	-5.43				
E2-3	-10.29	-5.54				
E2-4	-9.99	-5.17				
E2-5	-9.86	-5.09				
E2-6	-9.94	-5.33	-10.09	0.18	-5.33	0.17
E5-1	-10.31	-5.25				
E5-2	-10.18	-5.27				
E5-3	-10.31	-5.36				
E5-4	-10.11	-5.27				
E5-5	-10.28	-5.46	-10.23	0.09	-5.32	0.09
F10-1	-10.09	-4.69				
F10-2	-10.10	-4.68				
F10-3	-9.23	-3.80	-9.81	0.50	-4.39	0.51
F11-1	-9.07	-4.18				
F11-2	-9.20	-4.23				
F11-3	-8.89	-4.07				
F11-4	-8.65	-4.18	-8.95	0.24	-4.16	0.07
F13-1	-9.92	-4.67				
F13-2	-10.57	-4.53				
F13-3	-11.00	-5.25				
F13-4	-10.84	-5.15	-10.58	0.47	-4.90	0.35
F14-1	-9.72	-4.23				
F14-2	-10.56	-4.51				
F14-3	-10.34	-4.35				
F14-4	-11.09	-4.50				
F14-5	-10.65	-4.44	-10.47	0.50	-4.40	0.12
F8-1	-9.95	-5.16				
F8-2	-9.84	-5.09				
F8-3	-10.84	-4.76				
F8-4	-10.89	-4.63	-10.38	0.56	-4.91	0.25
F9-1	-10.23	-3.99				
F9-2	-9.54	-4.34				
F9-3	-10.09	-4.89	-9.95	0.36	-4.41	0.46
FIA_A1	-8.20	-3.48				

FIA_A2	-6.70	-3.23				
FIA_A3	-6.23	-2.95	-7.04	1.02	-3.22	0.27
FIB_A1	-10.48	-5.71				
FIB_A2	-10.37	-5.83				
FIB_A3	-10.23	-5.73				
FIB_A4	-10.45	-6.08				
FIB_A5	-9.87	-5.85				
FIB_A6	-9.43	-5.85				
FIB_A7	-9.24	-5.66	-10.01	0.51	-5.82	0.14
FIC_A1	-6.43	-3.63				
FIC_A2	-6.01	-3.36				
FIC_A3	-7.52	-3.53				
FIC_A4	-7.46	-3.86				
FIC_A5	-6.94	-4.36				
FIC_A6	-7.17	-3.98	-6.92	0.60	-3.79	0.36
FID-A1	-11.63	-4.56				
FID-A2	-11.04	-5.05				
FID-A3	-11.11	-5.42				
FID-A4	-10.83	-5.26				
FID_A5	-10.98	-4.63				
FID_A6	-11.18	-4.58				
FID_A7	-11.21	-4.84				
FID_A8	-11.30	-4.34				
FID_A9	-11.33	-4.40				
FID_A10	-11.39	-4.42	-11.20	0.23	-4.75	0.38
FIE_A1	-8.18	-4.81				
FIE_A2	-8.88	-4.62				
FIE_A3	-8.81	-4.63				
FIE_A4	-8.73	-4.65				
FIE_A5	-7.74	-4.40				
FIE_A6	-8.65	-4.70	-8.50	0.45	-4.63	0.13
FIF_A1	-9.31	-4.51				
FIF_A2	-9.62	-5.09				
FIF_A3	-9.71	-4.69				
FIF_A4	-9.51	-4.75				
FIF_A5	-9.12	-4.00				
FIF_A6	-9.26	-3.77	-9.42	0.23	-4.47	0.49

Appendix 9 – All trace element data obtained for speleothem BT for elements Mg, Sr, Ba, U, Y, Fe, La, Ce, Cu, and Pr.

Sample Depth (mm)	Mg : Ca	Fe : Ca	Cu : Ca	Sr : Ca	Y : Ca	Ba : Ca	La : Ca	Ce : Ca	Pr : Ca	Bi : Ca	U : Ca
1	9.76E-03	5.30E-03	9.75E-06	3.45E-04	1.95E-06	8.97E-06	1.62E-06	2.18E-06	2.86E-07	3.80E-05	7.02E-06
5	9.27E-03	1.05E-02	8.54E-06	2.92E-04	6.11E-09	5.64E-06	2.11E-08	4.77E-08	2.27E-09	1.38E-04	1.64E-06
9	9.45E-03	5.22E-03	6.16E-06	2.83E-04	8.54E-09	8.03E-06	1.24E-08	1.62E-08	6.30E-10	1.99E-04	1.65E-06
13	1.02E-02	5.13E-03	2.80E-06	2.89E-04	8.53E-09	5.41E-06	6.72E-09	9.19E-09	5.25E-10	4.01E-05	1.63E-06
17	1.08E-02	5.19E-03	1.77E-06	2.79E-04	5.52E-09	7.77E-06	2.57E-09	4.55E-09	3.17E-10	9.81E-05	1.56E-06
21	1.01E-02	5.16E-03	3.50E-06	2.77E-04	8.61E-09	5.43E-06	5.23E-08	3.03E-07	9.19E-10	5.12E-05	1.57E-06
25	9.85E-03	5.14E-03	1.97E-06	2.71E-04	6.58E-09	5.07E-06	1.94E-08	4.10E-08	3.79E-10	4.33E-06	1.48E-06
29	1.07E-02	5.14E-03	1.86E-06	3.01E-04	6.18E-09	5.56E-06	1.70E-09	3.39E-09	6.45E-11	1.24E-05	1.53E-06
33	1.09E-02	5.18E-03	2.08E-06	2.84E-04	6.93E-09	5.27E-06	3.75E-09	5.60E-09	4.68E-10	8.61E-06	1.56E-06
37	1.02E-02	9.77E-03	1.19E-05	2.79E-04	5.75E-09	5.74E-06	5.49E-09	1.30E-08	5.91E-10	2.62E-04	1.53E-06
41	1.01E-02	5.17E-03	2.72E-06	2.76E-04	6.92E-09	1.58E-05	1.29E-08	1.99E-08	5.38E-10	7.25E-05	1.64E-06
45	1.12E-02	5.17E-03	3.46E-06	2.84E-04	5.85E-09	5.45E-06	5.01E-09	7.30E-09	7.38E-10	6.59E-05	1.54E-06
49	1.08E-02	5.30E-03	4.85E-06	2.86E-04	5.03E-09	6.11E-06	1.99E-08	2.60E-08	4.49E-10	4.19E-04	1.58E-06
53	9.62E-03	5.21E-03	2.83E-06	2.68E-04	6.17E-09	5.09E-06	1.64E-08	2.45E-08	4.45E-10	3.92E-05	1.51E-06
57	9.69E-03	5.76E-03	3.37E-06	2.46E-04	7.10E-09	5.34E-06	3.17E-09	6.69E-09	9.07E-10	1.21E-04	1.50E-06
61	1.19E-02	5.21E-03	2.79E-06	2.85E-04	5.49E-09	5.16E-06	1.00E-08	1.59E-08	5.58E-10	1.47E-05	1.41E-06
65	1.08E-02	5.19E-03	3.21E-06	2.83E-04	4.66E-09	5.33E-06	4.31E-09	6.17E-09	3.53E-10	1.29E-04	1.50E-06
69	1.07E-02	5.31E-03	3.03E-05	2.84E-04	1.53E-08	6.14E-06	1.71E-07	2.34E-07	3.71E-09	1.88E-04	1.50E-06
73	1.08E-02	5.19E-03	5.58E-06	2.71E-04	5.66E-09	5.75E-06	1.02E-08	1.25E-08	5.99E-10	6.06E-04	1.44E-06

77	1.09E-02	5.23E-03	2.21E-06	2.61E-04	4.44E-09	4.66E-06	8.11E-09	1.09E-08	2.32E-10	1.17E-04	1.40E-06
81	1.18E-02	5.45E-03	2.28E-05	2.88E-04	8.54E-09	8.07E-06	1.05E-07	7.68E-08	8.18E-09	3.32E-03	1.39E-06
85	1.13E-02	5.11E-03	3.64E-06	2.78E-04	5.15E-09	4.85E-06	5.49E-09	7.88E-09	7.05E-10	6.00E-05	1.39E-06
89	1.25E-02	5.16E-03	3.94E-06	3.00E-04	6.49E-09	5.97E-06	1.91E-08	2.37E-08	6.29E-10	9.39E-05	1.40E-06
93	1.16E-02	5.29E-03	4.88E-06	3.01E-04	1.68E-08	6.12E-06	4.75E-08	7.19E-08	3.30E-09	1.49E-05	1.53E-06
97	1.06E-02	5.16E-03	6.76E-06	3.18E-04	2.03E-08	5.92E-06	6.36E-08	9.48E-08	5.97E-09	1.10E-05	1.67E-06
101	1.04E-02	5.16E-03	3.22E-06	3.33E-04	5.61E-09	5.93E-06	1.27E-08	1.62E-08	4.91E-10	9.20E-05	1.72E-06
105	1.01E-02	5.14E-03	4.94E-06	3.12E-04	9.01E-09	5.49E-06	1.29E-07	1.68E-07	1.38E-09	9.53E-05	1.69E-06
109	1.08E-02	5.15E-03	3.27E-06	3.17E-04	7.21E-09	6.38E-06	1.11E-08	1.83E-08	6.08E-10	3.95E-05	1.64E-06
113	1.11E-02	5.17E-03	8.40E-06	3.07E-04	7.18E-09	6.08E-06	2.14E-08	2.86E-08	8.85E-10	1.46E-04	1.60E-06
117	1.14E-02	5.71E-03	5.78E-06	3.31E-04	1.65E-08	5.72E-06	2.75E-08	4.81E-08	4.18E-09	1.60E-05	1.85E-06
121	1.09E-02	5.11E-03	1.19E-05	3.22E-04	1.34E-08	6.24E-06	1.87E-07	2.56E-07	3.17E-09	6.31E-05	1.71E-06
125	1.14E-02	5.20E-03	3.63E-06	3.35E-04	1.93E-08	5.74E-06	1.00E-07	2.02E-07	2.11E-08	3.46E-05	1.68E-06
129	1.25E-02	5.17E-03	3.46E-06	3.15E-04	1.48E-08	5.80E-06	1.21E-08	1.70E-08	1.78E-09	2.68E-05	1.62E-06
133	1.17E-02	5.14E-03	5.06E-06	3.00E-04	8.69E-09	6.21E-06	2.75E-08	3.66E-08	5.64E-10	9.71E-05	1.80E-06
137	1.31E-02	5.15E-03	3.32E-06	3.00E-04	6.87E-09	5.94E-06	1.03E-08	1.41E-08	5.50E-10	4.33E-05	1.68E-06
141	1.14E-02	5.25E-03	3.64E-06	3.28E-04	6.30E-09	6.25E-06	1.55E-07	1.49E-07	9.33E-10	1.08E-05	1.75E-06
145	1.16E-02	5.12E-03	4.02E-06	3.20E-04	7.18E-09	6.25E-06	6.42E-08	7.07E-08	1.05E-09	1.77E-05	1.74E-06
149	1.13E-02	5.98E-03	7.03E-06	3.07E-04	7.17E-09	5.99E-06	6.32E-08	8.85E-08	8.10E-10	1.98E-05	1.77E-06
153	1.14E-02	5.09E-03	5.38E-06	2.84E-04	6.21E-09	7.37E-06	3.46E-08	4.92E-08	7.13E-10	9.70E-05	1.74E-06
157	1.19E-02	5.16E-03	1.85E-06	2.72E-04	7.10E-09	6.33E-06	6.92E-09	1.09E-08	4.04E-10	2.50E-06	1.68E-06
161	1.20E-02	5.13E-03	3.20E-06	2.74E-04	8.29E-09	1.18E-05	4.78E-08	6.79E-08	1.01E-09	1.97E-05	1.65E-06
165	1.20E-02	5.11E-03	2.77E-06	2.63E-04	7.53E-09	5.08E-06	3.07E-08	4.41E-08	4.96E-10	1.63E-05	1.56E-06
169	1.23E-02	5.11E-03	2.66E-06	2.86E-04	5.88E-09	5.48E-06	2.45E-08	3.63E-08	6.24E-10	4.76E-05	1.62E-06
173	1.14E-02	5.11E-03	3.81E-06	2.98E-04	8.56E-09	7.53E-06	6.82E-08	1.03E-07	1.06E-09	5.15E-05	1.82E-06
177	1.09E-02	5.10E-03	3.01E-06	3.10E-04	8.29E-09	6.08E-06	1.67E-08	2.52E-08	7.00E-10	8.21E-06	1.85E-06
181	1.18E-02	5.11E-03	3.85E-06	2.65E-04	7.58E-09	5.61E-06	1.41E-08	2.28E-08	7.36E-10	1.76E-05	1.68E-06

