

The nature and extent of reactions between CO₂-rich water and fractured continental flood basalts

by

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Abstract

Continental flood basalts have been considered as an unconventional reservoir for geological carbon storage where vesiculated basalt intervals serve as reservoirs and massive basalt zones as a caprock. However, the presence of fractures in the massive layer may lead to CO₂ leakage. The objective of this study is to understand the reactions of CO₂-saturated fluid on fractured basalt and the respective changes in the fracture and adjacent connected pore network geometry at an early stage of the evolving geochemical system.

Batch reaction experiments, high-resolution sample characterisation, and modeling are used to better evaluate basalts as CO₂ storage reservoirs. The nature and extent of initial reactions between CO₂-rich water and fractures including the connected pore network were determined.

Reactions of CO₂-saturated water with powdered massive (MB) and with vesicular basalts (VB) was studied at three different P/T conditions to understand the mobilisation of ions from crystalline basalt at far-from-equilibrium conditions. Reaction path modeling was undertaken for experiments involving MB to estimate the amount of dissolved and precipitated minerals. Mobilisation of ions was unexpectedly low at high experimental pressure and temperature conditions suggesting concurrent mineral precipitation, which was confirmed by the model. Secondary minerals formed a coating on the surface of the primary minerals, which controlled the primary mineral dissolution rate. The nature of secondary minerals was studied in a separate experiment involving basalt wafers at pressure and temperature conditions representing a depth of approximately 800 m. Mostly clay minerals and zeolites were observed at the surface of the wafers and in suspension, which agreed with the change in water composition. Certain clay minerals and zeolites were highly supersaturated based on the outlet fluid composition. Siderite (FeCO₃) was close to equilibrium. The volume of dissolved and precipitated minerals was quantified in a third experiment using an artificially fractured basalt core at pressure and temperature conditions representing a depth of approximately 800 m. Net mineral precipitation occurred and the pore network structure changed, while only a very minor reduction in the net connected pore network volume was observed. These observations provide evidence for concurrent dissolution and precipitation processes leading to complex changes in the pore network geometry

In conclusion, precipitation of secondary silicate minerals dominates at an early stage of CO₂-saturated water and basalt reaction and the presence of fractures in basalt enhances the geochemical reactions.

Declaration

- This thesis is my original work towards the completion of my PhD except where indicated.
- Due acknowledgment has been made in the text where material from other researchers have been used.
- The thesis is fewer than the maximum word limit in length, exclusive of tables, maps, bibliographies, and appendices or that the thesis is 33,000 words as approved by the Research Degrees Committee.

Meghalim Phukan

Preface

The sections of this PhD research have been presented at the following seminars and conferences

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Parts of the thesis will be published in the following in preparation manuscripts

- ❖ Meghalim Phukan, Hong Phuc Vu, Ralf R. Haese, “Mineral dissolution and precipitation reactions and their net-balance in basalt and CO₂-saturated water at 80 bars and 60°C”
- ❖ Meghalim Phukan, Apoorv Jyoti, Ralf R. Haese, “The impact of mineral dissolution and precipitation on the pore network adjacent to the fractures”

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Nomenclature

Symbol	Definition	Units
ϕ	Porosity	-
M_d	Dry mass	<i>g</i>
M_w	Wet mass	<i>g</i>
V_g	Volume of the core	
Ω	Saturation index	-
Q	Ion activity product	-
K	Equilibrium constant	-
r	Net release rate	<i>mol. m². s⁻¹</i>
A	Volume of HCL	<i>ml</i>
R_i	Mineral dissolution rate	<i>mol sec⁻¹</i>
m	Mass	<i>g</i>
Δn	Change in number	-
Δt	Change on time	<i>s⁻¹</i>
<	Less than sign	-
>	Greater than sign	-
N	Normality	<i>eq/L</i>
r_k	Reaction rate	<i>mol. m². s⁻¹</i>
A_s	Mineral surface area	<i>m²</i>
k_+	Rate constant	<i>mol. m². s⁻¹</i>
k_{25}	Rate constant at 25° C	<i>mol. m². s⁻¹</i>
k_{60}	Rate constant at 60° C	<i>mol. m². s⁻¹</i>
k_{100}	Rate constant at 100° C	<i>mol. m². s⁻¹</i>
Ea	Activation energy	<i>kJ. mol⁻¹</i>
R	Ideal gas constant	<i>J. mol⁻¹. K⁻¹</i>
Π	Product function	-
a_j	Activity of promoting or inhibiting species	-
m_j	Molality of promoting or inhibiting species	-
P_j	Species power in the rate law	-
α	Order of reaction	-
β	Order of reaction	-
C_i	Initial concentration of ion	<i>mol. L⁻¹</i>
V	Residence volume	<i>L</i>
S. A	Total surface area	<i>m²</i>
D_{eq}	Equivalent diameter	<i>m</i>
N_{Veq}	Equivalent pore volume size	-
π	pi	-

List of Abbreviations

Abbreviations	Expansion
MORB	Mid-oceanic ridge basalt
CFB	Continental flood basalts
LIP	Large igneous provinces
CRBG	Columbia River Basalt Group
CAMP	Central Atlantic magmatic Province
DTB	Deccan Trap basalt
PFB	Port Fairy basalt
SB	Stapafell basalt
GWB	Geochemist's Workbench
PHREEQC	PH REDox EQUilibrium
BSCP	Big Sky Carbon Sequestration Partnership
MB	Massive basalt
VB	Vesicular basalt
NVP	Newer Volcanic Province
CSIRO	Commonwealth Scientific and Industrial Research Organisation
XRF	X-ray fluorescence
XRD	X-ray diffraction
SEM	Scanning electron microscopy
EDS	Energy dispersive spectroscopy
BSE	Back-Scattered Electrons
XPL	cross polarized light
PPL	plane polarised light
EPMA	Electron Microprobe Analysis
FTIR	Fourier Transform Infrared Spectroscopy
ICP-OES	Inductively coupled plasma with optical emission spectroscopy
PTFE	Polytetrafluoroethylene
BET	Brunauer- Emmett-Teller
DI	Deionised water
Micro-CT	Micro-computer tomography
2D	Two dimensional
3D	Three dimensional
CPN	Connected pore network
PSD	Pore size distribution

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Chapter 1: Introduction

1.1 Background: Geological carbon sequestration

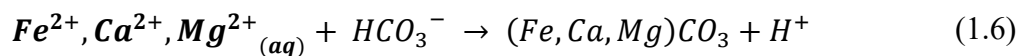
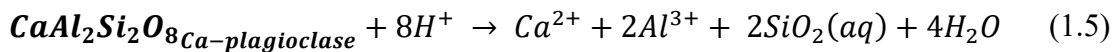
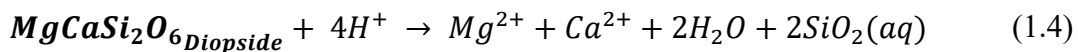
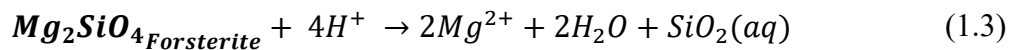
The global environmental change driven by an increase in the atmospheric CO₂ concentration requires a reduction in anthropogenic CO₂ emissions to restrain global warming to 1.5° C (UN 2015b, Erbach 2016, IEA 2016). Carbon capture and storage is a potentially viable greenhouse mitigation option to reduce large CO₂ emissions to the atmosphere (Bachu and Stewart 2002, Coninck et al. 2005, Holloway 2005, Gislason et al. 2010, Luquot et al. 2013). The released CO₂ is captured from point sources such as a coal fired power plant and transported through a pipeline to a nearby storage site, where the CO₂ is permanently disposed (Arning et al. 2019). Geological carbon sequestration (GCS) is a method of injecting CO₂ into deep geological porous formations such depleted/exhausted oil and gas beds, coal beds and saline formations found in sedimentary basins (Metz et al. 2005, Benson and Cole 2008, Pham et al. 2011).

CO₂ is a non-ideal gas which reduces its volume when compressed and changes to a supercritical state at given conditions, for example at 31°C and 73.4 bars. The injected supercritical CO₂ displaces the formation water in the pores and migrates upwards due to its lower density than the surrounding pore fluid. This upward migration of CO₂ can be contained by structural or stratigraphic trapping. Structural traps are formed by folded rocks. Closed faults may act as barriers to fluid migration, but open faults and fractures may serve as preferential fluid pathways. Stratigraphic traps are formed when properties of the rock changes such as permeability due to changes in the conditions of sediment deposition (Bachu et al. 2007, Van Pham et al. 2012, Lu et al. 2013). During the CO₂ plume migration through the porous rock, some of the CO₂ is snapped from the main plume and trapped in the pores, which is called residual trapping. Solubility and mineral trapping refer to the dissolution of CO₂ into the brine and the formation of carbonate minerals, respectively. The CO₂ dissolution depends on various factors, namely (a) the partial pressure of the CO₂, (b) hydraulic pressure in the formation rock, and (c) temperature and salinity of the formation water. Mineral trapping is considered the safest form of CO₂ storage as CO₂ is permanently immobilised (Oelkers et al. 2008, Romanov et al. 2015).

The injection of CO₂ into the water saturated rock triggers a several chemical reactions. Firstly, the injected CO₂ dissolves in the formation water, followed by dissociation of carbonic acid (H₂CO₃) which liberates protons (H⁺ ions) as shown in Eq (1.1) and (1.2) (Matter and Kelemen 2009, Takaya et al. 2019). The abundance of protons lowers the pH of the fluid.



The proton reacts with the primary minerals and basaltic glass. The dissolution reactions release the cations such as Ca²⁺, Mg²⁺, Fe²⁺, Na⁺, Al³⁺, K⁺ and Si. A few dissolution reactions of major primary mineral in basalt are shown by Eq (1.3), (1.4), and (1.5) (Gislason et al. 1987, Oelkers and Gislason 2001, Matter and Kelemen 2009, Gislason et al. 2010).



Once the concentration of the divalent cations (Ca²⁺, Mg²⁺, and / or Fe²⁺) and the carbonate ion (CO₃²⁻) concentration are high enough, carbonate minerals can precipitate (Eq. 1.6), permanently trapping CO₂ in the subsurface. However, the mineral dissolution reactions not only releases Ca²⁺, Mg²⁺ and / or Fe²⁺ but other ions such as Si and Al³⁺ as well. Consequently, secondary silicate minerals such as smectites (e.g. montmorillonite-(Na,Ca)_{0.33}(Al,Mg)₂(Si₄O₁₀)(OH)₂ · nH₂O), clays (e.g. kaolinite-Al₂(Si₂O₅)(OH)₄) and zeolites (e.g. analcime-Na(AlSi₂O₆) · H₂O) may also precipitate (Hellevang et al. 2017, Snæbjörnsdóttir et al. 2018, Wolff-Boenisch and Galeczka 2018) whereby carbonate mineral forming cations are consumed.

The mineral trapping capacity is typically low in CO₂ storage reservoirs consisting of sedimentary formations due to a lack of Ca, Mg, and Fe in the common primary minerals (quartz, feldspar, clay minerals) (Matter and Kelemen 2009, Matter et al. 2016). In addition, the dissolution rate of silicate minerals is low in sedimentary rocks. Hence, the transformation of CO₂ to carbonate minerals takes a very long time (Gislason and Oelkers 2014). The storage

capacity of sandstone reservoirs is usually high; therefore, they are often a first choice, despite their low mineral trapping. More recently, basalts deposits have been considered as an alternative but unconventional CO₂ storage reservoir due to the high reactivity of primary minerals and the high capacity to form carbonate minerals. Over the last two decades, there have been several studies at laboratory and field-scale regarding safe storage of anthropogenic CO₂ in basaltic reservoirs such as mid-oceanic ridge basalt (MORB) and continental flood basalts (CFB). CFB are found associated with large igneous provinces (LIP).

1.2 CO₂ storage potential in an unconventional basalt reservoir

Both MORB and CFB are comprised of mafic and ultramafic rocks. The presence of carbonate mineral forming divalent cations such as Mg²⁺, Ca²⁺, and Fe²⁺ in basalt is > 25 % by weight. However, basalt deposits lack a conventional cap rock. (McGrail et al. 2006, Gysi et al. 2011, Marieni et al. 2020).

Basalts cover about 10 % of the earth's surface and the ocean floor comprises additional large quantities (Dessert et al. 2003, McGrail et al. 2006, Goldberg et al. 2008, Oelkers et al. 2008, Gislason et al. 2010, Luhmann et al. 2017). Table 1.1 shows LIPs around the globe (McGrail et al. 2003).

Major large basalt flows deposits are located in the U.S.A, China, and India. Considering the large greenhouse gas emissions particularly from China and India, these basalt formations may act as good storage candidates for CO₂ in the future.

Site-specific assessments and an evaluation of risks associated with CO₂ injection and storage are required to obtain government and public approval and understand the financial liability by the operator (Coninck et al. 2005, Oelkers et al. 2008, Huerta et al. 2009). One of the risks is the migration of CO₂ from the targeted storage reservoir into the overlying formations including shallow aquifers and back to the atmosphere. CO₂ may leak from the targeted reservoir in different ways including through undetected high permeability zones or through leaky abandoned wells (Huerta et al. 2009, Huerta et al. 2016). Basalts are naturally fractured and comprise vertical and horizontal joints which control the flow of the fluid. Hence, these

fractures and joints might cause CO₂ migration outside the storage reservoir and may result in CO₂ leakage.

Table 1.1: Areal extents and volumes of major LIP's

Large Igneous Province	Location	Area km ²	Volume km ³
Columbia River Basalt Group (CRBG)	North-western U.S.A	200,000	224,000
Central Atlantic magmatic Province (CAMP)	Eastern U.S.A and Canada, northern South America, Northwest Africa	11 million km ²	2-3 × 10 ⁶
Deccan Trap Province	India and Pakistan	600,00	512,000
Emeishan basalt	Southwest China	> 250,000	> 300,000
Hannuoba-Chifeng basalt	Northeast China	20,000	1400*
Kerguelen Plateau	Southern Indian Ocean	2,300,000	9,100,000
Keweenawan Plateau	North Central U.S.A	160,000	640,000*
North Atlantic Igneous Province	U.K and Greenland	1,300,000	6,600,000
Ontong Java Plateau	Southwestern Pacific	1,900,000	44,400,000
Parana-Etendeka traps	Brazil, Namibia and Angola	2,200,000	> 1,000,000
Siberian traps	Eastern Siberia	340,000	400,000
Ethiopia-Yemen CFB	Yemen and Ethiopia	> 600,000	> 350,000

*Estimated volume based on area and average thickness of the flows

For geological CO₂ storage to be effective, the migration of CO₂ in the subsurface needs to be predictable, controlled and monitored to ensure long-term containment, in other words, one needs to ensure that little or no CO₂ leaks to the Earth's atmosphere for thousands of years (Shipton et al. 2006). A broad range of methods have been developed to characterize the subsurface as part of the site-specific assessment and to monitor the migration of CO₂ during and post-injection (Matter et al. 2007, Goldberg et al. 2010, Zakharova et al. 2012, Alfredsson et al. 2013, Sigfusson et al. 2015).

1.3 Basalt characterization

The primary properties used to determine the potential use of basalt as a CO₂ storage reservoir are the petrophysical nature (porosity and permeability), chemical composition, mineral composition and the characteristics of joints and fractures (geometry and orientation).

1.3.1. Structure of basalt flow deposits

The structural and petrophysical characteristics of basalt flow deposits have been studied extensively including in the context of sequestration of CO₂ (Kulkarni et al. 2000, McGrail et al. 2006, Prasad et al. 2012, Alfredsson et al. 2013).

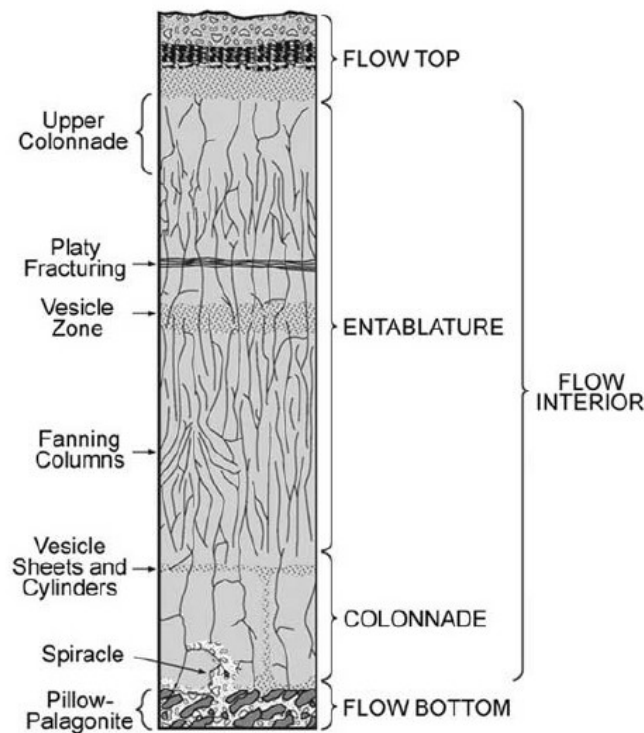


Figure 1.1: Major structural features of a flow unit of an idealized flood basalt flow (McGrail et al. 2006)

Fig. 1.1 shows a complex internal flow features of a flow unit of the Columbia River Basalt lava flow (U.S.A) which is a continental flood basalt (CFB). Many CFB are formed during phased eruptive events and results in stacked sequence of basalt flows or flow units with different thickness. The flow tops of each flow unit is highly vesicular and porous compared to the flow interior, as it has undergone rapid cooling when it contact with the overlying flow, importantly the atmosphere and water above (Goldberg et al 2010). The vesicular layer is typically fractured due to the regional stress field in the earth's crust, so that vesicles are connected. The flow interior is dense with low permeability. The flow interior (massive) acts as a cap rock and the flow top (vesicular layer) as the targeted CO₂ injection zone. The principle feature of a single lava flow is the flow top which has the potential to sequester CO₂. Most

vesicular tops are comprised of 15 to 30 % of lava flow thickness but it might vary from few centimetres to the entire thickness of a lava flow.

The lava flow deposits of the Deccan Trap Province in western India are made up of the sequential layers of vesicular amygdaloidal flows and compact massive flows ranging from few centimetres to tens of meters. The top section of vesicular amygdaloidal basalt is often around 6 m thick and is composed of glass, amygdales, and pyroclastic material. Amygdales are vesicles within igneous rocks and are often filled by secondary minerals, typically quartz, chalcedony, calcite or zeolites. The middle part (2-4 m) is relatively homogenous and comprises fewer amounts of amygdales and pyroclastic material. The lower part comprises unfilled vesicles and amygdales (Kulkarni et al. 2000). The total porosity within a basalt flow deposit may vary widely with up to 70 % of connected pores (McGrail et al. 2006). The flow interior of basalt flow is dense and low in permeability potentially to act as a cap rock between different flows (McGrail et al. 2006). The layered structure of basalt flows with highly permeable flow tops and dense and impermeable flow interiors make it a prospective candidate for safe and permanent CO₂ storage.

The basalt at the well-known CarbFix injection site in the southwest of Iceland is classified as mid-oceanic ridge basalt (MORB) and the site is located in between high-temperature geothermal systems. The geothermal gradient at the injection site is 80°C/km. The site is dominated by basaltic and ultrabasic lava flows and glassy hyloclastites (Bjornsson and ISOR, IG 2004, Alfredsson et al. 2013). The volcanic rocks have crystalline interior sandwiched between scoria on top and bottom (Alfredsson et al. 2013). Scorias are highly vesicular (30 %), dark coloured mafic volcanic rocks mostly composed of glassy fragments.

Joints are formed due to tensional stress during a differential thermal contraction during the cooling of the lava flow deposit. The vertical column (flow interior) in basalt is formed by colonnade and entablature joints which provide possible pathways for CO₂ leakage to an overlying flow (Fig. 1.1). Some joints with varying aperture size also extend into the overlying vesicular zone. Aperture has been defined as the width in the joints, fractures or cracks and its size ranges from few micrometres to > 2 mm (Engelder 1987, Zhao and Wang 2006).

1.3.2 Hydraulic properties

Physical properties of rocks are important to predict the hydraulic conductivity and direction of the CO₂ plume and the CO₂-saturated water. Systematic and hydrological investigations which included pump tests, reactive transport modeling of CO₂-saturated water along the rock surface, and tracer tests have been performed to obtain the effective matrix and fracture porosity, nature and position of the openings through which groundwater moves (Kulkarni et al. 2000, Aradóttir et al. 2012). High transmissivity and connected porosity make the basalt rock suitable for CO₂ injection and storage. Transmissivity is the measure of how much water can be transmitted horizontally and is directly related to thickness and hydraulic conductivity of its layer. Water transmission in flood basalts usually occurs in the vesicular and interflow zones where lateral flow of water occurs between confining massive zones. The reported transmissivity ranges from 0.0372 m² s⁻¹ to 0.00093 m² s⁻¹ (Kulkarni et al. 2000, McGrail et al. 2006).