185	1.21E-02	5.09E-03	4.84E-06	2.83E-04	7.22E-09	6.80E-06	5.54E-08	8.69E-08	1.43E-09	1.70E-04	1.77E-06
189	1.17E-02	5.08E-03	3.20E-06	2.69E-04	5.67E-09	5.69E-06	1.31E-08	2.09E-08	6.46E-10	2.45E-05	1.74E-06
193	1.11E-02	5.17E-03	2.57E-06	2.46E-04	7.79E-09	5.01E-06	9.54E-09	1.68E-08	2.84E-10	1.25E-05	1.55E-06
197	1.37E-02	5.14E-03	2.52E-06	2.67E-04	6.04E-09	5.43E-06	1.89E-08	2.49E-08	7.05E-10	1.00E-05	1.36E-06
201	1.05E-02	5.10E-03	3.54E-06	3.09E-04	7.33E-09	5.86E-06	1.54E-08	2.26E-08	4.88E-10	1.20E-05	1.68E-06
205	9.70E-03	5.09E-03	2.61E-06	3.15E-04	1.15E-08	6.02E-06	1.87E-08	3.11E-08	1.49E-09	8.10E-06	1.84E-06
209	1.06E-02	5.13E-03	4.31E-06	2.86E-04	6.43E-09	5.89E-06	3.08E-08	4.30E-08	1.08E-09	3.74E-05	1.68E-06
213	1.17E-02	5.08E-03	2.77E-06	2.71E-04	6.11E-09	5.25E-06	6.31E-09	9.59E-09	3.66E-10	3.44E-05	1.59E-06
217	1.26E-02	5.11E-03	2.74E-06	2.79E-04	7.35E-09	5.49E-06	8.48E-09	1.44E-08	3.78E-10	1.31E-05	1.66E-06
221	1.18E-02	5.08E-03	5.20E-06	2.43E-04	1.01E-08	6.07E-06	1.86E-08	2.62E-08	5.98E-10	1.78E-05	1.75E-06
225	1.05E-02	5.12E-03	3.93E-06	3.01E-04	3.38E-09	5.80E-06	4.99E-09	6.49E-09	3.61E-10	2.60E-05	1.76E-06
229	8.51E-03	5.08E-03	2.79E-06	3.06E-04	6.92E-09	5.91E-06	2.44E-09	4.34E-09	3.09E-10	7.35E-06	2.12E-06
233	9.30E-03	5.08E-03	2.38E-06	2.28E-04	7.72E-09	4.48E-06	6.08E-09	8.39E-09	4.88E-10	1.27E-05	1.56E-06
237	1.07E-02	5.07E-03	3.11E-06	2.52E-04	4.81E-09	8.34E-06	1.59E-08	2.14E-08	4.88E-10	4.45E-05	1.57E-06
241	9.32E-03	5.05E-03	9.63E-06	2.66E-04	5.71E-09	4.72E-06	1.11E-08	4.00E-08	4.97E-10	1.22E-05	1.63E-06
245	9.17E-03	5.22E-03	2.85E-06	3.22E-04	1.17E-08	5.48E-06	1.30E-07	1.68E-07	3.59E-09	7.76E-06	1.85E-06
249	9.23E-03	5.05E-03	2.74E-06	3.26E-04	4.69E-09	7.22E-06	1.89E-08	2.15E-08	3.46E-10	2.32E-05	1.80E-06
253	9.26E-03	5.05E-03	4.85E-06	3.25E-04	5.95E-09	5.35E-06	2.68E-08	3.81E-08	1.07E-09	2.95E-05	1.84E-06
257	8.53E-03	5.06E-03	3.09E-06	2.81E-04	8.39E-09	6.33E-06	4.52E-08	3.00E-08	1.40E-09	1.72E-05	1.86E-06
261	1.07E-02	5.06E-03	5.57E-06	2.93E-04	3.72E-09	5.46E-06	1.21E-08	2.75E-08	1.25E-09	2.10E-05	1.70E-06
265	9.33E-03	5.09E-03	2.38E-06	2.84E-04	7.05E-09	6.51E-06	1.37E-08	1.64E-08	8.47E-10	8.68E-06	1.74E-06
269	1.03E-02	5.00E-03	2.42E-05	2.54E-04	5.83E-09	4.54E-06	1.02E-08	1.24E-08	5.74E-10	5.58E-06	1.45E-06
273	9.43E-03	5.34E-03	2.56E-06	3.00E-04	6.62E-09	5.57E-06	2.22E-08	2.38E-08	8.84E-10	1.46E-05	1.70E-06
277	9.83E-03	5.01E-03	1.77E-06	2.98E-04	5.07E-09	6.54E-06	1.16E-08	1.43E-08	3.68E-10	9.84E-07	1.68E-06
281	9.68E-03	5.02E-03	4.91E-06	3.01E-04	7.18E-09	1.35E-05	1.66E-08	2.41E-08	7.99E-10	6.84E-06	1.74E-06
285	1.01E-02	5.03E-03	3.72E-06	2.98E-04	6.75E-09	2.29E-05	1.72E-08	2.82E-08	5.37E-10	1.46E-06	1.85E-06
289	9.29E-03	5.00E-03	3.99E-06	2.84E-04	6.94E-09	5.31E-06	2.16E-08	2.82E-08	6.39E-10	1.67E-05	1.98E-06

293	1.14E-02	4.96E-03	2.84E-06	2.70E-04	7.56E-09	5.40E-06	1.57E-08	2.26E-08	1.16E-09	4.71E-06	1.70E-06
297	1.20E-02	4.93E-03	3.98E-06	2.88E-04	6.89E-09	5.99E-06	2.04E-08	2.75E-08	1.09E-09	5.92E-06	1.74E-06
301	1.10E-02	4.96E-03	6.38E-06	2.84E-04	6.80E-09	8.31E-06	2.94E-08	4.24E-08	1.02E-09	4.55E-06	1.74E-06
305	1.01E-02	4.86E-03	4.16E-06	2.76E-04	6.14E-09	5.33E-06	1.58E-08	1.65E-08	9.95E-10	1.57E-05	1.90E-06
309	1.21E-02	4.92E-03	4.72E-06	2.75E-04	5.47E-09	6.04E-06	1.07E-08	1.36E-08	5.68E-10	1.06E-05	1.65E-06
313	1.10E-02	4.92E-03	2.68E-06	3.00E-04	6.58E-09	5.97E-06	6.55E-09	9.75E-09	5.54E-10	3.51E-06	1.81E-06
317	1.15E-02	4.93E-03	2.05E-06	2.51E-04	5.12E-09	5.44E-06	6.64E-09	8.87E-09	5.80E-10	3.76E-06	1.75E-06
321	1.04E-02	4.94E-03	3.66E-06	3.44E-04	1.43E-08	6.82E-06	1.97E-08	3.28E-08	1.72E-09	7.70E-06	2.20E-06
325	9.35E-03	4.87E-03	3.06E-06	3.63E-04	5.74E-09	7.16E-06	1.54E-08	2.11E-08	1.06E-09	2.47E-05	2.37E-06
329	1.06E-02	4.90E-03	1.66E-06	2.97E-04	3.18E-09	5.90E-06	3.42E-09	4.48E-09	2.32E-10	1.97E-06	2.09E-06
333	9.79E-03	4.89E-03	2.22E-06	2.72E-04	6.15E-09	5.06E-06	1.04E-08	1.77E-08	8.77E-10	3.89E-06	1.79E-06
337	1.04E-02	4.88E-03	2.15E-06	2.48E-04	5.31E-09	5.14E-06	8.22E-09	1.17E-08	2.89E-10	4.81E-06	1.78E-06
341	1.17E-02	4.85E-03	4.27E-06	2.63E-04	6.62E-09	5.74E-06	7.56E-09	1.08E-08	7.07E-10	8.53E-06	1.66E-06
345	9.94E-03	4.88E-03	7.24E-06	2.68E-04	6.26E-09	5.04E-06	2.81E-08	3.58E-08	1.27E-09	4.91E-05	1.77E-06
349	9.33E-03	4.85E-03	2.32E-06	2.62E-04	7.63E-09	4.51E-06	3.14E-05	5.13E-05	2.37E-07	1.56E-06	1.73E-06
353	9.99E-03	4.87E-03	4.26E-06	2.78E-04	7.41E-09	5.68E-06	7.35E-09	9.08E-09	7.33E-10	2.25E-06	1.81E-06
357	9.47E-03	4.85E-03	3.39E-06	2.89E-04	6.29E-09	9.75E-06	1.43E-08	2.01E-08	8.40E-10	6.56E-06	1.76E-06
361	1.28E-02	4.84E-03	4.11E-06	2.54E-04	5.55E-09	4.85E-06	1.92E-08	2.81E-08	6.75E-10	6.03E-06	1.53E-06
365	1.01E-02	4.79E-03	3.77E-06	2.77E-04	7.80E-09	7.49E-06	1.25E-08	1.86E-08	1.36E-09	3.62E-05	1.84E-06
369	9.50E-03	4.77E-03	4.52E-06	2.78E-04	7.21E-09	5.89E-06	4.90E-08	7.10E-08	9.98E-10	1.20E-05	1.97E-06
373	9.85E-03	4.78E-03	4.45E-06	2.53E-04	1.02E-08	8.04E-06	1.66E-08	2.51E-08	1.72E-09	9.72E-05	1.88E-06
377	9.20E-03	4.98E-03	3.57E-06	2.43E-04	2.13E-08	4.48E-06	1.94E-08	2.10E-08	3.00E-09	3.57E-06	1.68E-06
381	8.66E-03	4.78E-03	6.35E-06	2.92E-04	6.32E-09	4.79E-06	1.45E-08	2.17E-08	5.90E-10	1.60E-05	1.92E-06
385	1.05E-02	4.85E-03	1.71E-06	2.66E-04	4.81E-09	4.43E-06	7.40E-09	4.91E-08	3.81E-10	2.15E-06	1.67E-06
389	9.14E-03	4.91E-03	2.51E-06	2.86E-04	6.28E-09	4.60E-06	1.50E-08	2.41E-08	1.23E-09	6.78E-05	1.84E-06
393	9.75E-03	4.89E-03	2.46E-06	2.93E-04	5.91E-09	4.62E-06	1.91E-08	2.73E-08	3.87E-10	2.69E-06	1.76E-06
397	8.65E-03	4.78E-03	1.81E-06	3.31E-04	5.18E-09	6.74E-06	1.34E-08	2.04E-08	1.05E-09	3.81E-06	2.07E-06

401	9.92E-03	4.81E-03	2.24E-06	2.95E-04	4.60E-09	7.53E-06	1.06E-08	1.79E-08	1.11E-09	2.98E-06	1.81E-06
405	1.06E-02	4.84E-03	2.61E-06	2.96E-04	7.93E-09	5.79E-06	1.02E-08	1.02E-08	8.06E-10	5.05E-06	1.76E-06
409	1.02E-02	4.82E-03	3.01E-06	3.06E-04	1.00E-08	5.00E-06	2.48E-08	4.69E-08	2.50E-09	2.81E-06	1.81E-06
413	1.02E-02	4.96E-03	3.90E-06	3.00E-04	6.92E-09	5.33E-06	3.33E-08	3.51E-08	2.85E-09	1.70E-06	1.79E-06
417	9.83E-03	4.84E-03	2.10E-06	3.22E-04	5.57E-09	5.28E-06	5.90E-09	8.13E-09	3.95E-10	5.04E-06	1.94E-06
421	9.49E-03	4.90E-03	4.53E-06	2.99E-04	6.12E-09	4.85E-06	2.81E-08	3.72E-08	9.61E-10	6.92E-06	1.85E-06
425	9.05E-03	4.98E-03	3.43E-06	3.00E-04	1.05E-08	4.69E-06	2.01E-08	2.65E-08	5.72E-10	6.83E-06	1.87E-06
429	1.02E-02	5.19E-03	4.67E-06	3.02E-04	6.73E-09	5.94E-06	5.54E-09	8.95E-09	4.84E-10	1.58E-06	1.81E-06
433	1.11E-02	4.89E-03	3.29E-06	3.01E-04	7.22E-09	5.34E-06	1.95E-08	2.80E-08	8.25E-10	3.05E-06	1.83E-06
437	1.15E-02	4.82E-03	4.32E-06	3.28E-04	8.61E-09	9.04E-06	2.39E-08	4.03E-08	1.32E-09	2.95E-06	2.05E-06
441	1.21E-02	4.84E-03	2.55E-06	3.41E-04	2.98E-08	5.99E-06	2.21E-08	2.55E-08	3.92E-09	8.14E-06	2.09E-06
445	1.40E-02	4.85E-03	5.42E-06	2.76E-04	1.33E-08	4.40E-06	2.80E-08	5.22E-08	8.25E-10	3.43E-05	1.88E-06
449	1.44E-02	4.92E-03	4.98E-06	2.93E-04	8.39E-09	4.80E-06	1.25E-08	1.83E-08	5.54E-10	4.04E-06	1.98E-06
453	1.75E-02	4.93E-03	3.89E-06	3.33E-04	9.66E-09	6.01E-06	2.40E-08	3.06E-08	5.42E-10	8.21E-07	2.00E-06
457	1.63E-02	4.94E-03	6.40E-06	2.99E-04	1.02E-08	1.59E-05	1.33E-08	1.82E-08	7.30E-10	4.16E-06	2.18E-06
461	1.74E-02	4.84E-03	4.92E-06	3.01E-04	6.85E-09	4.41E-06	1.15E-07	1.62E-07	3.19E-10	2.18E-06	1.95E-06
465	1.81E-02	4.90E-03	3.65E-06	3.15E-04	5.46E-09	6.55E-06	3.24E-07	8.26E-07	5.23E-09	3.65E-06	2.07E-06
469	1.86E-02	4.89E-03	5.43E-06	3.70E-04	4.54E-09	5.63E-06	1.98E-08	2.77E-08	8.79E-10	7.33E-06	1.92E-06
473	2.12E-02	4.91E-03	5.37E-06	4.21E-04	4.92E-08	1.91E-05	7.73E-08	1.04E-07	1.14E-08	1.06E-05	2.22E-06
477	2.41E-02	4.89E-03	9.60E-06	4.65E-04	9.30E-09	6.45E-06	2.08E-07	3.15E-07	2.92E-09	1.81E-05	1.88E-06
481	2.50E-02	4.88E-03	5.32E-06	4.80E-04	9.18E-09	7.74E-06	2.03E-08	3.14E-08	2.08E-09	4.01E-06	2.08E-06
485	2.30E-02	4.89E-03	6.68E-06	4.52E-04	5.74E-09	1.03E-05	1.59E-08	2.29E-08	6.93E-10	5.27E-06	2.17E-06
489	2.39E-02	4.85E-03	7.35E-06	4.61E-04	9.13E-09	7.97E-06	3.51E-08	4.79E-08	8.14E-10	6.36E-06	2.31E-06
493	2.26E-02	4.89E-03	7.51E-06	4.60E-04	6.74E-09	8.89E-06	3.49E-08	4.59E-08	9.09E-10	1.25E-05	2.38E-06
497	2.51E-02	4.90E-03	3.25E-06	4.44E-04	5.61E-09	6.85E-06	6.90E-09	9.19E-09	1.68E-10	9.90E-07	1.82E-06
501	2.37E-02	4.91E-03	7.15E-06	5.07E-04	9.73E-09	1.11E-05	4.04E-08	7.68E-08	1.21E-09	2.56E-06	2.28E-06
505	2.32E-02	4.90E-03	6.96E-06	4.76E-04	1.35E-08	8.11E-06	2.03E-08	2.84E-08	7.29E-10	5.12E-06	2.30E-06

509	2.33E-02	4.89E-03	5.76E-06	5.20E-04	1.63E-08	9.37E-06	1.48E-08	2.35E-08	9.27E-10	2.25E-06	2.43E-06
513	2.62E-02	4.91E-03	1.73E-05	5.51E-04	2.92E-08	1.29E-05	5.16E-08	6.85E-08	6.24E-09	3.69E-06	2.37E-06
517	2.38E-02	4.86E-03	7.74E-06	5.24E-04	1.56E-08	9.80E-06	3.37E-08	4.72E-08	1.07E-09	5.36E-06	2.48E-06
521	2.46E-02	4.88E-03	1.37E-05	5.28E-04	1.72E-08	9.17E-06	5.88E-08	7.73E-08	1.19E-09	6.21E-06	2.30E-06
525	2.52E-02	4.85E-03	6.49E-06	5.07E-04	2.03E-08	9.67E-06	2.25E-08	3.20E-08	3.15E-10	9.42E-06	2.28E-06
529	2.49E-02	4.82E-03	8.44E-06	5.50E-04	1.30E-08	1.00E-05	3.81E-08	5.85E-08	8.51E-10	9.76E-06	2.62E-06
533	2.49E-02	4.86E-03	9.38E-06	5.55E-04	1.35E-08	3.21E-05	1.46E-08	2.39E-08	9.10E-10	8.64E-07	2.48E-06
537	2.46E-02	4.86E-03	1.01E-05	5.42E-04	2.34E-08	9.48E-06	1.34E-07	1.97E-07	3.05E-09	7.27E-06	2.46E-06
541	2.53E-02	4.86E-03	1.47E-05	5.55E-04	2.42E-08	1.20E-05	5.48E-08	8.09E-08	2.05E-09	5.22E-06	2.67E-06
545	2.63E-02	4.86E-03	9.23E-06	5.70E-04	1.68E-08	1.26E-05	5.26E-08	7.75E-08	1.35E-09	5.36E-06	2.61E-06
549	2.70E-02	4.94E-03	7.60E-06	5.96E-04	1.99E-08	1.24E-05	3.32E-08	5.02E-08	1.42E-09	2.10E-06	2.54E-06
553	2.54E-02	4.90E-03	1.12E-05	5.92E-04	2.81E-08	1.28E-05	1.91E-07	1.26E-07	5.13E-09	9.31E-06	2.62E-06
557	2.47E-02	4.90E-03	1.32E-05	5.98E-04	2.92E-08	1.30E-05	1.18E-07	2.63E-07	3.08E-09	1.63E-05	2.62E-06
561	2.37E-02	5.11E-03	1.23E-05	6.33E-04	5.47E-08	1.52E-05	2.10E-07	2.41E-07	9.39E-09	1.31E-05	2.76E-06
565	2.57E-02	4.92E-03	9.69E-06	6.73E-04	2.83E-08	1.44E-05	5.50E-08	8.00E-08	1.16E-09	5.85E-06	2.83E-06
569	2.71E-02	4.91E-03	6.09E-06	6.37E-04	1.37E-08	1.22E-05	1.75E-08	2.80E-08	8.96E-10	1.68E-06	2.41E-06
573	2.49E-02	4.93E-03	7.68E-06	6.69E-04	2.00E-08	1.27E-05	4.22E-08	6.09E-08	1.33E-09	6.34E-06	2.74E-06
577	2.43E-02	4.94E-03	9.97E-06	6.70E-04	2.68E-08	2.15E-05	6.49E-08	9.52E-08	1.56E-09	8.09E-06	2.75E-06
581	2.59E-02	4.91E-03	8.18E-06	6.75E-04	2.33E-08	1.28E-05	2.26E-08	3.36E-08	8.87E-10	1.04E-05	2.63E-06
585	2.61E-02	4.92E-03	8.74E-06	7.17E-04	1.86E-08	1.27E-05	4.42E-08	6.59E-08	1.89E-09	1.14E-05	2.79E-06
589	2.54E-02	4.94E-03	1.94E-05	7.13E-04	2.41E-08	1.23E-05	9.82E-08	1.38E-07	5.52E-09	4.16E-05	2.65E-06
593	2.48E-02	4.88E-03	1.62E-05	7.54E-04	1.43E-08	1.27E-05	5.30E-08	8.42E-08	1.61E-09	1.03E-05	2.97E-06
597	2.29E-02	4.92E-03	7.75E-06	7.25E-04	2.35E-08	1.30E-05	1.37E-07	1.03E-06	2.58E-09	6.88E-06	3.07E-06
601	2.37E-02	4.89E-03	8.36E-06	6.71E-04	1.80E-08	1.36E-05	2.59E-08	3.92E-08	1.71E-09	6.09E-06	2.68E-06
605	2.41E-02	4.94E-03	8.08E-06	6.78E-04	1.49E-08	1.14E-05	8.49E-08	1.22E-07	1.87E-09	1.11E-05	2.74E-06
609	2.40E-02	4.92E-03	8.35E-06	6.67E-04	1.63E-08	1.11E-05	3.09E-08	4.67E-08	2.35E-09	1.91E-05	2.77E-06
613	2.60E-02	4.91E-03	8.51E-06	7.32E-04	1.39E-08	1.13E-05	4.22E-08	6.02E-08	1.73E-09	2.25E-05	2.60E-06

617	2.43E-02	4.89E-03	7.95E-06	6.69E-04	1.84E-08	1.62E-05	4.69E-08	5.23E-08	1.21E-09	1.76E-05	2.89E-06
621	2.68E-02	4.88E-03	5.05E-06	6.54E-04	8.08E-09	1.19E-05	2.87E-08	3.96E-08	1.16E-09	2.53E-05	2.80E-06
625	2.69E-02	4.90E-03	5.61E-06	6.40E-04	6.92E-09	1.17E-05	2.27E-08	3.18E-08	1.40E-09	9.85E-06	2.76E-06
629	2.77E-02	5.01E-03	5.11E-06	6.55E-04	7.10E-09	1.14E-05	3.18E-08	4.45E-08	6.91E-10	4.50E-06	2.70E-06
633	2.62E-02	4.89E-03	5.80E-06	6.60E-04	8.88E-09	1.25E-05	2.32E-07	2.17E-07	1.60E-08	1.01E-05	2.99E-06
637	2.73E-02	4.89E-03	6.32E-06	6.47E-04	8.14E-09	1.09E-05	3.60E-08	4.25E-08	1.52E-09	9.64E-06	2.81E-06
641	2.75E-02	4.91E-03	5.04E-06	6.23E-04	7.00E-09	1.11E-05	1.49E-08	1.82E-08	4.60E-10	2.39E-06	2.73E-06
645	2.73E-02	4.89E-03	9.67E-06	5.82E-04	6.37E-09	1.21E-05	1.28E-08	1.58E-08	2.36E-10	6.21E-06	2.58E-06
649	2.54E-02	4.87E-03	8.37E-06	5.58E-04	5.48E-09	1.06E-05	8.00E-08	1.23E-07	4.53E-09	1.16E-05	2.60E-06
653	2.45E-02	4.88E-03	8.96E-06	5.38E-04	8.23E-09	1.12E-05	2.25E-08	3.28E-08	7.98E-10	8.62E-06	2.55E-06
657	2.50E-02	4.87E-03	5.79E-06	5.38E-04	5.48E-09	1.04E-05	2.26E-08	4.09E-08	6.16E-10	1.02E-05	2.65E-06
661	2.55E-02	4.90E-03	6.12E-06	5.20E-04	5.65E-09	9.57E-06	1.54E-08	1.87E-08	3.70E-10	4.17E-06	2.42E-06
665	2.35E-02	4.90E-03	6.39E-06	5.52E-04	8.85E-09	1.21E-05	7.56E-09	1.53E-08	-9.92E-11	8.58E-07	2.80E-06
669	2.44E-02	4.92E-03	1.94E-05	5.09E-04	1.24E-08	1.81E-05	5.45E-08	6.53E-08	2.62E-09	5.89E-06	2.56E-06
673	2.44E-02	4.88E-03	8.89E-06	4.88E-04	2.61E-08	1.22E-05	3.74E-08	5.21E-08	2.37E-09	4.46E-06	2.56E-06
677	2.56E-02	4.85E-03	6.75E-06	4.90E-04	1.14E-08	1.22E-05	1.25E-08	1.76E-08	3.29E-10	1.76E-05	2.49E-06
681	2.52E-02	4.87E-03	8.39E-06	4.74E-04	2.39E-08	1.42E-05	3.05E-08	5.27E-08	1.81E-09	6.43E-06	2.52E-06
685	2.49E-02	4.85E-03	6.76E-06	4.68E-04	1.93E-08	1.09E-05	2.07E-07	2.83E-07	1.07E-09	2.43E-06	2.45E-06
689	2.44E-02	4.92E-03	8.42E-06	4.42E-04	1.37E-08	9.82E-06	2.37E-08	3.46E-08	-1.06E-11	2.62E-06	2.19E-06
693	2.41E-02	4.88E-03	6.72E-06	4.72E-04	2.17E-08	1.10E-05	1.80E-08	3.04E-08	5.63E-10	2.62E-06	2.54E-06
697	2.40E-02	4.83E-03	8.28E-06	4.60E-04	2.62E-08	1.03E-05	2.50E-08	4.35E-08	9.62E-10	2.12E-06	2.30E-06
701	2.48E-02	4.85E-03	7.82E-06	4.70E-04	1.38E-08	1.14E-05	3.53E-08	5.34E-08	1.69E-09	6.38E-06	2.54E-06
705	2.31E-02	4.86E-03	4.80E-06	4.73E-04	4.48E-09	1.05E-05	3.09E-09	3.71E-09	-1.89E-10	2.42E-07	2.77E-06
709	2.06E-02	4.85E-03	6.94E-06	4.32E-04	6.75E-09	9.48E-06	3.55E-07	4.29E-07	1.40E-09	3.09E-06	2.65E-06
713	2.13E-02	4.87E-03	4.82E-06	4.22E-04	4.34E-09	1.02E-05	8.71E-09	1.23E-08	2.36E-10	1.70E-06	2.24E-06

717	2.35E-02	4.92E-03	9.70E-06	4.49E-04	1.94E-08	1.45E-04	2.94E-08	4.87E-08	3.56E-09	2.32E-06	2.26E-06
721	2.47E-02	4.85E-03	4.81E-06	4.70E-04	5.88E-09	8.27E-06	1.93E-08	2.83E-08	1.80E-10	3.23E-06	2.47E-06
725	2.48E-02	4.85E-03	5.97E-06	4.38E-04	4.70E-09	9.93E-06	1.60E-08	1.72E-08	3.09E-11	7.21E-07	2.49E-06
729	2.62E-02	4.84E-03	6.07E-06	4.70E-04	5.52E-09	1.02E-05	1.93E-08	2.51E-08	5.30E-10	3.27E-06	2.62E-06
733	2.55E-02	4.86E-03	5.75E-06	4.55E-04	4.80E-09	1.01E-05	1.00E-08	1.29E-08	3.51E-11	2.89E-06	2.58E-06
737	2.50E-02	4.82E-03	5.72E-06	4.47E-04	6.18E-09	9.75E-06	1.25E-08	1.74E-08	5.27E-11	4.08E-06	2.65E-06
741	2.45E-02	4.86E-03	7.43E-06	4.34E-04	6.27E-09	1.10E-05	2.28E-08	2.98E-08	-2.25E-11	9.09E-06	2.28E-06
745	2.47E-02	4.87E-03	6.29E-06	4.44E-04	1.50E-08	9.99E-06	4.77E-08	7.84E-08	7.94E-09	5.80E-06	2.61E-06
749	2.49E-02	4.84E-03	8.72E-06	4.44E-04	6.46E-09	9.92E-06	2.25E-08	2.95E-08	8.40E-10	5.49E-06	2.43E-06
753	2.44E-02	4.86E-03	7.26E-06	4.29E-04	6.78E-09	1.08E-05	7.94E-08	1.35E-06	1.96E-09	9.16E-06	2.46E-06
757	2.33E-02	4.86E-03	6.43E-06	4.09E-04	7.55E-09	1.05E-05	1.40E-08	2.44E-08	1.07E-09	5.59E-06	2.52E-06
761	2.35E-02	4.88E-03	5.25E-06	4.17E-04	4.54E-09	1.03E-05	8.53E-09	1.17E-08	4.77E-10	1.85E-06	2.63E-06
765	2.37E-02	4.85E-03	5.60E-06	4.29E-04	5.01E-09	1.07E-05	9.91E-09	1.66E-08	4.95E-10	2.69E-06	2.60E-06
769	2.28E-02	4.84E-03	6.62E-06	4.01E-04	6.43E-09	1.02E-05	7.26E-09	9.89E-09	3.64E-10	1.95E-06	2.50E-06
773	2.20E-02	4.89E-03	8.92E-06	4.33E-04	6.03E-09	1.07E-05	7.76E-09	1.31E-08	2.86E-10	2.73E-06	2.74E-06
777	2.25E-02	4.84E-03	5.82E-06	4.71E-04	1.19E-08	1.10E-05	1.15E-08	1.86E-08	5.37E-10	1.93E-06	2.82E-06
781	2.29E-02	4.86E-03	6.05E-06	4.06E-04	1.59E-08	9.78E-06	8.34E-08	1.14E-07	1.39E-09	7.11E-06	2.68E-06
785	2.51E-02	4.86E-03	5.33E-06	4.06E-04	2.82E-08	9.09E-06	6.08E-08	8.72E-08	4.73E-09	5.48E-06	2.50E-06
789	2.44E-02	4.81E-03	5.18E-06	3.49E-04	4.41E-09	8.34E-06	5.38E-08	7.15E-08	6.30E-10	3.60E-06	2.44E-06
793	2.61E-02	4.82E-03	5.88E-06	3.66E-04	4.80E-09	9.59E-06	3.62E-08	4.76E-08	4.39E-10	4.28E-06	2.51E-06
797	2.33E-02	4.85E-03	1.13E-05	4.02E-04	3.80E-09	9.34E-06	3.63E-08	4.52E-08	7.83E-10	7.59E-06	2.53E-06
801	2.38E-02	4.85E-03	4.43E-06	4.36E-04	5.44E-09	8.72E-06	1.15E-08	1.69E-08	6.11E-10	2.81E-05	2.40E-06
805	2.27E-02	4.81E-03	7.50E-06	4.54E-04	1.89E-08	1.07E-05	2.32E-08	3.53E-08	1.51E-09	5.25E-06	2.52E-06
809	2.22E-02	4.82E-03	7.72E-06	4.50E-04	3.29E-08	1.09E-05	1.23E-08	2.78E-08	1.03E-09	2.51E-06	2.49E-06
813	2.23E-02	4.83E-03	6.01E-06	4.72E-04	1.61E-08	1.09E-05	1.60E-08	2.85E-08	7.36E-10	5.20E-06	2.51E-06
817	2.23E-02	4.85E-03	6.85E-06	4.44E-04	3.32E-08	1.10E-05	1.32E-08	2.71E-08	1.13E-09	2.97E-05	2.44E-06
821	2.18E-02	4.82E-03	7.86E-06	4.29E-04	1.82E-08	9.91E-06	1.32E-08	2.23E-08	4.73E-10	2.13E-06	2.38E-06