1.3.3 Chemical and mineral composition

The bulk chemical composition of Columbia River from Grand Rhone basalt formation and Deccan basalt from western India contains upto 25 % of combined molar concentration of Ca, Mg and Fe. For e.g. 8-10 wt. % CaO, 5-6 wt. % MgO, and 13-14 wt. % Fe₂O₃ and these metals are readily liberated when subjected to acidic CO₂-saturated water and form solid carbonate minerals under favourable conditions (McGrail et al. 2006). The major minerals of the Columbian River and Deccan basalts are plagioclase feldspar and pyroxenes with minor amount of olivine (McGrail et al. 2006, Schaef et al. 2009, Xiong et al. 2017, Xiong et al. 2018). The MgO and Fe₂O₃ wt. % is higher in olivine containing basalt. The vesicular zone of Deccan Trap basalt is generally coarse-grained whereas the compact layer is fine-grained (Guha Roy et al. 2016). Secondary minerals phases such as carbonate and clay minerals along with zeolites were observed in the weathered Deccan Trap outcrop sample (Kulkarni et al. 2000, McGrail et al. 2006).

The primary mineral composition at the CarbFix study site in Iceland is as follows: plagioclase > pyroxene > olivine and a minor amount of magnetite – ilmenite, volcanic glass and quartz. The groundmass of basalt is composed of fine glassy material, plagioclase, and feldspar

(Gudbrandsson et al. 2008, Gudbrandsson et al. 2011). Glassy material is referred to volcanic glass, an amorphous product resulted from rapid cooling of magma. Secondary smectites and zeolites were also detected in the joints and cracks at the CarbFix site in Iceland prior to injection (Alfredsson et al. 2013).

1.4 Basalt mineral reactivity in the context of CO₂ storage

The rate of mineral and glass dissolution in basalts under CO₂ storage conditions mainly depend on the CO₂ solubility in the formation water and temperature. The CO₂ solubility and total alkalinity control the pH of the fluid. The dissolution of olivine and pyroxene is dominated at a low pH of around 2-4, while plagioclase dissolution is dominated at a higher pH > 4. Fig. 1.2 shows the comparison of the normalised Si release rate from different basalt minerals against pH within a narrow temperature range (25 to 30°C). Crystalline minerals have a lower dissolution rate compared to basaltic glass of similar chemical composition (Gudbrandsson et al. 2008, Oelkers et al. 2008).

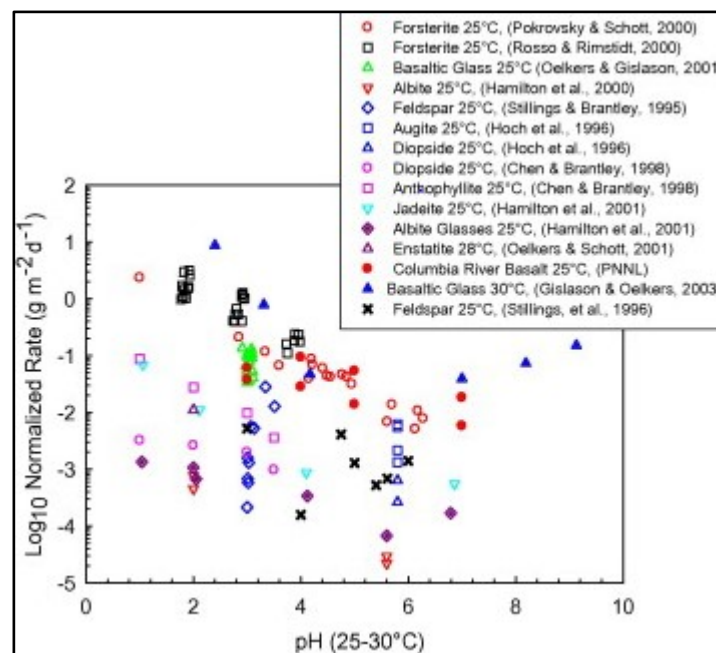


Figure 1.2: Si release rates ($\text{g m}^{-2} \text{d}^{-1}$) as a function of pH at a temperature range of 25–30°C. (Schaefer et al. 2009)

An increase in temperature increases the overall dissolution rate of minerals. As CO₂ saturated water is acidic, the dissolution of olivine and pyroxene releases Mg and Fe into the solution favouring the formation of siderite, magnesite or Mg-Fe carbonate solid solution instead of Ca-

rich carbonate minerals. This trend was additionally confirmed by CO₂-water-basalt experiments in the laboratory that showed predominantly the formation of Fe- and Mg-rich carbonate minerals at high CO₂ partial pressure, Mg- and Ca-rich carbonate minerals at intermediate and Ca-carbonate mineral is most common at low CO₂ partial pressure conditions (Matter and Kelemen 2009, Gysi and Stefánsson 2012a, Gysi and Stefánsson 2012b). Studies on natural analogues sites with a low CO₂ partial pressure showed calcite, clays, zeolites, and quartz/chalcedony as secondary minerals (Matter and Kelemen 2009, Gysi et al. 2011), whereas at sites with a high CO₂ partial pressure dominant minerals were quartz, Fe-, Mg-, and Ca-carbonate minerals (Matter and Kelemen 2009). The increase in the CO₂ partial pressure leads to a higher fraction of carbonate minerals formation as shown in Fig. 1.3 (Gysi and Stefánsson 2012a, Gysi and Stefánsson 2012b, Gislason et al. 2014).

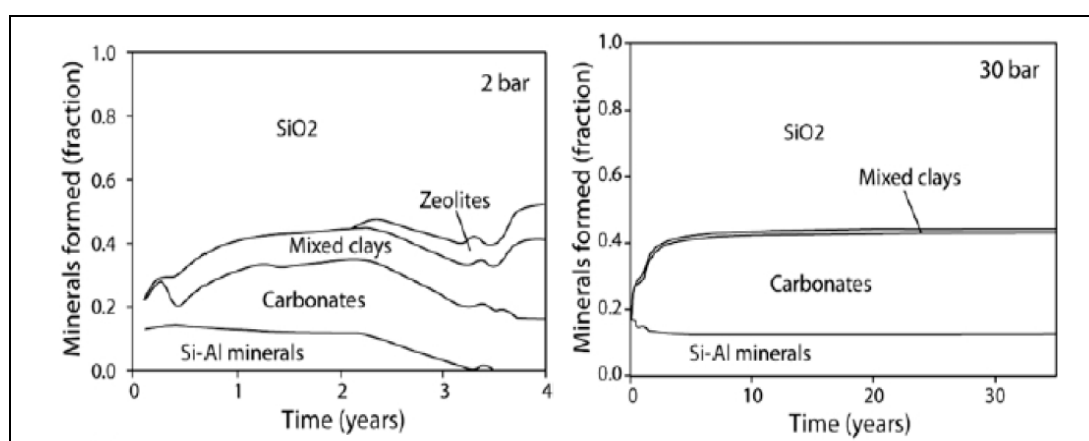


Figure 1.3: Batch reactor simulations of basaltic glass dissolution at 25°C (Gislason et al. 2014). The fraction of carbonate mineral precipitation increases with increasing pCO₂.

However, studies concluded that carbonate minerals only precipitates when the system has high pCO₂, pH and the fluid is rich in divalent cations (Hellevang et al. 2017, Snæbjörnsdóttir et al. 2018, Wolff-Boenisch and Galeczka 2018). The dissolution of aluminium silicate minerals not only releases divalent cations but also silicon and aluminium and at low pH and in systems with low divalent cation concentrations, it favours the formation of clays and zeolites. Thereby, it diminishes the efficiency of basalt carbonation (Hellevang et al. 2017, Wolff-Boenisch and Galeczka 2018).

1.5 Geochemical modeling

Geochemical modeling has helped to predict the nature of the secondary minerals but there is still a large difference between modeling, experimental and field studies mainly due to uncertainties in the estimation of reactive surface area of minerals in field experiments (Gysi and Stefánsson 2012b). Aqueous speciation is performed based on experimental outlet fluid concentration data to determine the state of mineral saturation. Reaction path simulations when coupled with experimental and natural observations provide a better understanding of the basalt alterations (Stefánsson and Gíslason 2001, Gysi and Stefánsson 2008, Gysi et al. 2011, Gysi and Stefánsson 2012a, Gysi and Stefánsson 2012b, Van Pham et al. 2012, Snæbjörnsdóttir et al. 2018). The software package, The Geochemist's Workbench (GWB) and PHREEQC ((PHREDOX EQUilibrium (in C language)) are commonly used to perform aqueous speciation calculation and to simulate the complex reactions between formation water and the minerals. The dissolution of the primary minerals and the precipitation of secondary minerals is commonly predicted under variable P/T conditions using reaction path modeling.

1.6 Field and laboratory studies on CO₂ storage in basalt

Field demonstration projects in MORB (Iceland) and CFB (United States) assessed the feasibility of CO₂ storage in basalts. The CarbFix project in Iceland is located near the Hellisheidi geothermal power plant, east of Reykjavik. Pure CO₂ of 175 tons in Phase I and CO₂-H₂S mixture of 73 tons in Phase II was injected into the basaltic aquifer at a depth of 400~800 m (Snæbjörnsdóttir et al. 2014, Matter et al. 2016). The CO₂ was dissolved into the water before injection by sparging the gaseous CO₂ into the water at surface. The initial low pH of the water promoted mineral dissolution in the basalt formation. The fluid-mineral system gradually approached a new equilibrium while carbonate minerals were formed (Gíslason et al. 2014, Gíslason et al. 2014). On the other hand, pure supercritical CO₂ was injected into the porous Columbian River Basalt (CRB) layers at a depth of more than 800 m in the Big Sky project (BSCP) at Wallula, USA. The pre-injection pressure and temperature at this depth are 36°C and 77 bars and the injected CO₂ was heated to 44°C prior to injection. The overlain impermeable basalt layers are predicted to prohibit the escape of buoyant CO₂ back to the surface (McGrail et al. 2006). However, there is a potential risk of CO₂ leakage through open joints and fractures in the massive basalt intervals.

The advantage of the CarbFix method is that the dissolved CO₂ reduces the risk of CO₂ leakage back to the atmosphere as CO₂-saturated water is denser than CO₂-free water (Sigfusson et al. 2015). Moreover, the dissolution of CO₂ in water immediately promotes the carbonation of host rocks in the presence of sufficient mineral-bound divalent metals. The major disadvantage of this method is the need for a substantial amount of water, and only a small fraction (4-5 %) of the mass injected is CO₂. In addition, the transportation and the storage cost of CO₂ via the dissolved water injection method is about two times the cost of direct CO₂ inject at the BSCP injection site (Gislason et al. 2014). CarbFix project results suggest about 95 % of the injected CO₂ was converted into calcite minerals in less than 2 years. Moreover, the injected gas mixture of CO₂-H₂S mineralized within months at the CarbFix2 site (Gunnarsson et al. 2018). Formation of ankerite nodules were observed in the core sample after 2 years of injection in case of the BSCP pilot study (McGrail et al. 2016).

Currently, the CarbonSAFE Cascadia project team is evaluating the CO₂ storage potential of an ocean basalt reservoir offshore from U.S.A and Canada. This project aims to collect industrial-scale CO₂, transport and store it in the offshore reservoir (Goldberg et al. 2018).

Laboratory scale studies were performed on CRB and Icelandic basalt samples at different experimental conditions to study the dissolution and precipitation of minerals (Bjornsson and ISOR, IG 2004, Gysi and Stefánsson 2012c, Galeczka et al. 2013, Galeczka et al. 2014). In recent years many other basalt formations across the globe have been investigated at laboratory scale with regards to carbon sequestration. Experiments performed on Deccan basalt samples in a batch reactor at 100°C observed the formation of carbonate minerals (Prasad et al. 2012, Kumar et al. 2017). Additionally, secondary silicates formed at low CO₂ partial pressure of 5-10 bar pCO₂ under short experimental duration (Kumar et al. 2017). The semi-quantitative model estimated a CO₂ storage potential of 94.15 kg per 1 m³ in the Miocene basalt of Kuanshi-Chutung area, Northwestern Taiwan, based on an isotopic analysis of the calcite and serpentine in the natural analogue (Lu et al. 2011). Schaef and his co-workers have investigated the geochemical reactions of CRB and few other continental flood basalts from India, South Africa and Canada with pCO₂ of 100 bar and within a temperature range of 60°C-100°C. Calcite formation along with minor amounts of siderite and magnesite were observed during their experimental study (Schaef et al. 2010, Schaef et al. 2011).

Mineral precipitation along potential leakage pathways such as joints and fractures due to the interaction of CO₂-saturated fluid and the basalt rock can be beneficial in two ways: (1) It could serve as additional storage volume (2) It could contain the buoyant supercritical CO₂ from leaking in the long term due to self-sealing of those preferential leakage pathways. Experiments where advection was the dominate transport regime of CO₂-rich water showed enhanced dissolution, and did not observe mineral precipitation and any net solid phase volume increase (Adeoye et al. 2017, Luhmann et al. 2017a, Luhmann et al. 2017b). However, in experiments where transport of the CO₂-enriched fluid was diffusion-controlled, a major reduction in the fracture volume was observed indicating mineral precipitation. Menefee and colleagues (2018), observed a reduction of 35 % - 48 % in the fracture volume of a basalt core at 100°C and 150°C within 10 days when reacted with water enriched with NaHCO₃⁻. A reduction in the fracture volume between 5.4 % and 15 % were also observed at a similar temperature without any synthetic supply of carbonate ions, but over a duration of 40 weeks (Xiong et al. 2018). Experimental studies in cement have confirmed that mineral precipitation within fractures can occur during CO₂ migration and may seal the fracture if the initial aperture is small and the fluid residence time is high. Other controlling factors are the fracture or joint roughness and the chemical composition of the fluid (Singurindy and Berkowitz 2005, Huerta et al. 2012). In the context of CO₂ leakage, a long residence time together with a low aperture are expected to lead to self-sealing of the pathway and ensures long-term CO₂ containment.

1.7 Research gap

Several laboratory studies showed the high capacity of basalt rock to mineralise CO₂ in form of carbonate minerals over a long reaction period or when the pH is buffered. However, the nature and extent of early reactions between CO₂-enriched water and fractured basalt has not been addressed. It could be that different minerals precipitate at an early stage compared to minerals precipitating at a later stage. Equally, the cation release rate as a net balance between concurrent dissolution and precipitation may change over time as the geochemical system evolves. My PhD thesis focuses on understanding reactions of CO₂-saturated fluid on fractured basalt and the respective changes in the fracture and adjacent connected pore network geometry at an early stage of the evolving geochemical system. My studies are carried out at reservoir conditions representing a depth > 800 m, with the initial pH of the fluid solely reflecting the solubility of CO₂ at the given depth conditions.

1.8 Research objectives

The theme of my research is the study of geochemical reactions between CO₂-enriched water and fractured massive (MB) basalts; and to compare the release rates of elements with vesicular (VB); over short experimental periods under reservoir conditions. The following three objectives were addressed:

1. What is the nature of mineral precipitation upon interaction with CO₂-saturated water with massive basalts at a depth of 800 m?
2. What are the release rates of elements (major cations and Si) from massive and vesicular basalt at variable pressure and temperature conditions at far-from-equilibrium conditions?
3. How and to what extent do mineral dissolution and precipitation change the geometry of fractures and their adjacent connected pore network in a massive basalt upon interaction with CO₂-saturated water at conditions representing a depth of 800 m?

1.9 Overview of the Thesis

The current thesis is subdivided into 5 chapters with three main chapters addressing the study objectives. The structure of the thesis is presented in Fig. 1.4

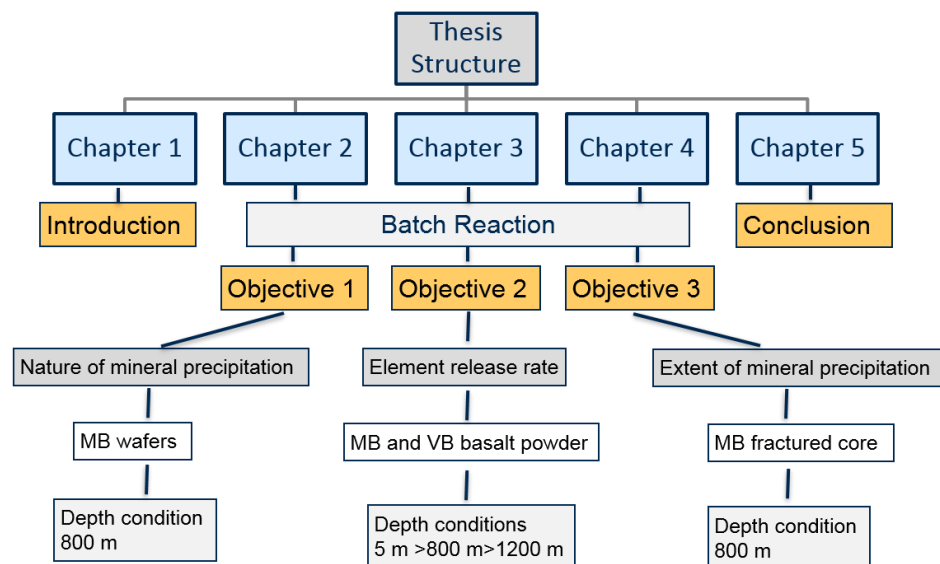


Figure 1.4: Structure of the PhD thesis; MB-massive basalt; VB-vesicular basalt

In this chapter 1 of the thesis, literature related to carbon storage in the basalt reservoirs is introduced. A research gap is identified in this chapter which is the motivation for this thesis.

The objective and structure of the thesis are also described here.

Chapter 2 addresses objective 1 and includes the characterisation of rock samples used in this study (CFB from Port Fairy, Australia). This study aims to understand the nature of mineral precipitation under deep (~ 800 m) subsurface conditions and over a relatively short reaction time. The interaction of CO₂-saturated formation water with basalt wafers was studied in batch reactor experiments at a pressure of 80 bars and 60°C for a period of 44 days. The minerals precipitating at a low pH of ≈ 4 could act as potential sealants of joints and fractures in fractured basalt reservoirs.

Chapter 3 addresses objective 2. This study aims to understand the mobilisation and availability of major cations such as Ca²⁺, Mg²⁺, Fe²⁺, and Si from crystalline basalt at the far-from-equilibrium conditions, which are required for the formation of secondary minerals. Interaction of CO₂-saturated water was studied with powdered massive (MB) and vesicular basalts (VB) at three different pressure and temperature conditions for 7 days in a stirred batch reactor. The release of elements from basalts was investigated as a function of reaction time for both VB and MB to assess and compare the reactivity of the minerals of both basalts. Additionally, an experiment was performed for MB to understand the impact of different rock:water ratios on the element release rate. Reaction path modeling was undertaken for MB by matching the end cation concentration and pH to the experiments to estimate the amount of dissolved and precipitated minerals. The influence of surface passivation of the primary mineral was tested in the model to match the changes in water composition over time.

Chapter 4 addresses objective 3. This study was performed to understand the influence of concurrent dissolution and precipitation processes on fractured massive basalt rock under diffusion-controlled conditions. A static experiment was conducted at realistic P/T conditions representing an injection depth ~ 800 m in the subsurface where artificial fractures and the adjacent connected pore network in a core were exposed to CO₂-saturated water. Changes in the fracture and pore space geometry were analyzed using non-destructive imaging techniques. Changes in the connected pore network, surface area, dissolved and precipitated minerals were quantified.

Chapter 5 presents the conclusion and recommendations for future studies.

Chapter 2: The nature of mineral precipitation and its self-sealing potential of leakage pathways in fractured massive basalt upon CO₂-saturated water interaction at 80 bars and 60°C

Abstract

Continental flood basalts are currently considered as unconventional CO₂ storage reservoirs, given that several knowledge gaps remain, for example, whether fractures and joints in the storage complex may lead to CO₂ leakage. This study determines whether CO₂-rich fluid and rock interactions leads to mineral precipitation outcompeting mineral dissolution. This process would potentially seal joints and fractures at a depth of approximately 800 meters and thereby contribute to CO₂ containment. The interaction of CO₂-saturated formation water with basalt wafers was studied in a batch reactor experiment at a pressure of 80 bars and 60°C for a period of 44 days. Primarily stilbite (a zeolite) and montmorillonite (a smectite) were observed in suspension and kaolinite, Fe-oxides, Na-nontronite, and Mg-rich carbonate minerals were additionally identified as authigenic minerals on the surface of the basalt wafers at the end of the incubation. These observations are in agreement with the state of mineral saturation based on the water composition throughout the incubation except for Mg-carbonate mineral. All dissolved cation concentrations declined between incubation day 6 and 44 suggesting net precipitation of secondary minerals leading to a net decrease in porosity. The secondary mineral coating on wafers led to surface passivation of the primary minerals. Carbonate minerals were undersaturated throughout the incubation suggesting limited carbon mineral trapping capacity under the given conditions.

2.1 Introduction

The permanent disposal of carbon dioxide in the subsurface has been considered a viable option to reduce global warming (Coninck et al. 2005, Metz et al. 2005). Sedimentary basins have been studied for a relatively long time and are in principle considered as a conventional storage reservoir for CO₂. In this case, mineralisation of CO₂ might take thousands of years to occur. Continental flood basalts are considered unconventional CO₂ storage reservoirs and are not widely studied in the context of geological carbon storage. Continental flood basalts consist of alternating layers of vesicular and massive basalts, where the former could serve as reservoir and the latter as a caprock. However, vertical joints and subvertical fractures are often present in basalt and may serve as conduits for buoyancy-driven CO₂ migration and could compromise CO₂ containment.