825	2.18E-02	4.81E-03	6.50E-06	4.42E-04	2.02E-08	1.05E-05	9.33E-09	1.92E-08	4.39E-10	1.47E-05	2.50E-06
829	2.09E-02	4.81E-03	5.72E-06	4.22E-04	1.44E-08	1.01E-05	1.16E-08	1.79E-08	4.44E-10	1.86E-06	2.64E-06
833	2.17E-02	4.91E-03	6.44E-06	4.34E-04	1.98E-08	1.18E-05	1.49E-08	2.22E-08	9.11E-10	5.17E-06	2.49E-06
837	2.11E-02	4.82E-03	6.27E-06	3.86E-04	2.06E-08	9.85E-06	2.26E-08	3.42E-08	1.11E-09	3.84E-06	2.31E-06
841	2.04E-02	4.84E-03	6.26E-06	3.80E-04	1.72E-08	9.35E-06	3.03E-08	4.24E-08	7.51E-10	1.36E-06	2.40E-06
845	2.05E-02	4.77E-03	9.60E-06	4.32E-04	2.31E-08	1.71E-05	1.77E-08	3.14E-08	9.83E-10	2.14E-06	2.43E-06
849	2.10E-02	4.84E-03	6.03E-06	4.27E-04	2.66E-08	1.07E-05	1.24E-08	2.50E-08	4.54E-10	2.32E-06	2.36E-06
853	2.10E-02	4.81E-03	5.14E-06	4.49E-04	2.94E-08	1.08E-05	6.82E-09	1.43E-08	4.66E-10	4.86E-07	2.39E-06
857	2.11E-02	4.82E-03	5.80E-06	4.29E-04	2.98E-08	1.09E-05	4.68E-08	7.58E-08	1.40E-09	1.41E-06	2.29E-06
861	2.03E-02	5.18E-03	5.02E-06	4.43E-04	2.62E-08	1.11E-05	2.02E-08	3.55E-08	1.03E-09	9.48E-07	2.51E-06
865	1.98E-02	4.83E-03	4.84E-06	4.30E-04	1.88E-08	1.01E-05	9.84E-09	1.75E-08	3.57E-10	1.93E-07	2.41E-06
869	1.99E-02	4.82E-03	5.49E-06	4.08E-04	2.46E-08	1.00E-05	8.78E-09	1.78E-08	2.92E-10	5.06E-07	2.35E-06
873	1.81E-02	4.83E-03	5.04E-06	3.97E-04	2.44E-08	1.07E-05	9.31E-09	1.88E-08	6.15E-10	1.30E-06	2.42E-06
877	1.95E-02	4.80E-03	5.17E-06	3.88E-04	2.25E-08	9.76E-06	2.62E-08	4.21E-08	1.41E-09	4.23E-07	2.43E-06
881	1.99E-02	4.81E-03	4.17E-06	3.90E-04	1.85E-08	9.29E-06	8.57E-09	1.74E-08	3.38E-11	4.14E-06	2.42E-06
885	1.77E-02	4.81E-03	4.01E-06	3.72E-04	1.50E-08	9.53E-06	1.19E-08	2.06E-08	5.14E-10	5.33E-07	2.42E-06
889	1.81E-02	4.79E-03	7.04E-06	3.58E-04	1.45E-08	1.04E-05	3.92E-08	5.57E-08	1.37E-09	6.06E-06	2.70E-06
893	1.95E-02	4.79E-03	3.88E-06	3.69E-04	1.31E-08	8.90E-06	6.50E-09	1.27E-08	4.50E-10	9.48E-07	2.68E-06
897	1.86E-02	4.74E-03	3.21E-06	4.40E-04	1.21E-08	8.66E-06	1.59E-08	3.01E-08	1.01E-10	8.00E-06	2.34E-06
901	1.74E-02	4.80E-03	2.15E-05	4.24E-04	1.76E-08	8.86E-06	2.55E-08	3.77E-08	1.24E-09	1.77E-06	2.27E-06
905	1.58E-02	4.83E-03	4.78E-06	4.59E-04	9.44E-09	8.85E-06	1.76E-08	2.36E-08	5.28E-10	1.80E-06	2.55E-06
909	1.53E-02	4.80E-03	5.32E-06	4.54E-04	1.25E-08	1.05E-05	1.25E-08	1.95E-08	5.96E-10	1.12E-06	2.60E-06
913	1.80E-02	4.80E-03	5.92E-06	4.30E-04	1.97E-08	1.07E-05	1.82E-08	3.18E-08	1.35E-09	4.43E-06	2.69E-06
917	1.90E-02	4.79E-03	5.05E-06	4.20E-04	2.45E-08	9.98E-06	1.83E-08	3.56E-08	6.14E-10	3.72E-06	2.38E-06
921	1.92E-02	4.79E-03	4.93E-06	4.18E-04	1.96E-08	9.58E-06	2.10E-08	3.25E-08	1.63E-09	2.30E-06	2.52E-06
925	1.95E-02	4.79E-03	4.06E-06	4.04E-04	1.32E-08	8.45E-06	7.95E-09	1.68E-08	2.67E-10	6.84E-07	2.48E-06
929	1.71E-02	4.79E-03	4.49E-06	3.85E-04	1.61E-08	8.71E-06	3.34E-08	4.98E-08	7.27E-10	1.12E-06	2.35E-06

933	1.72E-02	4.79E-03	1.23E-05	3.64E-04	1.31E-08	8.60E-06	1.93E-08	2.65E-08	7.02E-10	9.58E-07	2.41E-06
937	1.66E-02	4.81E-03	4.37E-06	4.22E-04	1.29E-08	8.97E-06	9.63E-09	1.59E-08	2.09E-10	1.70E-05	2.34E-06
941	1.52E-02	4.76E-03	3.41E-06	4.59E-04	1.01E-08	1.00E-05	1.47E-08	2.16E-08	1.05E-09	4.70E-07	2.61E-06
945	1.56E-02	4.81E-03	3.88E-06	4.51E-04	1.27E-08	1.03E-05	3.27E-08	4.90E-08	1.79E-09	2.02E-06	2.67E-06
949	1.54E-02	4.99E-03	5.77E-06	4.60E-04	1.92E-08	9.12E-06	1.32E-07	1.42E-07	4.23E-09	1.13E-05	2.33E-06
953	1.45E-02	4.83E-03	9.99E-06	4.45E-04	1.14E-08	8.39E-06	2.33E-08	3.52E-08	8.14E-10	2.51E-06	2.45E-06
957	1.54E-02	4.87E-03	3.52E-06	4.57E-04	1.89E-08	8.62E-06	1.62E-08	2.66E-08	1.80E-09	4.80E-06	2.40E-06
961	1.75E-02	4.80E-03	3.01E-06	4.14E-04	1.30E-08	7.25E-06	1.71E-08	2.56E-08	1.18E-09	1.99E-06	2.43E-06
965	1.78E-02	4.82E-03	2.76E-06	4.51E-04	1.02E-08	7.68E-06	5.83E-09	8.63E-09	3.66E-10	4.24E-07	2.17E-06
969	1.66E-02	4.89E-03	5.82E-06	4.55E-04	1.34E-08	7.52E-06	4.15E-08	5.45E-08	1.02E-09	2.55E-06	2.34E-06
973	1.77E-02	1.07E-02	1.40E-05	4.54E-04	1.01E-07	7.39E-06	1.03E-07	1.28E-07	1.19E-08	1.19E-05	2.28E-06
977	1.45E-02	4.78E-03	4.08E-06	5.03E-04	1.29E-08	8.61E-06	5.81E-08	7.87E-08	1.64E-09	1.42E-06	2.61E-06
981	1.54E-02	4.75E-03	2.84E-06	4.97E-04	1.34E-08	9.17E-06	3.56E-08	4.70E-08	1.08E-09	6.63E-07	2.48E-06
985	1.61E-02	4.75E-03	2.59E-06	5.10E-04	1.21E-08	1.03E-05	1.63E-08	2.58E-08	6.90E-10	4.59E-07	2.39E-06
989	1.46E-02	4.78E-03	3.84E-06	4.65E-04	1.19E-08	8.49E-06	1.23E-08	2.13E-08	7.34E-10	5.94E-07	2.50E-06
993	1.73E-02	4.77E-03	2.55E-06	4.06E-04	1.21E-08	8.22E-06	1.17E-08	2.09E-08	7.16E-10	1.16E-06	2.43E-06
997	1.55E-02	4.78E-03	4.14E-06	4.67E-04	1.40E-08	8.33E-06	8.17E-07	1.65E-06	2.81E-09	8.03E-07	2.41E-06
1001	1.76E-02	4.82E-03	4.94E-06	4.73E-04	1.43E-08	1.03E-05	3.51E-08	5.14E-08	1.55E-09	1.30E-05	2.39E-06
1005	1.57E-02	4.78E-03	3.20E-06	4.80E-04	1.17E-08	9.54E-06	1.07E-08	1.96E-08	6.56E-10	1.98E-06	2.45E-06
1009	1.79E-02	4.86E-03	3.99E-06	4.55E-04	1.43E-08	8.83E-06	1.94E-08	3.21E-08	1.04E-09	5.43E-06	2.60E-06
1013	1.61E-02	4.81E-03	4.07E-06	4.82E-04	1.29E-08	8.71E-06	1.21E-08	2.38E-08	6.79E-10	6.41E-06	2.35E-06
1017	1.59E-02	4.83E-03	3.85E-06	4.49E-04	1.28E-08	8.72E-06	1.10E-08	2.36E-08	7.17E-10	2.69E-06	2.33E-06
1021	1.85E-02	4.86E-03	1.72E-06	3.96E-04	1.45E-08	7.73E-06	1.49E-08	2.07E-08	1.15E-09	1.41E-06	2.23E-06
1025	1.62E-02	4.94E-03	3.44E-06	4.00E-04	1.26E-08	6.89E-06	8.46E-09	1.48E-08	7.20E-10	2.24E-06	2.34E-06
1029	1.51E-02	4.90E-03	4.12E-06	4.38E-04	1.12E-08	7.55E-06	1.75E-08	5.24E-08	1.48E-09	1.81E-06	2.37E-06
1033	1.50E-02	4.81E-03	2.15E-06	4.53E-04	7.84E-09	8.19E-06	1.08E-08	1.46E-08	5.64E-10	9.51E-07	2.52E-06
1037	1.47E-02	4.81E-03	2.26E-06	4.31E-04	8.60E-09	7.98E-06	5.35E-09	7.58E-09	6.01E-10	4.53E-07	2.47E-06

1041	1.46E-02	4.83E-03	3.56E-06	4.32E-04	1.29E-08	2.15E-05	9.37E-09	1.25E-08	7.68E-10	4.38E-07	2.56E-06
1045	1.46E-02	4.82E-03	1.73E-05	4.80E-04	8.66E-09	7.89E-06	5.36E-09	9.05E-09	4.06E-10	5.38E-07	2.62E-06
1049	1.52E-02	4.82E-03	6.18E-06	4.56E-04	1.11E-08	8.19E-06	5.61E-08	7.91E-08	7.57E-10	8.44E-07	2.59E-06
1053	1.51E-02	4.82E-03	5.54E-06	4.73E-04	8.99E-09	8.62E-06	6.80E-08	8.75E-08	9.74E-10	1.94E-06	2.51E-06
1057	1.68E-02	5.63E-03	7.61E-06	5.41E-04	1.30E-08	8.62E-06	5.84E-08	7.55E-08	1.67E-09	4.83E-06	2.51E-06
1061	1.71E-02	4.81E-03	4.00E-06	5.35E-04	1.09E-08	8.39E-06	1.55E-08	2.24E-08	1.15E-09	1.29E-06	2.46E-06
1065	1.72E-02	4.80E-03	1.01E-05	5.00E-04	1.45E-08	8.91E-06	3.47E-08	6.22E-08	1.74E-09	1.40E-05	2.52E-06
1069	1.87E-02	4.79E-03	4.96E-06	5.03E-04	1.21E-08	8.50E-06	2.04E-08	3.11E-08	7.14E-10	3.84E-06	2.74E-06
1073	1.83E-02	4.79E-03	5.45E-06	6.10E-04	2.24E-08	9.90E-06	4.16E-08	7.80E-08	7.11E-09	1.99E-06	2.59E-06
1077	1.88E-02	4.80E-03	5.09E-06	5.48E-04	1.67E-08	1.04E-05	9.31E-09	1.67E-08	6.53E-10	2.16E-06	2.64E-06
1081	1.99E-02	4.77E-03	1.48E-05	5.66E-04	1.68E-08	9.46E-06	2.86E-08	4.25E-08	9.30E-10	4.48E-06	2.60E-06
1085	1.69E-02	4.87E-03	6.06E-06	5.78E-04	1.35E-08	9.22E-06	1.11E-08	1.91E-08	3.81E-10	1.34E-06	2.42E-06
1089	1.95E-02	4.82E-03	6.38E-06	5.76E-04	1.42E-08	8.99E-06	3.39E-08	4.79E-08	1.06E-09	9.45E-06	2.31E-06
1093	1.81E-02	4.79E-03	4.99E-06	6.19E-04	1.44E-08	9.74E-06	1.90E-08	3.35E-08	1.91E-09	6.62E-06	2.41E-06
1097	2.11E-02	4.83E-03	5.75E-06	5.41E-04	1.88E-08	1.00E-05	1.09E-08	2.08E-08	5.00E-10	1.87E-05	2.49E-06
1101	2.11E-02	4.81E-03	5.32E-06	5.41E-04	2.03E-08	1.42E-05	2.76E-08	4.77E-08	1.06E-09	4.12E-06	2.51E-06
1105	2.05E-02	4.82E-03	6.42E-06	5.09E-04	2.22E-08	9.00E-06	3.20E-08	5.33E-08	2.07E-09	5.47E-06	2.45E-06
1109	1.74E-02	4.82E-03	4.58E-06	5.52E-04	1.12E-08	1.05E-05	9.01E-09	1.48E-08	4.30E-10	4.76E-06	2.52E-06
1113	1.72E-02	4.83E-03	4.13E-06	5.53E-04	1.02E-08	8.26E-06	1.03E-08	1.55E-08	3.17E-10	9.90E-07	2.44E-06
1117	1.79E-02	4.81E-03	5.19E-06	5.32E-04	1.45E-08	9.92E-06	7.54E-09	1.64E-08	1.22E-09	5.05E-07	2.53E-06
1121	1.89E-02	4.85E-03	5.91E-06	4.97E-04	1.29E-08	2.82E-05	1.43E-08	2.45E-08	6.27E-10	3.64E-06	2.43E-06
1125	1.71E-02	4.78E-03	3.85E-06	4.76E-04	1.35E-08	9.20E-06	1.98E-08	3.12E-08	3.22E-09	2.72E-06	2.51E-06
1129	1.70E-02	4.82E-03	4.10E-06	4.74E-04	1.07E-08	8.61E-06	6.84E-09	5.13E-08	2.39E-10	2.38E-06	2.42E-06
1133	1.80E-02	4.80E-03	4.25E-06	5.01E-04	8.85E-09	8.41E-06	5.16E-08	6.63E-08	5.42E-10	1.88E-06	2.43E-06
1137	1.80E-02	4.81E-03	4.16E-06	5.64E-04	1.07E-08	1.31E-05	3.36E-08	5.09E-08	1.47E-09	8.49E-06	2.49E-06
1141	1.81E-02	4.80E-03	3.66E-06	5.74E-04	9.70E-09	9.20E-06	2.78E-08	3.28E-08	1.30E-09	1.69E-06	2.47E-06
1145	1.71E-02	4.79E-03	9.87E-06	5.35E-04	1.13E-08	9.51E-06	3.24E-08	4.91E-08	6.27E-10	2.41E-06	2.60E-06