When CO₂ dissolves in water and its dissociation products are formed, the water becomes mildly acidic. At low pH basaltic glass and minerals slowly dissolve and mobilise ions including the divalent cations Ca²⁺, Mg²⁺, and Fe²⁺, which typically make up approximately 25 % by weight in basalt. Mineral dissolution consumes H⁺ ions and the mobilised cations may become involved in secondary mineral precipitation (McGrail et al. 2006, Gudbrandsson et al. 2008, Gislason and Oelkers 2014). The dissolution rates are mainly depending on pH and temperature, where the pH is typically controlled by the partial pressure of CO₂ and alkalinity (Gysi and Stefánsson 2012a). The dissolution rates of minerals are significantly lower than the dissolution rate of the basaltic glass of similar composition (Gislason et al. 2003). Furthermore, the dissolution of silica-aluminium minerals such as plagioclase and pyroxene not only release divalent cations but also silica and aluminium. The combination of ions enriched from the dissolution of basalt under mildly acidic conditions tends to lead to the formation of clays and zeolites and diminishes the efficiency of basalt carbonation (Gislason et al. 2014).

Reaction path models were run to predict the nature of mineral formation over a range of pressure and temperature conditions (Gysi and Stefánsson 2008, Gysi et al. 2011, Gysi and Stefánsson 2012a, Gysi and Stefánsson 2012b, Van Pham et al. 2012, Snæbjörnsdóttir et al. 2018) and suggested precipitation of smectites and zeolites along with chalcedony, kaolinite and goethite (Gysi and Stefánsson 2008, Gysi et al. 2011, Van Pham et al. 2012). Gysi and Stefánsson predicted that (Ca-Mg-Fe) smectites and Fe-rich carbonates are formed at pH < 6.5,

whereas zeolites, (Ca-Mg-Fe) smectites and different forms of carbonates precipitate at $\text{pH} > 6.5$, (Gysi et al. 2011). Recent experimental studies by Hellevang and colleagues (2017) and Xiong and colleagues (2017), observed the formation of smectite at $\text{pH} < 7$ whereas various forms of Ca-carbonates are formed together with smectite at a $\text{pH} > 9$. The Mg^{2+} and Fe^{2+} cations from the primary minerals are incorporated into clay minerals such as smectites and oxides which competes with the formation of magnesite and carbonate mineral solid solutions. Dissolved Ca is preferentially precipitated as zeolite rather than calcite (Aradóttir et al. 2012).

Mineral precipitation in natural joints and fractures in basalt has been observed to partly or fully inhibit fluid flow. In some instances, Si-Al minerals are the primary infilling of joints and fractures in basalts, for example, smectites, halloysite, and goethite were found in eastern Australian basalts (Eggleton et al. 1987) and upward migration of petroleum and associated CO_2 -rich brine replaced zeolites and clays with carbonate minerals in West Greenland basalts (Rogers et al. 2006). In other cases, saponite and calcite were observed as alternate vein filling minerals (Goldberg et al. 2008) and the interaction of basalt with meteoric fluid lead to the precipitation of carbonate minerals at a depth of 1-2 km (Lu et al. 2011). Upward migration of CO_2 -saturated brine along a fracture zone and CO_2 degassing at a shallow aquifer resulted in calcite precipitation due to an increase in pH (Todaka et al. 2009).

Experimental studies in cement have confirmed that calcite precipitation within fractures can occur upon CO_2 interaction and may seal the fracture if the initial aperture is small and the fluid residence time is long. Other controlling factors are the fracture or joint roughness and the chemical composition of the fluid (Singurindy and Berkowitz 2005, Huerta et al. 2012). A number of studies have evaluated mineral dissolution and precipitation in high-pressure batch reactors focussing on basalt dissolution and carbonation of minerals under CO_2 -saturated conditions. Most of the experiments are performed using powdered basaltic glass and basalt-forming minerals with a large surface area $> 4000 \text{ cm}^2/\text{g}$ and deionised water (DI) or mixture of analytical grade solutions as synthetic formation water (Gudbrandsson et al. 2008, Stockmann et al. 2011, Stockmann et al. 2013, Sissmann et al. 2014, Hellevang et al. 2017, Kumar et al. 2017).

This study aims to understand the nature of mineral precipitation under deep ($\sim 800 \text{ m}$) subsurface conditions assuming the CO_2 -enriched water reacts with the walls of the fractures and joints potentially leading to a self-sealing of the leakage pathway. We present results from

a batch reactor experiment using basalt wafers to study the interactions between basalt surface and CO₂-saturated fluid. The incubation water was prepared by equilibrating water with powdered basalt at elevated temperature and pressure. The experimental results by means of the fluid composition and secondary mineral formation were compared to mineral saturation indices from geochemical modeling.

2.2 Materials and Methods

2.2.1 Sample Location

The rock sample was sourced from Bamstone Port Fairy Bluestone Quarry, located in the southeast of Victoria, Australia. Port Fairy is situated in the Newer Volcanic Province (NVP) and is about 300 km N.E of Melbourne. The Newer Volcanic Province is the youngest reflection of the sporadic basaltic volcanism in south-east Australia and is estimated to be 1.9 million years old (Ollier 1985, Orth 1988, Matchan et al. 2011).

Mount Rouse is a composite volcano in the NVP which is located at about 60 km northeast of Port Fairy. The Rouse-Port Fairy flow is the longest amongst the major five flows originating from Mount-Rouse (Fig. 2.1). The age of this flow is estimated to be 320,000 years, one of the youngest basalt deposits of the NVP. The width of the flow varies from 200 m to 14 km (Ollier 1985). The flow filled the ancient valleys of Shaw and Moyne Rivers and these lava flows are identified by their stony rise feature and abundance of outcrops (Matchan and Phillips 2011). The thickness of individual flows varies from approximately 150 m to 5 m, typically decreasing in thickness from its source, Mount Rouse, to the coastline at Port Fairy.

The basalt sample from the quarry near Port Fairy was pristine and unweathered. Pre-experimental basalt samples characterization involved XRF (X-ray fluorescence), XRD (X-ray diffraction) and electron microprobe on thin sections. The above analysis could not be performed on post-experimental sample due to small sample size and poor crystallinity of secondary mineral precipitation.

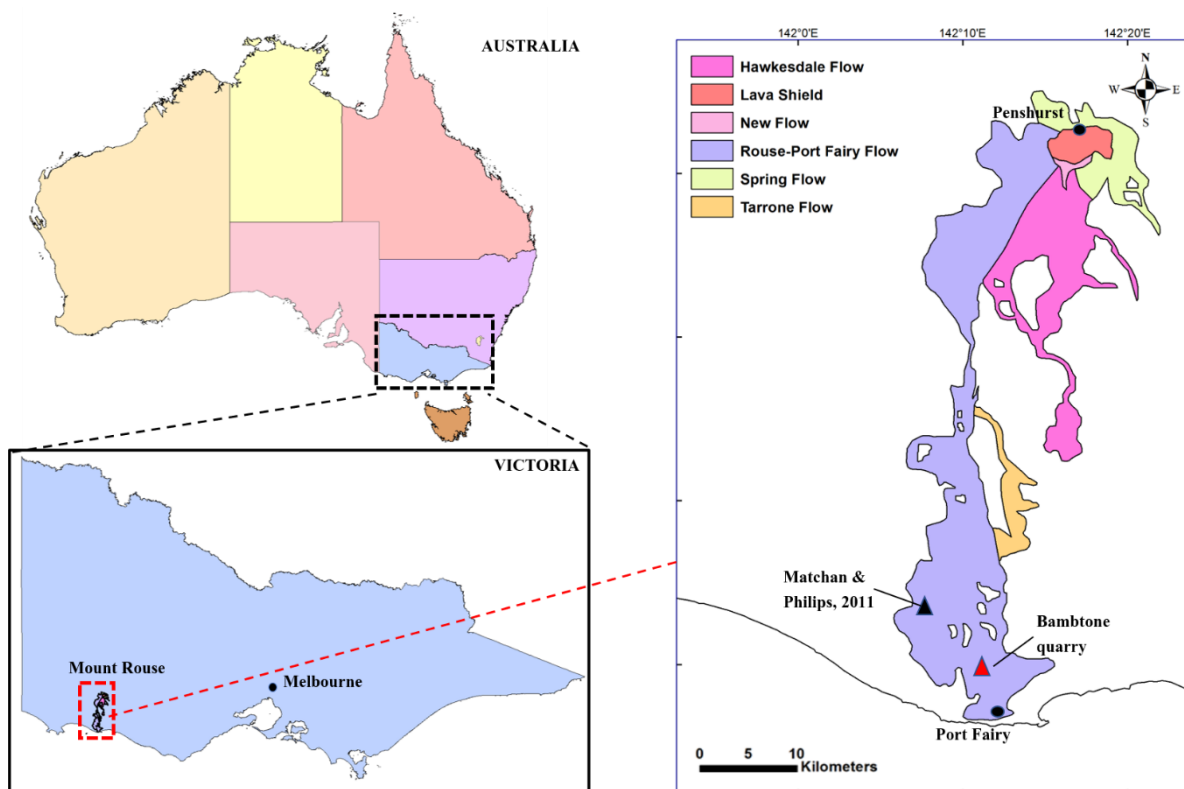


Figure 2.1: Sample location (Bamstone Quarry) and the distribution of basalt flow deposits originating from Mount Rouse as part of the Newer Volcanic Province in Victoria (modified after (Sutalo and Joyce 2004, Matchan and Phillips 2011)).

Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) analysis was performed for both pre- and post-experimental samples. Additionally, Fourier Transform Infrared Spectroscopy (FTIR) was performed on post-experimental samples. FTIR analysis can be performed on small sample size (< 1 g), which can also detect poorly crystalline minerals. The pre-experimental rock sample was performed to analyse the mineral and rock compositions. This information is important to understand the nature of dissolved mineral and secondary mineral precipitation based on release of cations in the fluid on interaction of CO₂-saturated water. Therefore, the selection of range of rock analysis techniques for both pre-and post-experimental sample are mostly based on sample size and degree of crystallinity of the new formed minerals.

2.2.2 Rock and mineral analysis

The bulk composition of the basalt was analysed by PANalytical AXIOS wavelength dispersive XRF spectrometer located at CSIRO, Adelaide. The mineral composition was

determined by SIEMENS D5005 Bragg-Brentano diffractometer at Australian National University, Canberra. The scan range was 4 to $84^\circ 2\theta$, at a step width of 0.02° , and a scan speed of 2 seconds per step. The data was interpreted using the SIEMENS software Diffracplus Eva (2003) for mineral identification, and Siroquant V3 for mineral quantification. The petrographic analysis was performed using both plane polarised light and cross polarised light (LEICA ICC50 W) on polished thin sections. Thin sections were also analysed on a Philips / FEI XL30 environmental SEM equipped with an OXFORD INCA EDS to determine the presence of amorphous phase (basaltic glass) and to perform semiquantitative analysis of the major minerals. Electron microprobe analysis (Cameca SX50) was performed on polished thin sections to identify and obtain the composition of unknown minerals and the matrix. Prior to microprobe analysis, Microbeam Digimax digitiser system attached to the optical microscope which was used to select and mark individual minerals on the thin sections.

Solid phase samples after the experiment were characterised using SEM-EDX and Fourier Transform Infrared (FTIR) analysis. Two gold-coated reacted basalt wafers (W5 and W10) were analysed by SEM-EDX to image surface features and perform qualitative elemental analysis of the selected spots. FTIR was used to identify minerals in the three solid phase samples. 64 scans with a wavelength range from 400 cm^{-1} to 4000 cm^{-1} were collected and averaged for each sample and the acquired spectra were compared with mineral specific spectra of the RRUF and Caltech mineral databases. The description of the specific minerals selected for spectrum comparison with the post-experimental solid phases are shown in Appendix 1.

Porosity and surface area of a massive basalt sample of $3.4 \times 3.5 \times 1\text{ mm}$ was also characterized by micro-CT scanner, a GE Nanotom M, at the School of Earth Sciences, The University of Melbourne. This miniature dimension of basalt sample was used to have an improved resolution of the scan. The porosity and surface area of the massive basalt sample were extracted through this scanning. It was scanned at a resolution of $3.55\text{ }\mu\text{m}$, a voltage of 55 kV, a current of $270\text{ }\mu\text{A}$ and power of 14.9 W. More details on calculation of porosity and surface area is presented in Chapter 4 (section 4.2.4.2). The porosity of the massive basalt core sample ($L = 4.8\text{ cm}$; $D = 3.7\text{ cm}$) was also measured by the weight difference between dry and water-saturated (Safiuddin and Hearn, 2005). The sample was oven-dried at 50°C (Contherm Digital Series) for 48 hours to ensure it has dried completely and then the dry mass (M_d) was measured. Thereafter, the sample was immersed in DI water in a closed vacuum chamber and connected

to a high vacuum pump (Edwards RV8). The core was submerged for 48 hours at 50 kPa and then wet mass (M_w) was measured. Porosity (ϕ) was calculated by the following equation, where, V_g is the geometrical volume of the core

$$\phi = \frac{M_w - M_d}{V_g} \quad (2.1)$$

2.2.3 Fluid analysis

Major cations in the fluid (Ca^{2+} , Mg^{2+} , Fe^{2+} , Na^+ , K^+ , Al^{3+}) and Si were analysed by inductively coupled plasma with optical emission spectroscopy (ICP-OES, Model 5110, Agilent). Total alkalinity was measured on unfiltered fluid samples by potentiometric titration (916 Ti-Touch titrator, Metrohm). Two endpoints pH values were set at 4.3 and 2.5. The pH electrode of the titrator was calibrated at pH 4 and 7 and the initial pH of the sample solution is noted. The sample was diluted with a ratio of 1:8. In this case, 2 mL of unfiltered sample was mixed with 14 mL of deionised water (DI). A standardised 0.01 M HCl solution was prepared and used to titrate the sample to determine the total alkalinity of the diluted sample (Snoeyink et al. 1980). The following equation was used in calculating the total alkalinity

$$\text{Alkalinity, mg} \left(\frac{\text{CaCO}_3}{\text{L}} \right) = \frac{A * N * 50,000}{\text{mL of sample}} \quad (2.2)$$

Where, A is the mL of HCl consumed to reach first endpoint pH of 4.3 and second endpoint pH of 2.5, N (0.01) is the normality of HCl (eq/L).

2.2.4 Experimental method

A total of 15 basalt wafers each with a size of 3.8 cm length, 1.2 cm breadth and thickness of 0.8 mm were prepared using a diamond cup wheel grinder. This dimension was chosen to accommodate maximum samples in the high-pressure titanium 5500 Compact Mini Bench Top Parr[®] Reactor for maximum surface area (Fig. 2.2). The wafers were sonicated in deionized water followed by acetone to remove fine particles on the surface and was oven-dried at 50°C for 24 hours. A sample holder was fabricated of polytetrafluoroethylene (PTFE) to hold the

basalt wafers intact inside the Parr[®] reactor. PTFE material was chosen because it is chemically inert under the given experimental conditions.

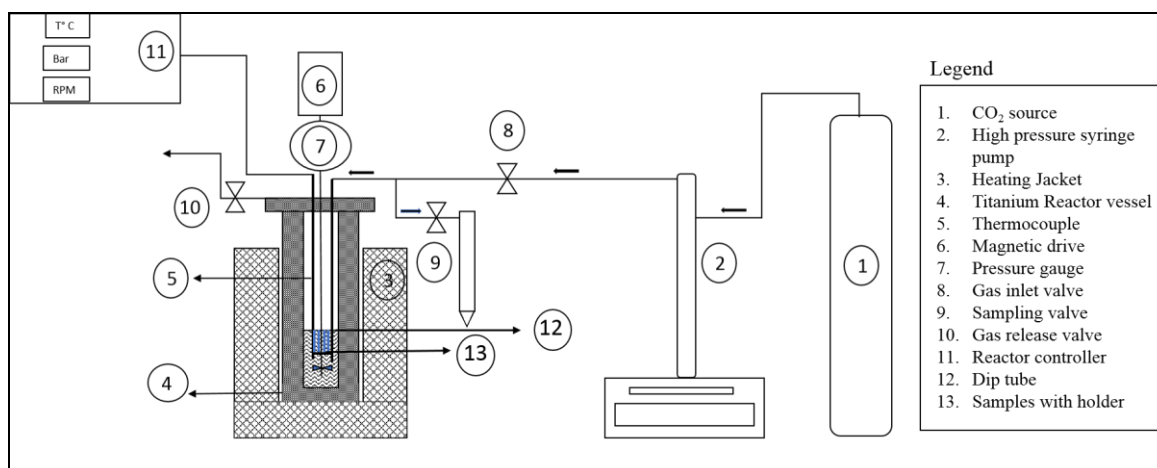


Figure 2.2: Schematic diagram of the high-pressure batch reactor

The sample holder had in total 15 grooves and each groove was 1 mm wide. The wafers were inserted into the grooves and the distance between each wafer was 1 mm. This distance was chosen to mimic an aperture size of a natural fracture. A high-pressure vessel (Parr-Instrument) of 450 mL was used to study mineral dissolution and precipitation in CO₂-saturated water for 44 days at 60°C and 80 bars.

The sample holder was attached to the cooling loop and the dip tube. The samples with the holder was immersed in 315 mL of synthetic formation water with a headspace of 89.5 mL for CO₂. The total mass of the wafers was 17.44 g. The fluid/wafers assembly was continuously stirred at a low rate (100 rpm) in order to avoid breaking of the wafers while keeping the fluid well mixed. The initial fluid/solid mass ratio was 18 and decreases to 14 at the end of the experiment as the fluid volume was reduced by 21 % due to fluid sampling. A syringe pump (500D, Teledyne Isco) was used to add CO₂ to the headspace at the beginning of the incubation, and whenever pressure drops occurred during the experiment. Prior to pressurization, CO₂ was purged at 5 bars for 30 minutes to remove oxygen from the fluid.

Fluid samples of 7 mL volume each were collected from the high-pressure sampling valve after a certain period of time (1, 2, 6, 9, 14, 19, 22, 36, 30, 34, 37 and 44 days). Fluid samples were used for immediate total alkalinity analysis and the remaining sample was filtered through 0.45 µm and acidified with concentrated HNO₃ to a pH < 2 prior to major cation analysis. At

the end of the experiment, the reactor was allowed to cool prior to depressurization. The depressurization of the reactor was performed at a very slow rate (1 bar per minute). This slow cooling and depressurization minimized potential mineral precipitation due to quenching. Three solid phase samples were collected. The residual fluid in the vessel was filtered and the suspended matter (SM) was collected. Deionized water was used for rinsing the internal parts including the fitted wafers and the wafer holder. The rinsed water was later filtered to collect the rinsed solid phase (RP). The precipitated material around the vessel was carefully scrapped off onto a filter paper (VP). The three solid phase samples and the wafers were freeze-dried prior to analysis. Additionally, the SM and RP were completely dissolved in HNO_3 acid at a temperature of 60°C for 2 hours. Major and minor cation concentrations were subsequently measured in diluted HNO_3 using ICP-OES to determine the composition and total mass of authigenic mineral phases in the SM and RP fractions.

Due to the unavailability of onsite formation water, it was prepared in the laboratory in the 450 ml Parr Reactor. A water composition similar to formation water at the Columbia River basalt site was prepared (Newcomb 1972), as shown in Table 2.7, by dissolving 20 g of powdered basalt with a grain size of $45\text{-}106\ \mu\text{m}$ and a specific surface area of $1.2936\ \text{m}^2/\text{g}$ in 380 ml of slowly stirred, CO_2 -saturated deionized water at 60°C and 80 bars for 48 hours. The grain size was determined by sieve fraction and the specific surface area by BET N_2 adsorption using a Micrometric 3-Flex analyser. Fluids were not sampled during the incubation period to avoid loss of fluid. The final composition of the synthetic formation water was later analysed by ICP-OES and is presented in Table.2.7. This process of creating formation water in the laboratory was undertaken to supply cations to enhance precipitation of secondary minerals.

2.2.5 Geochemical modeling

The solubility of CO_2 at 60°C and 80 bars was calculated using Duan and Sun model for ternary systems (Duan and Sun 2003). Aqueous speciation was performed using Geochemist's Workbench 11.0 (GWB) to determine the in-situ pH and whether certain minerals are under or supersaturated at certain times during the experiment (GWB11 2016).

The outlet fluid concentrations at each step was used to compute the mineral saturation index during the experiment. The following equation gives the mineral saturation index Ω

$$\Omega = \frac{Q}{K} \quad (2.3)$$

where Q is the ion activity product, and K is the mineral specific equilibrium constant.

The thermo.com V8. R6+ database was updated for the present study by entering the primary mineral compositions obtained through electron microprobe analysis (EPMA). The database was also updated with thermodynamic data of three different solid solutions of ankerite (Ca-Mg-Fe carbonate mineral) based on ideal mixing considering different ratios of calcite (CaCO_3), magnesite (MgCO_3) and siderite (FeCO_3) (Kerrick et al. 1975, Price 1985). The updated thermodynamic database with the details of the interested minerals are presented in Chapter 3. Aqueous speciation including the in-situ pH was derived by charge balance, using the calculated dissolved CO_2 saturation concentration and the measured cation and bicarbonate ion concentrations.