1149	2.18E-02	4.81E-03	4.30E-06	5.08E-04	2.64E-08	9.50E-06	1.75E-08	2.92E-08	1.47E-09	1.33E-06	2.49E-06
1153	1.90E-02	4.85E-03	1.53E-05	4.97E-04	1.78E-08	1.33E-05	2.51E-08	3.93E-08	1.62E-09	7.78E-06	2.38E-06
1157	1.86E-02	4.76E-03	4.32E-06	5.30E-04	1.08E-08	9.78E-06	1.56E-08	2.19E-08	5.43E-10	2.02E-06	2.58E-06
1161	1.83E-02	4.80E-03	4.75E-06	4.75E-04	1.36E-08	9.91E-06	1.17E-08	2.01E-08	3.92E-10	3.33E-06	2.62E-06
1165	1.82E-02	4.77E-03	4.26E-06	4.51E-04	1.11E-08	9.30E-06	1.12E-08	1.69E-08	1.31E-10	1.95E-06	2.53E-06
1169	1.93E-02	4.77E-03	7.13E-06	4.21E-04	1.76E-08	8.91E-06	1.22E-08	1.96E-08	5.40E-10	6.08E-05	2.75E-06
1173	1.99E-02	4.78E-03	4.37E-06	4.99E-04	1.46E-08	9.63E-06	1.18E-08	1.78E-08	1.42E-10	1.56E-06	2.41E-06
1177	1.89E-02	4.78E-03	4.58E-06	4.77E-04	1.00E-08	9.11E-06	8.03E-09	1.33E-08	2.53E-10	2.03E-06	2.56E-06
1181	1.85E-02	4.78E-03	3.74E-06	4.78E-04	1.26E-08	8.81E-06	1.02E-08	2.01E-08	2.82E-10	2.45E-06	2.73E-06
1185	2.05E-02	4.74E-03	8.80E-06	5.41E-04	1.11E-08	1.00E-05	5.03E-08	7.44E-08	9.90E-10	2.56E-06	2.50E-06
1189	1.92E-02	4.77E-03	3.71E-06	5.09E-04	9.19E-09	8.67E-06	6.25E-09	9.22E-09	1.37E-10	5.51E-06	2.60E-06
1193	2.07E-02	4.76E-03	4.01E-06	5.01E-04	9.91E-09	8.75E-06	1.41E-08	1.95E-08	6.04E-10	2.01E-06	2.45E-06
1197	2.00E-02	4.69E-03	5.03E-06	5.14E-04	1.01E-08	9.97E-06	1.08E-08	1.79E-08	3.07E-11	2.55E-06	2.60E-06
1201	2.11E-02	4.80E-03	5.35E-06	5.24E-04	1.31E-08	1.01E-05	2.76E-08	3.92E-08	3.63E-10	2.30E-06	2.56E-06
1205	2.20E-02	4.81E-03	6.18E-06	5.14E-04	1.97E-08	1.22E-05	2.66E-08	4.17E-08	8.60E-10	2.08E-06	2.91E-06
1209	2.09E-02	4.81E-03	6.08E-06	4.91E-04	1.60E-08	1.38E-05	4.06E-08	6.18E-08	5.72E-10	2.70E-06	2.86E-06
1213	2.19E-02	4.81E-03	5.91E-06	4.85E-04	1.87E-08	1.25E-05	2.10E-08	3.23E-08	3.23E-10	2.19E-06	2.77E-06
1217	2.11E-02	4.81E-03	5.03E-06	4.46E-04	1.69E-08	1.19E-05	1.78E-08	2.88E-08	1.19E-10	2.47E-06	2.79E-06
1221	1.89E-02	4.78E-03	6.19E-06	4.63E-04	1.52E-08	1.24E-05	2.66E-07	3.60E-07	1.85E-09	2.96E-06	2.50E-06
1225	2.03E-02	4.77E-03	8.49E-06	4.50E-04	1.39E-08	1.12E-05	8.34E-08	1.13E-07	1.24E-09	6.31E-06	2.74E-06
1229	2.14E-02	4.76E-03	6.39E-06	4.34E-04	1.54E-08	1.11E-05	1.17E-07	1.69E-07	1.30E-09	5.53E-06	2.63E-06
1233	2.06E-02	4.81E-03	5.82E-06	4.04E-04	1.48E-08	1.06E-05	1.71E-07	2.47E-07	7.86E-10	1.18E-05	2.69E-06
1237	2.15E-02	4.78E-03	4.51E-06	3.77E-04	1.26E-08	9.75E-06	6.75E-09	1.34E-08	6.31E-10	4.82E-06	2.39E-06
1241	2.13E-02	4.79E-03	9.97E-06	3.84E-04	1.96E-08	1.03E-05	5.57E-07	7.91E-07	2.57E-09	2.40E-05	2.53E-06
1245	2.26E-02	4.79E-03	5.95E-06	4.25E-04	1.23E-08	1.04E-05	1.47E-08	2.07E-08	1.00E-09	2.55E-06	2.66E-06
1249	2.16E-02	4.80E-03	3.57E-05	4.03E-04	1.31E-08	1.14E-05	3.25E-08	6.08E-08	9.10E-10	1.19E-06	2.49E-06
1253	2.00E-02	4.78E-03	5.93E-06	3.72E-04	1.57E-08	1.13E-05	1.75E-08	2.81E-08	5.95E-10	2.82E-06	2.49E-06

1257	1.97E-02	4.74E-03	6.18E-06	3.26E-04	1.83E-08	1.43E-05	1.14E-08	2.34E-08	7.87E-10	2.34E-06	2.42E-06
1261	2.01E-02	4.78E-03	5.62E-06	3.56E-04	1.30E-08	1.05E-05	1.65E-08	2.66E-08	8.51E-10	4.56E-06	2.38E-06
1265	2.18E-02	4.78E-03	7.64E-06	4.49E-04	3.77E-08	1.12E-05	4.55E-08	7.96E-08	4.30E-09	5.62E-06	2.28E-06
1269	2.10E-02	4.78E-03	2.08E-04	3.80E-04	1.52E-08	1.13E-05	3.24E-08	4.17E-08	6.02E-10	1.26E-06	2.33E-06
1273	2.00E-02	4.77E-03	6.16E-06	3.79E-04	2.07E-08	1.17E-05	2.83E-08	4.44E-08	9.32E-10	3.61E-06	2.41E-06
1277	2.01E-02	4.73E-03	1.09E-05	4.17E-04	1.28E-08	1.16E-05	2.44E-08	3.51E-08	6.92E-10	1.24E-06	2.51E-06
1281	1.92E-02	4.76E-03	6.10E-06	4.66E-04	1.61E-08	1.24E-05	2.84E-08	4.00E-08	9.93E-10	1.68E-06	2.38E-06
1285	2.03E-02	4.81E-03	5.36E-06	4.76E-04	1.72E-08	1.35E-05	1.76E-08	2.78E-08	7.04E-10	9.46E-07	2.51E-06
1289	2.07E-02	4.81E-03	5.31E-05	4.67E-04	4.20E-08	1.55E-05	6.10E-07	8.22E-07	8.47E-09	9.12E-06	2.37E-06
1293	2.01E-02	4.79E-03	5.25E-06	4.71E-04	2.38E-08	1.61E-05	3.46E-08	4.05E-08	2.03E-09	1.44E-06	2.40E-06
1297	1.99E-02	4.79E-03	5.19E-06	4.50E-04	1.72E-08	1.08E-05	2.27E-08	3.64E-08	7.20E-10	1.15E-06	2.19E-06
1301	2.10E-02	4.73E-03	4.47E-06	4.32E-04	1.24E-08	1.05E-05	1.41E-08	1.84E-08	8.69E-10	4.74E-07	2.26E-06
1305	1.79E-02	4.77E-03	4.79E-06	4.02E-04	1.24E-08	9.61E-06	2.17E-08	3.48E-08	7.21E-10	3.75E-06	2.21E-06
1309	1.96E-02	4.80E-03	4.11E-06	4.72E-04	9.26E-09	9.90E-06	1.50E-08	2.10E-08	8.86E-10	1.98E-06	2.10E-06
1313	2.27E-02	4.81E-03	5.32E-06	4.55E-04	1.11E-08	1.27E-05	2.11E-08	3.07E-08	6.08E-10	2.74E-06	2.23E-06
1317	2.26E-02	4.82E-03	5.75E-06	4.18E-04	1.27E-08	1.09E-05	3.27E-08	4.88E-08	1.22E-09	2.33E-06	2.19E-06
1321	2.17E-02	4.79E-03	6.98E-06	4.04E-04	1.63E-08	1.33E-05	3.37E-08	4.68E-08	7.94E-10	2.86E-06	2.32E-06
1325	2.18E-02	4.79E-03	5.90E-06	3.39E-04	1.91E-08	1.12E-05	2.97E-08	4.13E-08	1.10E-09	9.00E-07	2.01E-06
1329	2.31E-02	4.81E-03	6.21E-06	3.58E-04	1.37E-08	1.29E-05	4.00E-08	6.82E-08	1.05E-09	3.04E-06	2.05E-06
1333	2.41E-02	4.88E-03	6.08E-06	3.88E-04	1.01E-08	1.23E-05	2.49E-08	4.39E-08	6.65E-10	2.81E-06	2.20E-06
1337	2.24E-02	4.81E-03	4.53E-06	3.63E-04	9.35E-09	1.15E-05	3.37E-08	4.56E-08	8.58E-10	1.69E-06	2.16E-06
1341	2.32E-02	4.80E-03	4.66E-06	3.73E-04	1.12E-08	1.08E-05	2.85E-08	4.23E-08	8.79E-10	2.21E-06	2.01E-06
1345	2.19E-02	4.79E-03	5.32E-06	3.78E-04	1.18E-08	1.15E-05	3.33E-08	4.31E-08	8.15E-10	1.43E-05	2.12E-06
1349	2.09E-02	4.83E-03	5.23E-06	3.34E-04	3.06E-08	1.10E-05	5.37E-08	8.61E-08	2.25E-09	1.20E-05	1.95E-06
1353	2.10E-02	5.00E-03	3.76E-06	3.25E-04	9.19E-09	9.47E-06	1.33E-08	1.97E-08	4.15E-10	5.27E-06	1.95E-06
1357	2.14E-02	4.84E-03	9.22E-06	3.54E-04	2.93E-08	1.09E-05	5.07E-08	6.90E-08	1.98E-09	2.68E-06	1.97E-06
1361	2.31E-02	4.99E-03	1.10E-05	4.00E-04	3.71E-08	1.44E-05	4.03E-08	6.04E-08	3.03E-09	3.93E-06	2.23E-06

1365	2.05E-02	4.88E-03	5.36E-06	3.93E-04	5.10E-08	1.17E-05	5.39E-08	8.50E-08	7.54E-09	2.40E-06	2.33E-06
1369	2.12E-02	4.77E-03	5.85E-06	3.94E-04	2.68E-08	1.22E-05	2.99E-08	4.11E-08	2.50E-09	5.24E-06	2.59E-06
1373	2.20E-02	4.74E-03	6.21E-06	3.75E-04	2.15E-08	1.77E-05	3.27E-08	4.79E-08	1.96E-09	4.23E-06	2.73E-06
1377	2.51E-02	4.75E-03	6.59E-06	3.99E-04	2.01E-08	1.30E-05	2.62E-08	3.89E-08	2.85E-09	9.18E-06	2.38E-06
1381	2.34E-02	4.73E-03	5.84E-06	4.08E-04	2.75E-08	1.33E-05	2.66E-08	4.24E-08	2.90E-09	2.13E-06	2.43E-06
1385	2.24E-02	4.76E-03	5.72E-06	4.34E-04	2.46E-08	1.40E-05	2.56E-08	3.98E-08	1.95E-09	7.17E-07	2.57E-06
1389	2.32E-02	4.78E-03	5.29E-06	3.69E-04	2.11E-08	1.22E-05	1.58E-08	2.78E-08	1.13E-09	2.61E-05	2.33E-06
1393	2.52E-02	4.77E-03	5.28E-06	3.88E-04	1.05E-08	1.19E-05	1.45E-08	2.32E-08	8.53E-10	1.11E-06	2.14E-06
1397	2.41E-02	4.78E-03	6.08E-06	4.14E-04	1.60E-08	1.33E-05	2.78E-08	3.84E-08	1.07E-09	2.67E-06	2.45E-06
1401	2.42E-02	4.77E-03	5.24E-06	3.94E-04	1.56E-08	1.35E-05	4.35E-08	5.60E-08	1.49E-09	5.23E-06	2.39E-06
1405	2.38E-02	4.85E-03	5.79E-06	3.74E-04	1.37E-08	1.49E-05	1.81E-08	3.04E-08	7.37E-10	2.55E-06	2.22E-06
1409	2.20E-02	4.77E-03	7.02E-06	3.55E-04	2.48E-08	1.36E-05	1.14E-08	2.02E-08	8.45E-10	1.45E-06	2.05E-06
1413	2.29E-02	4.76E-03	6.98E-06	4.00E-04	2.65E-08	1.46E-05	1.17E-08	2.14E-08	1.03E-09	2.51E-06	2.30E-06
1417	2.33E-02	4.76E-03	7.24E-06	4.14E-04	1.59E-08	1.54E-05	2.73E-08	4.16E-08	1.52E-09	1.35E-05	2.36E-06
1421	2.40E-02	4.75E-03	8.19E-06	4.08E-04	1.96E-08	1.30E-05	4.80E-08	5.48E-08	1.82E-09	4.79E-06	2.34E-06
1425	2.28E-02	4.77E-03	8.79E-06	3.76E-04	2.07E-08	1.36E-05	3.51E-08	5.04E-08	1.57E-09	2.06E-05	2.07E-06
1429	2.17E-02	1.17E-02	9.98E-06	3.68E-04	1.67E-08	1.29E-05	3.08E-08	4.41E-08	1.54E-09	8.56E-06	2.03E-06
1433	2.20E-02	4.77E-03	6.63E-06	3.74E-04	1.32E-08	1.18E-05	2.54E-08	3.55E-08	1.14E-09	1.84E-05	2.17E-06
1437	2.22E-02	4.77E-03	5.57E-06	3.86E-04	1.69E-08	1.21E-05	2.06E-08	2.59E-08	2.09E-09	6.53E-06	2.17E-06
1441	2.24E-02	4.82E-03	6.50E-06	3.95E-04	1.39E-08	1.39E-05	2.04E-08	2.98E-08	8.34E-10	6.46E-06	2.28E-06
1445	2.16E-02	4.78E-03	6.86E-06	3.81E-04	1.62E-08	1.30E-05	2.26E-08	3.50E-08	6.38E-10	6.57E-06	2.34E-06
1449	2.27E-02	4.81E-03	6.11E-06	4.10E-04	1.39E-08	1.38E-05	1.62E-08	2.58E-08	6.26E-10	6.75E-06	2.23E-06
1453	2.27E-02	4.78E-03	5.16E-06	4.13E-04	1.10E-08	1.29E-05	1.84E-08	2.55E-08	6.11E-10	2.65E-05	2.35E-06
1457	2.24E-02	4.80E-03	5.76E-06	3.91E-04	1.82E-08	1.63E-05	3.26E-08	5.17E-08	1.17E-09	3.14E-06	2.24E-06
1461	2.18E-02	4.78E-03	5.69E-06	3.88E-04	1.45E-08	1.34E-05	1.55E-08	2.32E-08	4.24E-10	6.79E-06	2.35E-06
1465	2.14E-02	4.77E-03	5.85E-06	3.86E-04	1.51E-08	1.45E-05	1.06E-08	1.89E-08	6.84E-10	5.72E-06	2.38E-06
1469	2.10E-02	4.80E-03	5.42E-06	3.70E-04	1.84E-08	1.40E-05	2.49E-08	4.44E-08	2.89E-09	3.95E-06	2.36E-06