2.3 Results

2.3.1 Chemical and mineralogical composition of basalt

The bulk chemical composition of the Port Fairy basalt (PFB) is compared with Columbia River (CRB), Deccan Trap basalt (DTB) and Stapafell basalt (SB) as shown in Table 2.1.

The CRB sample comes from a vesicular zone of the Grande Rhonde basalt formation and the DTB sample was taken at an outcrop from western India (McGrail et al. 2006). The sample from Stapafell Mountain is from a basaltic dyke, SW Iceland (Gudbrandsson et al. 2011). The chemical composition of Stapafell is similar to basaltic glass collected from the same area and it is close to the composition of mid-ocean ridge basalt (Oelkers and Gislason 2001, Gislason and Oelkers 2003).

The percentage of SiO_2 is around 50 wt. %. The total wt. % of Ca, Mg and Fe is about 30 % and sum of Na, and K cations is 4.4 % in Port Fairy basalts. The Fe concentration follow in the order $\text{SB} > \text{PFB} > \text{DTB} > \text{CRB}$. Port Fairy basalt is richer in monovalent cation and it proceeds in the following order: $\text{PFB} > \text{DTB} > \text{CRB} > \text{SB}$.

The Loss of ignition (LOI) was minimal in the Port Fairy sample. LOI is a test used in inorganic analytical chemistry which consist of heating the sample at a specific temperature. This results in escape of volatile substance until its mass no longer change. The low LOI in Port Fairy sample indicates minor presence of water molecule or hydrated mineral group.

Table 2.1: Chemical composition of basalt samples from Port Fairy obtained by XRF analysis and compared with average chemical composition of Columbia River Basalt (U.S.A), Deccan Trap Basalts (India) and Stapafell (Iceland). Concentrations are given in wt. %.

Component	PFB	CRB ^a	DTB ^a	SB ^b
SiO ₂	49.2	51.1	50.7	47.9
TiO ₂	2.0	2.11	3.39	1.6
Al ₂ O ₃	13.7	15.0	12.9	13.4
Fe ₂ O ₃	12.1	13.3	14.38	12.3
MnO	0.2	0.17	0.22	0.2
MgO	10.0	5.16	5.03	10.2
CaO	9.0	8.84	9.76	12.2
Na ₂ O	3.3	2.76	2.62	1.5
K ₂ O	1.1	0.44	0.66	0.3
P ₂ O ₅	0.4	0.46	0.39	0.2
	< 0.005			
Cl	< 50			
LOI (XRF)	-0.88			-0.5
Sum	100.88	99.34	100.05	

^a(McGrail et al. 2006); ^b(Gudbrandsson et al. 2011); LOI: loss of ignition

Plagioclase (23.2 % andesine), alkali feldspar (21.3 % anorthoclase), olivine (16.6 % forsterite) and pyroxene (21.2 % diopside) were found to be major crystalline components (Table 2.2).

Plagioclase feldspar is of Na-rich andesine composition whereas alkali feldspar is K-rich anorthoclase. This is in good agreement with XRF data. A trace amount of nepheline and pseudobrookite is also present. Additionally, an XRD amorphous phase was also detected (16.6 %). XRD spectrum of MB is presented in the Appendix, Fig A1.1.

Table 2.2:Port Fairy Basalt mineral composition of basalt determined by XRD

Port Fairy Basalt	wt. %	sd
Amorphous material	16.6	1.7
Andesine	23.2	1
Anorthoclase	21.3	1.4
Diopside	21.2	1
Forsterite	16.6	1
Nepheline	trace	
Pseudobrookite	1.2	0.4

Basalt often contains volcanic glass, which is detected as an amorphous phase by XRD analysis (Kanakiya et al. 2017). Petrographic analysis on thin sections under the optical and scanning electron microscope (SEM) could not identify any volcanic glass (Fig A.1.2). Petrographic analysis using both plane polarised light (PPL) and cross polarised light (XPL) enables accurate mineral identification as different minerals exhibit unique colours and textures when viewed under different light.

Personal communication with the XRD team at Australian National University, Canberra indicated that a mixture of very finely grained minerals often does not generate identifiable sharp XRD peaks and hence, they are classified as “amorphous phase”. The rock is comprised predominantly of plagioclase, olivine and clinopyroxene (Fig. 2.3).

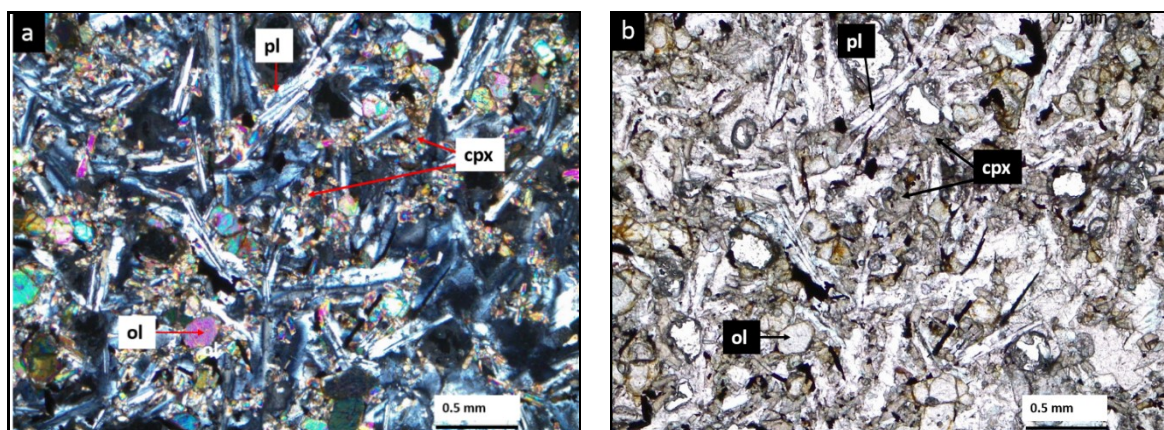


Figure 2.3: Photomicrographs of samples of basalts from Port Fairy showing the major mineralogy a) under cross polarized light (XPL); b) under plane polarised light (PPL); Pl-plagioclase; Cpx-clinopyroxene; Ol-olivine

The opaque minerals were identified as ilmenite and apatite. The clinopyroxenes are elongated and finer than olivine and show less intense colour. The clinopyroxene could be augite due to its dark brown appearance suggesting a high titanium concentration. The presence of titanium in clinopyroxene was verified through microprobe analysis and SEM-coupled with BSE (back scattered electrons) (Fig. 2.4).

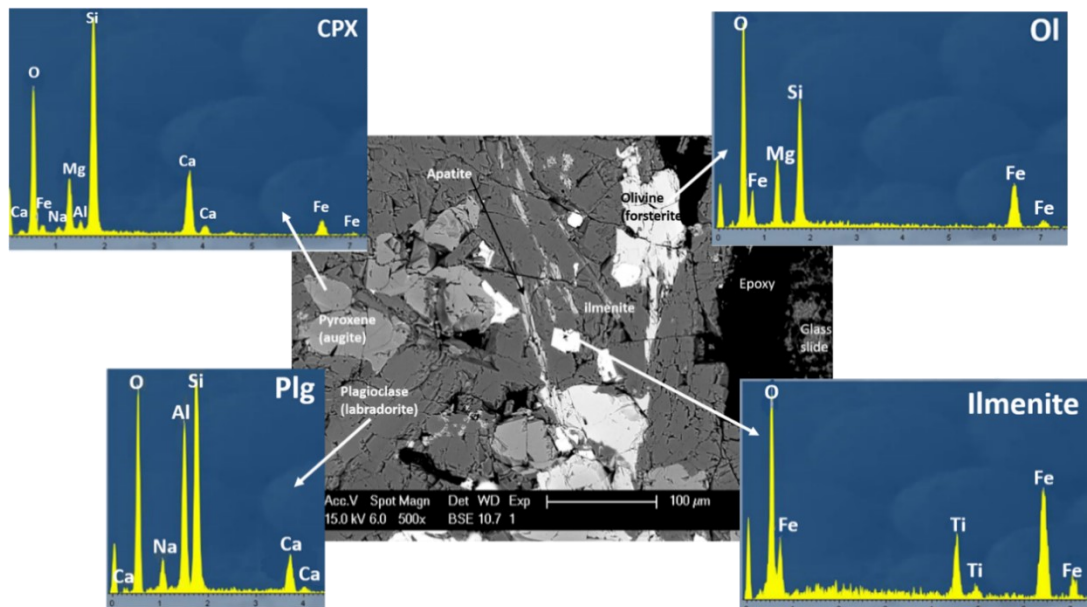


Figure 2.4: Back-scattered image from a polished thin section of massive basalt showing the qualitative chemical composition of main minerals in MB.

The microprobe analysis represents the chemical composition of the major primary minerals as wt. % in form of oxides as shown in Table 2.3, which was formulated using standard mineral formula, specified with mineral group, normalised with oxygen. The results from microprobe analysis specified the chemical composition of the main minerals suggesting the presence of Na-rich plagioclase (labradorite) and Mg-rich olivine (forsterite) as phenocrysts. The presence of apatite mineral was $< 2\%$ and thereby microprobe analysis was not performed on apatite mineral. Anorthoclase was merely observed in the thin section under the optical microscope but in general Na and K-rich minerals were detected in the microprobe analysis. This could be due to the presence of very fine-grained Na-rich plagioclase matrix with a little K^+ impurity and hence it is here referred to as Na-rich matrix mineral.

Table 2.3: Quantitative chemical composition of the major primary minerals of the Port Fairy Basalt obtained through microprobe analysis

Component (wt.%)	Pyroxene	Olivine	Plagioclase	Na-rich matrix	Opaque
SiO ₂	48.65	38.39	53.74	52.24	0.01
TiO ₂	2.46	0.03	0.13	0.12	50.65
Al ₂ O ₃	3.53	0.06	29.09	29.8	0.03
Cr ₂ O ₃	0.02	0.03	0.00	0.03	0.00
FeO	9.76	21.63	0.55	0.49	47.02
V ₂ O ₃	0.11	0.02	0.02	0.01	0.26
MnO	0.18	0.25	0.00	0.00	0.65
MgO	13.00	39.78	0.08	0.11	1.89
ZnO	0.01	0.09	0.06	0.00	0.00
NiO	0.04	0.26	0.02	0.00	0.00
K ₂ O	0.00	0.01	0.31	0.26	0.00
Na ₂ O	0.59	0.01	5.31	4.54	0.03
CaO	21.00	0.29	11.06	12.0	0.03
Nb ₂ O ₅	0.05	0.06	0.04	0.00	0.00
Sum	99.40	100.86	100.3	99.7	100.5

The composition of major minerals determined by microprobe is given in Table 2.4.