1473	2.02E-02	4.81E-03	7.38E-06	3.66E-04	1.98E-08	1.33E-05	2.96E-08	4.66E-08	1.62E-09	8.88E-06	2.15E-06
1477	2.12E-02	4.76E-03	6.07E-06	3.25E-04	1.91E-08	1.48E-05	1.27E-08	2.16E-08	6.70E-10	7.61E-06	2.11E-06
1481	2.14E-02	4.78E-03	6.54E-06	3.09E-04	1.22E-08	1.27E-05	2.82E-08	6.37E-08	6.66E-10	2.38E-06	2.43E-06
1485	2.26E-02	4.96E-03	5.87E-06	2.82E-04	1.16E-08	1.33E-05	2.34E-08	4.27E-08	8.16E-10	2.09E-06	2.29E-06
1489	2.12E-02	4.77E-03	7.17E-06	3.39E-04	2.50E-08	1.49E-05	2.26E-08	3.71E-08	2.63E-09	2.79E-06	2.19E-06
1493	2.12E-02	4.76E-03	5.36E-06	3.55E-04	1.54E-08	1.61E-05	1.39E-08	1.97E-08	1.69E-10	2.87E-06	2.35E-06
1497	2.06E-02	4.77E-03	5.70E-06	3.51E-04	2.16E-08	1.51E-05	1.48E-08	2.42E-08	2.86E-10	2.33E-06	2.29E-06
1501	2.09E-02	4.79E-03	4.59E-06	3.68E-04	1.10E-08	1.69E-05	1.70E-08	2.11E-08	5.59E-10	4.60E-06	2.35E-06
1505	1.94E-02	4.78E-03	5.39E-06	3.63E-04	1.46E-08	1.57E-05	2.06E-08	2.70E-08	6.57E-10	5.11E-06	2.38E-06
1509	1.91E-02	4.89E-03	6.37E-06	3.50E-04	2.06E-08	1.44E-05	4.60E-08	6.56E-08	3.67E-09	7.46E-06	2.15E-06
1513	1.91E-02	4.78E-03	7.95E-06	3.60E-04	1.37E-08	1.39E-05	2.96E-08	3.82E-08	8.72E-10	8.74E-06	2.10E-06
1517	2.14E-02	4.79E-03	5.76E-06	4.16E-04	1.44E-08	1.39E-05	2.71E-08	3.76E-08	7.94E-10	5.05E-05	2.08E-06
1521	2.18E-02	4.80E-03	6.03E-06	4.23E-04	1.62E-08	1.41E-05	4.17E-08	5.51E-08	1.59E-09	4.49E-06	2.22E-06
1525	2.15E-02	4.80E-03	5.02E-06	4.32E-04	1.38E-08	1.53E-05	2.56E-08	3.78E-08	7.54E-10	1.26E-05	2.36E-06
1529	1.97E-02	4.78E-03	5.84E-06	4.27E-04	1.69E-08	1.65E-05	2.28E-08	2.96E-08	5.92E-10	1.29E-05	2.44E-06
1533	1.91E-02	5.03E-03	7.69E-06	4.04E-04	3.86E-08	2.91E-05	5.70E-08	8.69E-08	8.99E-09	6.77E-06	2.44E-06
1537	1.88E-02	4.81E-03	8.39E-06	3.75E-04	2.24E-08	1.33E-05	7.64E-08	1.14E-07	3.71E-09	1.55E-05	2.39E-06
1541	1.76E-02	4.76E-03	5.46E-06	3.46E-04	8.65E-09	1.23E-05	2.12E-08	2.82E-08	5.87E-10	8.00E-06	2.38E-06
1545	1.90E-02	4.78E-03	6.77E-06	3.41E-04	6.23E-08	1.44E-05	2.78E-08	3.80E-08	9.66E-10	3.36E-05	2.29E-06
1549	1.81E-02	4.82E-03	4.76E-06	3.52E-04	1.62E-08	1.38E-05	1.03E-08	2.93E-08	1.29E-09	1.84E-05	2.32E-06
1553	2.05E-02	4.77E-03	5.60E-06	3.44E-04	1.83E-08	1.37E-05	8.18E-08	1.35E-07	1.22E-09	1.44E-06	2.21E-06
1557	1.88E-02	4.79E-03	4.24E-06	3.08E-04	1.07E-08	1.26E-05	6.76E-09	1.02E-08	2.83E-10	6.48E-06	2.12E-06
1561	2.29E-02	4.76E-03	1.95E-05	3.38E-04	1.24E-08	1.56E-05	4.79E-07	8.48E-08	2.34E-09	1.76E-05	2.18E-06
1565	2.27E-02	4.92E-03	8.96E-06	3.54E-04	1.96E-08	1.50E-05	1.07E-06	1.35E-06	5.56E-09	9.99E-06	2.32E-06
1569	2.32E-02	4.78E-03	9.04E-06	3.42E-04	4.50E-08	1.61E-05	9.04E-08	1.24E-07	5.00E-09	7.11E-06	2.26E-06
1573	2.35E-02	4.78E-03	5.55E-06	3.47E-04	1.63E-08	1.47E-05	1.38E-08	2.11E-08	9.55E-10	2.54E-06	2.26E-06
1577	2.41E-02	4.76E-03	7.08E-06	3.38E-04	2.41E-08	1.85E-05	1.51E-08	2.47E-08	7.23E-10	3.92E-06	2.27E-06

1581	2.58E-02	4.81E-03	6.68E-06	3.42E-04	9.26E-09	1.64E-05	4.92E-09	6.96E-09	2.44E-10	6.54E-07	2.26E-06
1585	2.65E-02	4.76E-03	1.16E-05	3.44E-04	1.92E-08	1.86E-05	3.56E-08	7.52E-08	4.62E-09	7.14E-06	2.32E-06
1589	2.58E-02	4.79E-03	1.90E-05	3.61E-04	1.49E-08	1.55E-05	1.20E-07	1.45E-07	3.12E-09	1.29E-05	2.26E-06
1593	2.54E-02	4.87E-03	7.43E-06	3.45E-04	1.19E-08	1.54E-05	2.32E-08	3.05E-08	4.39E-10	8.00E-06	2.29E-06
1597	2.50E-02	4.79E-03	6.68E-06	3.22E-04	8.87E-09	1.80E-05	2.86E-08	3.52E-08	1.17E-09	8.43E-06	2.14E-06
1601	2.60E-02	4.78E-03	6.81E-06	3.52E-04	1.27E-08	1.60E-05	2.44E-08	2.70E-08	6.84E-10	4.19E-06	2.33E-06
1605	2.65E-02	4.80E-03	7.60E-06	3.68E-04	2.80E-08	1.94E-05	2.33E-08	4.18E-08	1.67E-09	2.56E-05	2.40E-06
1609	2.55E-02	4.87E-03	7.06E-06	3.89E-04	2.31E-08	1.81E-05	1.16E-08	2.17E-08	6.13E-10	2.87E-06	2.43E-06
1613	2.70E-02	4.80E-03	5.74E-06	3.91E-04	1.82E-08	1.66E-05	1.84E-08	3.00E-08	7.24E-10	3.69E-06	2.31E-06
1617	2.64E-02	4.78E-03	6.29E-06	4.28E-04	1.53E-08	1.74E-05	1.11E-08	1.63E-08	3.56E-10	3.55E-06	2.50E-06
1621	2.71E-02	4.79E-03	5.62E-06	4.25E-04	1.49E-08	1.69E-05	3.74E-08	2.54E-08	5.55E-09	1.52E-06	2.44E-06
1625	2.67E-02	4.77E-03	6.40E-06	4.03E-04	2.24E-08	1.64E-05	9.24E-09	1.72E-08	2.93E-10	3.69E-06	2.32E-06
1629	2.71E-02	4.80E-03	6.20E-06	4.38E-04	1.49E-08	1.71E-05	2.08E-08	2.43E-08	8.36E-10	2.19E-06	2.27E-06
1633	2.69E-02	4.75E-03	5.88E-06	4.26E-04	3.37E-08	1.87E-05	5.78E-08	6.15E-08	3.74E-09	7.88E-06	2.42E-06
1637	2.82E-02	4.80E-03	5.90E-06	4.32E-04	9.84E-09	1.75E-05	9.67E-09	1.55E-08	9.23E-10	7.92E-07	2.21E-06
1641	2.89E-02	4.77E-03	6.44E-06	4.57E-04	1.32E-08	1.91E-05	1.81E-08	2.51E-08	5.54E-10	3.08E-06	2.31E-06
1645	2.75E-02	4.78E-03	7.73E-06	4.78E-04	2.06E-08	2.11E-05	3.83E-08	1.19E-07	1.94E-09	2.36E-06	2.43E-06
1649	2.72E-02	5.00E-03	9.82E-06	4.81E-04	1.87E-08	2.14E-05	6.39E-08	8.35E-08	1.03E-09	4.04E-06	2.61E-06
1653	2.73E-02	4.79E-03	9.44E-06	5.12E-04	2.33E-08	2.08E-05	8.62E-08	8.60E-08	1.61E-09	3.67E-06	2.58E-06
1657	2.77E-02	4.75E-03	5.93E-06	5.24E-04	1.91E-08	3.23E-05	3.78E-08	6.67E-08	1.08E-09	9.89E-07	2.46E-06
1661	2.75E-02	4.76E-03	5.95E-06	5.13E-04	1.63E-08	3.23E-05	1.16E-08	1.60E-08	5.81E-10	1.26E-06	2.45E-06
1665	2.82E-02	4.77E-03	5.68E-06	5.00E-04	1.95E-08	1.93E-05	1.24E-08	1.92E-08	5.91E-10	1.01E-06	2.39E-06
1669	2.90E-02	4.80E-03	5.21E-06	4.42E-04	1.53E-08	1.80E-05	1.02E-08	1.71E-08	5.46E-10	1.77E-06	2.24E-06
1673	2.83E-02	4.78E-03	5.53E-06	4.23E-04	1.38E-08	1.71E-05	1.70E-08	2.29E-08	7.51E-10	1.02E-06	2.25E-06
1677	2.71E-02	4.92E-03	6.99E-06	4.46E-04	1.85E-08	1.82E-05	8.38E-09	1.38E-08	5.48E-10	3.98E-06	2.14E-06
1681	2.80E-02	4.75E-03	6.83E-06	4.75E-04	3.06E-08	1.84E-05	8.06E-09	1.90E-08	1.04E-09	6.79E-08	2.13E-06
1685	2.77E-02	4.77E-03	7.16E-06	4.73E-04	3.24E-08	2.04E-05	1.18E-08	2.15E-08	7.71E-10	2.54E-06	2.16E-06

1689	2.82E-02	4.78E-03	7.15E-06	4.74E-04	3.12E-08	1.90E-05	2.03E-08	3.55E-08	8.08E-10	3.19E-06	2.18E-06
1693	2.88E-02	4.75E-03	6.64E-06	4.72E-04	2.29E-08	1.82E-05	3.08E-08	5.46E-08	1.67E-09	1.38E-06	2.02E-06
1697	2.79E-02	4.78E-03	6.17E-06	4.88E-04	1.90E-08	1.70E-05	1.16E-08	1.87E-08	6.14E-10	4.37E-06	2.02E-06
1701	2.74E-02	4.84E-03	6.30E-06	5.01E-04	1.73E-08	2.20E-05	1.45E-08	2.60E-08	7.78E-10	2.88E-06	2.23E-06
1705	2.76E-02	4.91E-03	6.79E-06	4.95E-04	2.22E-08	1.90E-05	1.31E-08	2.33E-08	9.09E-10	1.67E-06	2.21E-06
1709	2.68E-02	4.76E-03	6.28E-06	4.76E-04	2.12E-08	2.19E-05	1.15E-08	2.02E-08	7.70E-10	1.71E-06	2.19E-06
1713	2.62E-02	4.78E-03	6.99E-06	4.79E-04	2.85E-08	1.93E-05	2.51E-08	3.96E-08	1.84E-09	9.12E-06	2.19E-06
1717	2.62E-02	4.79E-03	6.55E-06	4.99E-04	1.55E-08	1.90E-05	2.19E-08	2.83E-08	9.03E-10	1.82E-06	2.25E-06
1721	2.70E-02	4.74E-03	6.57E-06	5.03E-04	1.30E-08	1.92E-05	1.60E-08	2.29E-08	7.39E-10	9.99E-07	2.22E-06
1725	2.68E-02	4.84E-03	4.28E-06	4.88E-04	1.07E-08	1.73E-05	5.46E-09	8.63E-09	3.95E-10	3.65E-07	2.19E-06
1729	2.61E-02	4.77E-03	5.64E-06	4.67E-04	1.50E-08	1.73E-05	1.06E-08	1.83E-08	7.89E-10	1.90E-06	2.23E-06
1733	2.61E-02	4.77E-03	5.70E-06	4.54E-04	1.58E-08	1.63E-05	2.00E-08	2.92E-08	6.37E-10	2.12E-06	2.09E-06
1737	2.46E-02	4.77E-03	8.57E-06	4.10E-04	1.90E-08	2.29E-05	2.79E-08	3.64E-08	9.78E-10	3.91E-06	2.06E-06
1741	2.56E-02	4.75E-03	8.61E-06	4.12E-04	3.05E-08	1.80E-05	2.17E-08	3.74E-08	7.72E-10	2.43E-06	2.11E-06
1745	2.49E-02	4.78E-03	6.72E-06	4.21E-04	1.81E-08	1.64E-05	2.51E-08	3.34E-08	6.30E-10	4.80E-06	1.99E-06
1749	2.42E-02	4.78E-03	1.43E-05	4.10E-04	2.96E-08	1.91E-05	1.73E-08	3.08E-08	5.38E-10	2.09E-06	2.18E-06
1753	2.37E-02	4.79E-03	8.86E-06	4.73E-04	2.28E-08	2.20E-05	3.66E-08	6.07E-08	1.61E-09	6.07E-06	2.15E-06
1757	2.23E-02	4.79E-03	7.20E-06	4.54E-04	2.89E-08	3.61E-05	2.14E-08	3.61E-08	8.71E-10	1.45E-06	2.17E-06
1761	2.21E-02	4.77E-03	8.30E-06	4.18E-04	4.11E-08	1.91E-05	4.67E-08	6.09E-08	5.78E-09	5.73E-06	2.10E-06
1765	2.15E-02	4.88E-03	6.36E-06	4.32E-04	1.50E-08	1.72E-05	1.06E-08	1.67E-08	5.26E-10	2.85E-06	2.21E-06
1769	2.29E-02	4.77E-03	5.85E-06	4.24E-04	1.71E-08	1.56E-05	2.02E-08	3.18E-08	2.92E-09	1.63E-06	1.97E-06
1773	2.31E-02	4.77E-03	4.53E-06	3.89E-04	7.07E-09	1.46E-05	2.37E-08	1.97E-08	3.18E-10	9.34E-07	1.78E-06
1777	2.14E-02	4.80E-03	8.63E-06	3.87E-04	1.63E-08	1.66E-05	3.26E-08	5.12E-08	1.82E-09	5.96E-06	1.94E-06
1781	2.05E-02	4.76E-03	6.64E-06	3.99E-04	1.65E-08	1.67E-05	2.31E-08	7.27E-08	2.46E-09	5.54E-06	1.96E-06
1785	1.97E-02	4.82E-03	1.37E-05	3.87E-04	2.40E-08	1.57E-05	9.80E-08	1.26E-07	2.85E-09	1.61E-05	1.97E-06
1789	2.03E-02	4.74E-03	7.20E-06	3.90E-04	1.87E-08	1.52E-05	4.36E-08	9.71E-08	3.89E-09	7.29E-06	1.96E-06
1793	1.96E-02	4.78E-03	1.06E-05	3.96E-04	2.55E-08	1.78E-05	7.66E-08	1.14E-07	6.31E-09	1.80E-05	2.07E-06

1797	1.90E-02	4.80E-03	9.61E-06	3.69E-04	1.71E-08	1.48E-05	1.03E-07	1.20E-07	1.95E-09	1.04E-05	2.00E-06
1801	2.04E-02	4.78E-03	1.14E-05	3.60E-04	1.22E-08	1.28E-05	8.62E-08	1.05E-07	1.99E-09	1.34E-05	1.78E-06
1805	1.89E-02	4.78E-03	7.73E-06	3.66E-04	2.08E-08	1.35E-05	5.59E-08	7.11E-08	1.77E-09	6.30E-06	1.89E-06
1809	2.03E-02	4.79E-03	6.56E-06	3.62E-04	1.15E-08	1.38E-05	4.13E-08	5.23E-08	9.51E-10	4.21E-06	1.96E-06
1813	2.11E-02	4.76E-03	9.63E-06	3.52E-04	1.12E-08	1.38E-05	1.13E-07	3.14E-07	1.35E-09	3.50E-05	1.75E-06
1817	1.90E-02	4.74E-03	5.26E-06	3.73E-04	1.00E-08	1.28E-05	2.33E-08	3.08E-08	9.31E-10	3.39E-06	1.93E-06
1821	1.80E-02	4.81E-03	1.01E-05	4.02E-04	6.22E-08	1.65E-05	1.53E-07	2.46E-07	1.84E-08	1.48E-05	2.00E-06
1825	1.82E-02	4.75E-03	1.57E-05	3.93E-04	2.45E-08	1.52E-05	1.60E-07	2.81E-07	2.70E-09	2.11E-05	1.94E-06
1829	1.85E-02	4.79E-03	9.09E-06	3.90E-04	1.56E-08	1.49E-05	4.64E-08	6.05E-08	1.38E-09	1.22E-05	2.05E-06
1833	1.89E-02	4.72E-03	5.71E-06	3.83E-04	9.00E-09	1.31E-05	4.42E-08	6.56E-08	6.60E-10	7.49E-06	1.93E-06
1837	1.90E-02	4.77E-03	9.76E-06	3.87E-04	3.41E-07	1.41E-05	2.07E-07	2.58E-07	5.35E-08	5.43E-06	2.06E-06
1841	2.11E-02	4.79E-03	5.15E-06	3.88E-04	8.94E-09	1.30E-05	3.48E-08	4.37E-08	1.71E-09	2.78E-06	1.71E-06
1845	1.99E-02	4.75E-03	1.01E-05	3.89E-04	1.19E-08	1.25E-05	1.23E-07	1.77E-07	1.37E-09	6.31E-06	1.73E-06
1849	1.98E-02	4.74E-03	5.87E-06	4.15E-04	1.49E-08	1.31E-05	2.86E-08	3.75E-08	5.28E-10	5.20E-06	1.82E-06
1853	2.04E-02	4.77E-03	8.40E-06	4.07E-04	1.09E-08	1.34E-05	7.50E-08	1.02E-07	1.25E-09	1.82E-05	1.72E-06
1857	1.99E-02	4.81E-03	1.37E-05	4.12E-04	2.45E-08	1.54E-05	7.82E-08	1.03E-07	1.08E-09	1.64E-05	1.88E-06
1861	2.12E-02	4.74E-03	6.75E-06	4.01E-04	1.84E-08	1.45E-05	4.39E-08	5.33E-08	7.10E-10	7.81E-06	1.88E-06
1865	2.03E-02	4.76E-03	1.23E-05	3.84E-04	2.27E-08	1.60E-05	7.85E-08	9.90E-08	1.80E-09	4.70E-06	1.74E-06
1869	2.04E-02	4.77E-03	1.45E-05	4.08E-04	3.11E-08	1.68E-05	1.09E-07	1.62E-07	1.28E-09	5.62E-06	1.89E-06
1873	2.05E-02	4.77E-03	8.17E-06	4.21E-04	4.56E-08	1.70E-05	4.19E-08	6.44E-08	1.13E-09	1.65E-06	1.85E-06
1877	1.96E-02	4.75E-03	1.31E-05	4.26E-04	4.13E-08	1.74E-05	1.04E-07	1.69E-07	1.94E-09	2.07E-05	1.87E-06
1881	1.85E-02	4.76E-03	1.54E-05	4.09E-04	5.90E-08	1.64E-05	1.04E-07	1.43E-07	2.74E-09	1.20E-05	1.80E-06
1885	1.91E-02	4.76E-03	1.05E-05	4.16E-04	2.84E-08	1.86E-05	6.21E-08	9.62E-08	2.62E-09	8.25E-06	1.97E-06
1889	1.85E-02	4.80E-03	6.02E-06	4.11E-04	2.28E-08	1.59E-05	2.92E-08	4.10E-08	7.62E-10	4.98E-06	2.04E-06
1893	1.93E-02	4.96E-03	6.05E-06	3.75E-04	1.56E-08	1.42E-05	1.77E-08	2.58E-08	8.42E-10	3.04E-06	1.85E-06
1897	1.91E-02	4.81E-03	2.42E-05	3.78E-04	3.58E-08	1.68E-05	8.98E-08	1.15E-07	3.13E-09	7.47E-06	1.96E-06
1901	1.91E-02	4.78E-03	2.15E-05	3.85E-04	2.12E-08	1.53E-05	7.16E-08	1.90E-07	2.19E-09	1.91E-05	1.90E-06

1905	1.84E-02	4.83E-03	3.40E-05	3.76E-04	2.15E-08	1.56E-05	3.42E-07	4.03E-07	4.80E-09	2.39E-05	1.84E-06
1909	1.82E-02	4.78E-03	1.18E-04	3.45E-04	2.08E-08	1.52E-05	4.11E-07	5.16E-07	6.84E-09	4.24E-05	1.75E-06
1913	1.81E-02	4.77E-03	1.69E-05	3.60E-04	2.12E-08	1.58E-05	1.28E-07	1.67E-07	3.05E-09	1.30E-05	1.85E-06
1917	1.58E-02	4.74E-03	7.68E-06	3.84E-04	1.44E-08	1.55E-05	4.82E-08	1.22E-07	2.05E-09	6.91E-06	1.92E-06
1921	1.62E-02	4.76E-03	1.12E-05	3.58E-04	1.36E-08	1.37E-05	7.84E-08	1.40E-07	3.33E-09	5.49E-06	1.81E-06
1925	1.57E-02	4.76E-03	7.80E-06	3.80E-04	1.56E-08	1.34E-05	1.45E-07	1.77E-07	9.07E-09	8.98E-06	1.87E-06
1929	1.37E-02	4.81E-03	7.24E-06	3.77E-04	1.26E-08	1.30E-05	6.35E-08	7.68E-08	1.29E-09	1.76E-05	1.88E-06
1933	1.50E-02	4.74E-03	4.45E-06	3.60E-04	7.79E-09	1.22E-05	2.94E-08	4.06E-08	5.50E-10	3.67E-06	1.77E-06
1937	1.53E-02	4.79E-03	6.11E-06	3.43E-04	7.10E-09	1.45E-05	3.96E-08	5.09E-08	9.23E-10	3.97E-06	1.64E-06
1941	1.62E-02	4.80E-03	7.67E-06	3.76E-04	1.22E-08	1.26E-05	1.16E-07	1.52E-07	5.91E-09	1.51E-05	1.75E-06

Appendix 10 – All trace element data obtained for speleothem M2 for elements Mg, Sr, Ba, U, Y, Fe, La, Ce, Cu, and Pr.

Sample Depth (mm)	Mg : Ca	Fe : Ca	Cu : Ca	Sr : Ca	Y : Ca	Ba : Ca	La : Ca	Ce : Ca	Pr : Ca	U : Ca
1	6.00E-03	5.14E-03	3.01E-06	1.52E-04	2.25E-06	3.79E-06	1.48E-06	2.13E-06	3.11E-07	1.87E-06
5	5.80E-03	5.17E-03	8.72E-07	1.51E-04	6.63E-09	3.48E-06	4.54E-09	6.24E-09	8.86E-10	1.17E-06
9	5.47E-03	5.30E-03	1.22E-06	1.44E-04	3.70E-09	3.27E-06	5.28E-09	7.61E-09	4.22E-10	1.12E-06
13	5.37E-03	5.21E-03	5.39E-07	1.39E-04	3.06E-09	3.37E-06	2.00E-09	4.09E-09	5.64E-10	1.06E-06
17	4.92E-03	5.22E-03	1.02E-06	1.33E-04	7.63E-09	8.52E-06	4.80E-09	7.78E-09	2.97E-10	1.14E-06
21	5.54E-03	5.21E-03	5.64E-07	1.48E-04	4.44E-09	3.37E-06	9.41E-11	5.02E-10	1.37E-10	1.12E-06
25	5.35E-03	5.25E-03	1.16E-06	1.90E-04	5.25E-09	4.20E-06	8.23E-09	1.19E-08	4.31E-10	1.39E-06
29	8.11E-03	5.28E-03	2.46E-06	1.65E-04	1.08E-08	4.26E-06	3.77E-08	5.44E-08	6.06E-09	1.07E-06
33	6.99E-03	5.25E-03	1.14E-06	1.72E-04	4.78E-09	4.28E-06	1.77E-09	1.92E-09	3.51E-10	1.34E-06
37	5.90E-03	5.21E-03	4.49E-06	1.59E-04	6.33E-09	4.01E-06	3.45E-09	2.64E-08	8.97E-11	1.23E-06
41	6.27E-03	5.20E-03	7.80E-07	1.64E-04	6.08E-09	4.17E-06	3.76E-10	6.25E-11	1.84E-10	1.35E-06
45	6.92E-03	5.16E-03	1.29E-06	1.75E-04	5.34E-09	4.32E-06	2.57E-10	9.67E-10	1.06E-10	1.32E-06
49	6.96E-03	5.17E-03	1.10E-06	1.68E-04	7.91E-09	4.36E-06	4.69E-09	6.57E-09	3.36E-10	1.35E-06
53	6.27E-03	5.19E-03	1.04E-06	1.59E-04	5.77E-09	3.90E-06	2.18E-09	3.23E-09	1.91E-10	1.28E-06
57	6.07E-03	5.15E-03	1.02E-06	1.50E-04	6.12E-09	4.44E-06	2.99E-09	5.29E-09	5.73E-10	1.22E-06
61	5.61E-03	5.19E-03	8.49E-07	1.50E-04	4.72E-09	3.57E-06	8.26E-10	1.41E-09	1.94E-10	1.20E-06
65	4.99E-03	5.16E-03	1.18E-06	1.44E-04	5.29E-09	3.55E-06	2.20E-09	4.60E-09	3.03E-10	1.13E-06
69	4.99E-03	5.17E-03	1.42E-06	1.41E-04	5.06E-09	3.19E-06	7.15E-09	1.01E-08	1.48E-10	1.11E-06
73	4.82E-03	5.16E-03	1.12E-06	1.40E-04	8.53E-09	3.17E-06	7.81E-09	1.31E-08	9.56E-10	1.14E-06
77	5.03E-03	5.16E-03	8.56E-07	1.49E-04	6.87E-09	3.98E-06	8.52E-10	2.72E-09	1.92E-10	1.19E-06
81	5.71E-03	5.13E-03	8.80E-07	1.49E-04	3.79E-09	3.27E-06	4.28E-10	5.03E-10	1.51E-10	1.05E-06

85	6.45E-03	5.16E-03	1.22E-06	1.50E-04	6.11E-09	4.12E-06	6.68E-09	1.11E-08	3.77E-10	1.22E-06
89	6.86E-03	5.15E-03	9.53E-07	1.42E-04	5.96E-09	3.67E-06	3.93E-09	4.67E-09	2.30E-10	1.09E-06
93	5.55E-03	5.19E-03	7.37E-07	1.42E-04	4.68E-09	3.30E-06	6.33E-10	1.26E-09	2.75E-10	1.15E-06
97	5.46E-03	5.15E-03	1.23E-06	1.39E-04	4.76E-09	3.29E-06	4.37E-09	5.74E-08	2.60E-10	1.18E-06
101	5.62E-03	5.16E-03	1.39E-06	1.35E-04	5.13E-09	5.39E-06	1.26E-09	1.77E-09	3.25E-10	1.19E-06
105	5.30E-03	5.15E-03	8.43E-07	1.38E-04	4.11E-09	3.05E-06	-1.29E-10	-8.57E-11	-2.69E-11	1.13E-06
109	5.62E-03	5.18E-03	1.51E-06	1.29E-04	6.34E-09	3.13E-06	5.66E-10	1.79E-09	2.39E-10	1.14E-06
113	5.49E-03	5.14E-03	6.84E-07	1.41E-04	4.80E-09	3.28E-06	1.10E-09	9.85E-10	1.03E-10	1.17E-06
117	5.68E-03	5.12E-03	7.31E-07	1.48E-04	4.21E-09	3.78E-06	1.93E-09	2.78E-09	1.17E-10	1.26E-06
121	4.96E-03	5.14E-03	1.87E-06	1.57E-04	4.86E-09	4.07E-06	5.42E-09	7.75E-09	5.36E-10	1.37E-06
125	4.78E-03	5.13E-03	1.15E-06	1.74E-04	4.93E-09	4.39E-06	3.72E-09	5.00E-09	2.74E-10	1.53E-06
129	5.21E-03	5.13E-03	1.61E-06	1.63E-04	5.29E-09	4.24E-06	8.08E-09	8.84E-09	2.39E-10	1.53E-06
133	5.85E-03	5.18E-03	1.28E-06	1.41E-04	5.95E-09	7.65E-06	6.88E-09	1.03E-08	3.16E-10	1.01E-06
137	4.67E-03	5.08E-03	9.39E-07	1.55E-04	5.11E-09	7.81E-06	1.91E-09	3.17E-09	1.81E-10	1.29E-06
141	4.49E-03	5.12E-03	1.84E-06	1.47E-04	8.74E-09	3.62E-06	7.54E-09	9.04E-09	4.07E-10	1.49E-06
145	4.49E-03	5.10E-03	7.73E-07	1.44E-04	5.43E-09	3.79E-06	1.68E-09	2.46E-09	2.81E-10	1.30E-06
149	4.80E-03	5.11E-03	1.44E-05	1.44E-04	5.73E-09	3.39E-06	7.32E-09	8.79E-09	3.59E-10	1.18E-06
153	4.26E-03	5.10E-03	6.90E-07	1.58E-04	4.77E-09	4.10E-06	3.20E-09	5.05E-09	1.94E-10	1.37E-06
157	4.44E-03	5.15E-03	1.49E-06	1.71E-04	6.55E-09	5.41E-06	7.62E-09	1.06E-08	4.73E-10	1.40E-06
161	4.78E-03	5.15E-03	1.33E-06	1.60E-04	5.73E-09	3.41E-06	1.02E-08	1.49E-08	4.73E-10	1.28E-06
165	4.52E-03	5.12E-03	8.57E-07	1.44E-04	4.61E-09	2.89E-06	6.44E-09	7.12E-09	3.46E-10	1.11E-06
169	4.74E-03	5.10E-03	7.95E-07	1.57E-04	5.44E-09	3.54E-06	1.02E-09	9.88E-10	1.30E-10	1.27E-06
173	4.55E-03	5.13E-03	9.09E-07	1.57E-04	4.12E-09	3.61E-06	2.29E-09	2.78E-09	2.69E-10	1.32E-06
177	4.58E-03	5.12E-03	1.08E-06	1.67E-04	7.08E-09	3.72E-06	3.41E-09	3.88E-09	1.36E-10	1.41E-06
181	4.27E-03	5.12E-03	1.03E-06	1.53E-04	8.10E-09	3.51E-06	1.84E-09	2.07E-09	2.19E-10	1.39E-06
185	4.49E-03	5.10E-03	8.74E-07	1.65E-04	7.54E-09	4.09E-06	1.16E-09	1.79E-09	2.01E-10	1.42E-06
189	4.10E-03	5.15E-03	1.31E-06	1.50E-04	6.55E-09	4.48E-06	2.94E-09	4.73E-09	4.47E-10	1.25E-06

193	4.86E-03	5.25E-03	1.97E-06	1.69E-04	8.43E-09	4.06E-06	1.75E-08	2.25E-08	1.28E-09	1.35E-06
197	4.73E-03	5.17E-03	7.31E-07	1.56E-04	4.73E-09	4.06E-06	2.06E-09	2.81E-09	2.26E-10	1.25E-06
201	4.93E-03	5.15E-03	9.58E-07	1.53E-04	6.05E-09	3.96E-06	2.63E-09	4.04E-09	1.71E-10	1.31E-06
205	5.32E-03	5.14E-03	7.29E-07	1.39E-04	4.66E-09	3.34E-06	3.51E-09	3.30E-09	2.49E-10	1.14E-06
209	5.08E-03	5.14E-03	9.11E-07	1.36E-04	7.05E-09	3.69E-06	6.16E-09	7.67E-09	3.29E-10	1.18E-06
213	5.34E-03	5.17E-03	2.41E-06	1.32E-04	6.03E-09	3.01E-06	1.00E-08	1.58E-08	8.64E-10	1.07E-06
217	5.35E-03	5.14E-03	1.02E-06	1.38E-04	5.10E-09	4.97E-06	1.30E-08	7.05E-09	5.07E-10	1.14E-06
221	4.06E-03	5.13E-03	3.36E-06	1.48E-04	1.37E-08	3.78E-06	8.44E-09	1.30E-08	3.53E-10	1.57E-06
225	5.24E-03	5.18E-03	8.96E-07	1.54E-04	7.03E-09	3.32E-06	4.34E-09	8.95E-09	8.35E-10	1.43E-06
229	5.17E-03	5.13E-03	8.13E-07	1.55E-04	3.90E-09	3.09E-06	3.58E-09	5.48E-09	3.41E-10	1.33E-06
233	5.66E-03	5.12E-03	1.01E-06	1.40E-04	5.50E-09	3.21E-06	1.69E-09	1.34E-07	2.07E-10	1.13E-06
237	4.69E-03	5.09E-03	9.38E-07	1.45E-04	5.93E-09	3.11E-06	2.12E-09	3.06E-09	1.34E-10	1.21E-06
241	4.99E-03	5.10E-03	1.22E-06	1.58E-04	4.49E-09	3.32E-06	1.15E-08	6.06E-09	3.83E-10	1.25E-06
245	4.71E-03	5.12E-03	8.46E-07	1.52E-04	5.01E-09	3.32E-06	1.19E-09	1.66E-09	3.88E-11	1.31E-06
249	4.61E-03	5.13E-03	1.26E-06	1.34E-04	7.22E-09	2.86E-06	2.68E-09	4.06E-09	2.69E-10	1.17E-06
253	4.20E-03	5.12E-03	1.09E-06	1.36E-04	6.56E-09	3.05E-06	4.71E-10	1.93E-09	7.81E-11	1.26E-06
257	4.76E-03	5.12E-03	1.05E-06	1.46E-04	4.16E-09	3.31E-06	2.03E-09	3.37E-09	2.68E-10	1.31E-06
261	4.19E-03	5.13E-03	1.98E-06	1.48E-04	7.20E-09	3.53E-06	7.88E-09	1.11E-08	9.74E-10	1.47E-06
265	4.62E-03	5.15E-03	1.05E-06	1.41E-04	7.36E-09	3.19E-06	1.92E-09	3.11E-09	4.86E-10	1.33E-06
269	4.41E-03	5.12E-03	9.21E-07	1.37E-04	5.68E-09	9.15E-06	9.27E-10	2.41E-09	4.79E-10	1.27E-06
273	4.21E-03	5.10E-03	1.09E-06	1.38E-04	7.43E-09	3.38E-06	3.99E-09	6.70E-09	3.02E-10	1.54E-06
277	4.07E-03	5.10E-03	1.04E-06	1.42E-04	5.47E-09	3.48E-06	6.65E-10	1.50E-09	2.10E-10	1.54E-06
281	4.53E-03	5.08E-03	1.23E-06	1.43E-04	6.59E-09	6.55E-06	5.09E-09	9.38E-09	6.38E-10	1.38E-06
285	4.07E-03	5.07E-03	2.87E-06	1.54E-04	9.12E-09	3.70E-06	1.75E-08	2.55E-08	9.10E-10	1.59E-06
289	4.31E-03	5.10E-03	2.20E-06	1.64E-04	8.43E-09	4.23E-06	1.58E-08	2.92E-08	6.05E-10	1.65E-06
293	5.54E-03	5.10E-03	1.25E-06	1.56E-04	5.49E-09	5.56E-06	4.13E-09	6.57E-09	3.72E-10	1.38E-06
297	4.53E-03	5.10E-03	1.71E-06	1.48E-04	9.49E-09	3.66E-06	5.41E-09	7.90E-09	5.17E-10	1.41E-06

301	4.85E-03	5.09E-03	1.13E-06	1.41E-04	6.73E-09	3.54E-06	9.88E-09	1.25E-08	3.68E-10	1.34E-06
305	4.69E-03	5.08E-03	1.01E-06	1.50E-04	4.82E-09	3.63E-06	4.50E-09	7.64E-09	3.50E-10	1.42E-06
309	5.01E-03	5.12E-03	9.92E-07	1.57E-04	5.77E-09	3.95E-06	1.18E-08	1.32E-08	1.80E-10	1.42E-06
313	4.35E-03	5.08E-03	1.21E-06	1.50E-04	5.43E-09	3.87E-06	6.93E-09	1.13E-08	1.98E-10	1.54E-06
317	4.76E-03	5.07E-03	1.00E-06	1.39E-04	5.29E-09	3.86E-06	4.96E-09	6.39E-09	6.34E-10	1.44E-06
321	4.22E-03	5.09E-03	1.04E-06	1.33E-04	4.09E-09	3.21E-06	1.42E-09	2.43E-09	1.93E-10	1.35E-06
325	4.71E-03	5.11E-03	1.18E-06	1.41E-04	4.80E-09	3.51E-06	2.54E-09	4.81E-09	2.66E-10	1.39E-06
329	4.69E-03	5.07E-03	1.65E-06	1.45E-04	8.26E-09	1.07E-05	8.08E-09	1.08E-08	7.49E-10	1.37E-06
333	4.36E-03	5.07E-03	1.13E-06	1.45E-04	6.68E-09	3.56E-06	2.93E-09	4.36E-09	2.74E-10	1.47E-06
337	4.83E-03	5.10E-03	6.62E-07	1.45E-04	4.29E-09	3.80E-06	8.92E-10	1.44E-09	9.82E-11	1.30E-06
341	4.20E-03	5.07E-03	8.24E-07	1.49E-04	4.78E-09	3.58E-06	7.00E-10	1.48E-09	1.20E-10	1.51E-06
345	4.71E-03	5.09E-03	8.76E-07	1.37E-04	5.92E-09	4.92E-06	5.92E-09	9.14E-09	1.14E-09	1.19E-06
349	5.21E-03	5.12E-03	1.54E-06	1.44E-04	5.52E-09	3.47E-06	1.69E-08	1.37E-08	6.52E-09	1.15E-06
353	4.75E-03	5.09E-03	9.06E-07	1.50E-04	4.52E-09	3.59E-06	3.55E-09	5.12E-09	2.49E-10	1.42E-06
357	4.67E-03	5.09E-03	1.27E-06	1.48E-04	4.86E-09	3.54E-06	2.27E-09	3.30E-09	1.76E-10	1.47E-06
361	5.17E-03	5.10E-03	7.27E-07	1.46E-04	3.74E-09	6.96E-06	1.88E-09	3.68E-09	5.07E-10	1.37E-06
365	4.87E-03	5.06E-03	1.18E-06	1.46E-04	4.18E-09	3.55E-06	3.57E-09	5.39E-09	3.31E-10	1.40E-06
369	4.60E-03	5.10E-03	1.65E-06	1.50E-04	6.05E-09	4.00E-06	5.15E-09	9.31E-09	1.08E-09	1.46E-06
373	4.02E-03	5.07E-03	1.04E-06	1.53E-04	1.15E-08	3.65E-06	8.53E-09	1.50E-08	2.00E-09	1.62E-06
377	4.16E-03	5.04E-03	1.07E-06	1.57E-04	4.70E-09	3.81E-06	7.81E-09	6.94E-09	2.79E-10	1.61E-06
381	4.55E-03	5.05E-03	9.02E-07	1.53E-04	3.07E-09	3.71E-06	1.23E-09	2.46E-09	2.78E-10	1.51E-06
385	4.56E-03	5.06E-03	1.63E-06	1.59E-04	5.32E-09	4.19E-06	9.15E-09	1.31E-08	5.03E-10	1.45E-06
389	3.90E-03	5.05E-03	9.33E-07	1.60E-04	3.60E-09	3.75E-06	5.33E-09	7.49E-09	3.45E-10	1.65E-06
393	4.12E-03	5.05E-03	1.97E-06	1.49E-04	6.86E-09	3.61E-06	2.92E-08	3.19E-08	6.88E-10	1.59E-06
397	4.28E-03	5.06E-03	1.28E-06	1.66E-04	1.69E-07	4.49E-06	3.53E-09	6.36E-09	3.42E-10	1.58E-06
401	4.09E-03	5.09E-03	8.61E-07	1.53E-04	3.77E-09	3.50E-06	3.43E-09	5.51E-09	4.06E-10	1.57E-06
405	4.07E-03	5.11E-03	5.88E-06	1.71E-04	4.00E-09	3.91E-06	2.53E-09	4.14E-09	2.37E-10	1.65E-06

409	3.92E-03	5.04E-03	2.24E-06	1.56E-04	3.03E-09	3.65E-06	1.14E-08	1.78E-08	3.45E-10	1.68E-06
413	4.09E-03	5.07E-03	5.51E-05	1.64E-04	3.79E-09	5.86E-06	2.49E-09	3.44E-09	1.54E-10	1.63E-06
417	3.95E-03	5.06E-03	1.06E-06	1.59E-04	5.41E-09	3.71E-06	2.17E-09	3.89E-09	2.65E-10	1.70E-06
421	4.12E-03	5.04E-03	9.41E-07	1.63E-04	4.35E-09	3.69E-06	1.68E-09	2.69E-09	2.87E-10	1.67E-06
425	4.34E-03	5.04E-03	1.09E-06	1.61E-04	4.29E-09	6.30E-06	2.29E-09	4.18E-09	2.34E-10	1.74E-06
429	4.25E-03	5.06E-03	9.59E-07	1.56E-04	5.82E-09	3.80E-06	3.16E-09	5.83E-09	5.28E-10	1.68E-06
433	4.20E-03	5.06E-03	1.25E-06	1.50E-04	5.07E-09	3.81E-06	2.38E-09	3.97E-09	2.02E-10	1.60E-06
437	3.88E-03	5.05E-03	1.10E-06	1.51E-04	5.11E-09	3.55E-06	4.93E-09	7.20E-09	5.86E-10	1.67E-06
441	3.84E-03	5.05E-03	1.03E-06	1.41E-04	5.55E-09	3.35E-06	1.93E-09	2.65E-09	3.09E-10	1.60E-06
445	3.92E-03	5.07E-03	8.54E-07	1.54E-04	5.57E-09	4.20E-06	1.44E-09	2.18E-09	3.60E-10	1.71E-06
449	4.78E-03	5.08E-03	1.90E-06	1.39E-04	9.03E-09	3.78E-06	6.33E-08	9.01E-08	1.04E-09	1.37E-06
453	4.50E-03	5.05E-03	1.31E-06	1.49E-04	7.37E-09	4.19E-06	6.67E-09	1.29E-08	6.31E-10	1.67E-06