Table 2.4: Mineral composition determined by microprobe analysis

Mineral	Basalt mineral formula
Plagioclase (labradorite)	$Ca_{0.54}Na_{0.46}Fe_{0.04}Al_{1.55}Si_{2.43}O_8$
Pyroxene (augite)	$Ca_{0.86}Mg_{0.74}Fe_{0.30}Mn_{0.01}Ti_{0.07}Na_{0.04}Al_{0.36}Si_{1.87}O_6$
Olivine (forsterite)	$Mg_{1.54}Fe_{0.47}Mn_{0.01}Si_{0.9}O_4$
Ilmenite	$Fe_{1.60}Ti_{0.93}Mg_{0.07}Mn_{0.01}O_3$
Na-rich matrix ^a	$Na_{0.68}K_{0.039}Ca_{0.08}Fe_{0.08}Al_{1.10}Si_{2.46}O_8$

^a formulated using alkali feldspar (K-feldspar) formula

Ollier (1985) refers to the basalt from the Mt Rouse-Port Fairy flow as fine-grained and slightly vesicular. They observed 5-7 % of small fresh olivine (< 0.3 mm) phenocrysts in fine-grained groundmass made up of 30 % plagioclase laths (up to 0.2 mm length and 0.02 mm wide).

The remainder groundmass was made up of iron oxide granules, fine pyroxenes and small patches of feldspar. The groundmass was holocrystalline and less transparent due to its fine-grained structure (Ollier 1985). Other studies on the PF basalt (Irving and Green 1976, Orth 1988, Matchan and Phillips 2011) showed an olivine composition of 20 wt. % of the rock with subhedral phenocryst (average size 0.3-0.5 mm). Titanomagite was mainly observed as groundmass but also as phenocryst (up to size 1.2 mm). The clinopyroxene showed a zonation reflecting the variation of titanium in the crystal. They rarely observed any presence of glass. Magnetite and minor ilmenite formed around olivine pyroxene clusters. Apatite occurred as fine needles (~ 1 %) in interstitial plagioclase. The volume of vesicles makes up about 15 % and the sizes are observed up to 8 mm.

Overall, the PF basalt composition is of olivine tholeiite composition and is comparable to most continental flood basalts. The major minerals of the CRB and DTB are plagioclase feldspar and pyroxenes. Quartz and olivine are present in minor amounts. Secondary minerals such as carbonate minerals, clay minerals, and zeolites were detected in the weathered DTB outcrop sample (McGrail et al. 2006). The average composition of the mid-oceanic ridge basalt from Stapafell Mountain, SW Iceland suggests that the relative volume proportion of plagioclase: pyroxene: olivine is 44:39:17 of labradorite, augite and of forsterite composition respectively (Gudbrandsson et al. 2011). Thereby, the primary mineral composition of basalt from PFB is similar to other basalts in other regions which have been used in laboratory studies on mineral dissolution and precipitation in the context of geological carbon storage.

The porosity and total surface area of the PFB wafer sample as determined by micro-CT analysis is 11.8 % and 5488 cm^2 ($0.0314 \text{ m}^2/\text{g}$) respectively. The specific surface area of the basalt powder used for the preparation of formation water is 40 times larger than the specific surface area of wafers. The porosity measured by saturation and buoyancy technique is 12 %.

2.3.2 Characterisation of mineral phases formed during incubation

Following the opening of the reactor, solid particles were observed in the residual fluid as well as at the surface of the internal parts of the reactor and on the wall of the reactor vessel. Apart from the reacted wafers, three solid samples were collected from the vessel. Fig. 2.5 shows the solid precipitates from rinsed wafers (RP) and precipitates on the vessel wall (VP). FTIR peaks in all the solid samples were observed at around 3421 cm^{-1} , 2950 cm^{-1} , 2360 cm^{-1} , 1644 cm^{-1} , 1455 cm^{-1} , 1003 cm^{-1} and 433 cm^{-1} , which suggests the formation of smectites and zeolite.

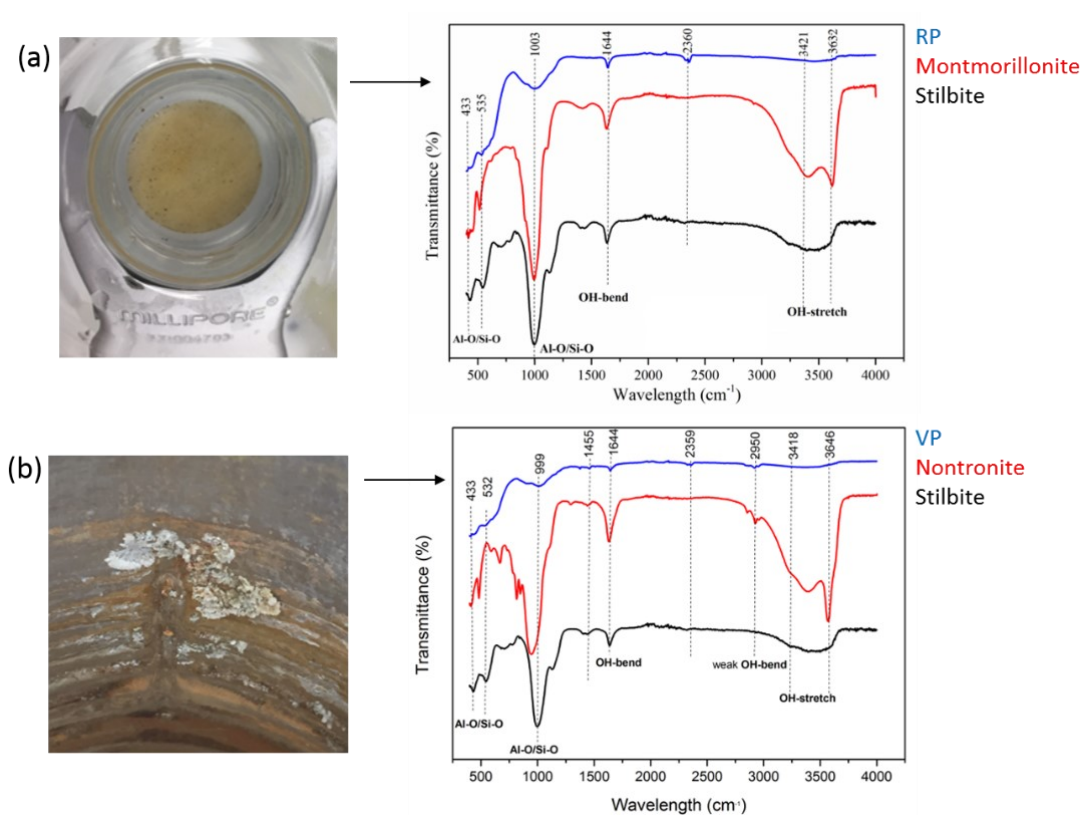


Figure 2.5: FTIR spectra of (a) solid phase from rinsed wafers (RP) matched with FTIR spectra of montmorillonite (a smectite) and stilbite (a zeolite) and (b) solid precipitate phase from vessel wall (VP) matched with FTIR spectra of nontronite (a smectite) and stilbite (a zeolite)

Table 2.5 presents the transmittance peaks and bands of smectites, zeolites, and major carbonate minerals. The zeolite group and smectite group have a broadband in the wavenumber region $3400\text{--}3200\text{ cm}^{-1}$ corresponding to symmetric and asymmetric stretching vibrations of OH groups. The zeolite group and smectite group have a broadband in the wavenumber region

3400-3200 cm^{-1} corresponding to symmetric and asymmetric stretching vibrations of OH groups. The bending vibration of water (H-O-H) occurs at around 1644 cm^{-1} . The peak around 2920 cm^{-1} is due to additional weak bending vibration of H-O-H bond. The stretching vibrations of Al-O, and Si-O are found at a range of 990-1003 cm^{-1} . The bands around 433 and 535 cm^{-1} are due to Al-O-Si deformation of the clay minerals. The main difference in the FTIR spectrum between the zeolites and the smectites is the double high-intensity peaks in smectite in the range of 3300-3600 cm^{-1} (Pechar and Rykl 1981, Byrappa and Kumar 2007, Adikary et al. 2015). Fig. 2.5a shows the matching peaks of rinsed wafer precipitates (RP) with stilbite, a common zeolite, and montmorillonite from the smectite group. Similarly, the peaks of vessel precipitate (VP) match the spectra for stilbite and nontronite belonging to the smectite group (Fig. 2.5b). The peaks of the solid sample at lower wavelengths $< 1000 \text{ cm}^{-1}$ are very weak compared to the sharp peaks of zeolites and smectites, which suggests the newly formed solid phases are poorly crystalline. From the above observations, it is concluded that the newly formed mineral phases are zeolites and smectite.

Table 2.5: Transmittance band of solid samples, zeolites, smectites and carbonates

Peak no	SM (cm^{-1})	RP (cm^{-1})	VP (cm^{-1})	z1 (cm^{-1})	z2 (cm^{-1})	z3 (cm^{-1})	sme1 (cm^{-1})	sme2 (cm^{-1})	c1 (cm^{-1})	c2 (cm^{-1})	c3 (cm^{-1})
1	–	3632	3646	–	–	–	3632	–	–	–	–
2	–	–	–	–	3594	3592	3569	3569	–	–	–
3	3382	3421	3418	3367	3403	3401	3403	3403	–	3448	3363
4	–	2923	2950	–	2920	–	2927	2925	–	–	–
5	2349	2359	2359	–	–	2360	2364	2362	2514	2528	2527
6	1643	1644	1644	1644	1627	1637	1633	1631	1794	1829	1811
7	1454	–	1455	–	1457	1440	–	1419	–	1432	1405
8	–	–	–	–	–	–	1394	–	1394	–	–
9	999.2	1003	999.2	1002	998	998	995	946	1091	1041	–
10	–	535	532	511	518	545	515	588	874	881	865
11	429	433	433	455	449	433	418	418	711	746	738

where SM, RP and VP are formed phases of suspended matter, rinsed wafer and vessel precipitate respectively;

Zeolites: z1- chabazite; z2 - heulandite and z3 – stilbite

Smectites: sme1 – montmorillonite; sme2 – nontronite

Carbonate minerals: c1 – calcite; c2 – magnesite and c3 - siderite

As the peaks of all three formed solid phases were similar, the spectrum of VP was tried to match with common carbonate minerals (calcite, magnesite and siderite) previously observed

in other experimental studies in context of CO₂ storage (Stockmann et al. 2011, Stockmann et al. 2013, Xiong and Giammer 2014, Matter et al. 2016, Xiong et al. 2017a, Xiong et al. 2017b, Menefee et al. 2018). However, the peaks do not match, confirming no precipitation of pure carbonate minerals. Fig. 2.6 shows the mismatch of peaks on the spectrum of the carbonate minerals with the peaks of VP spectrum.

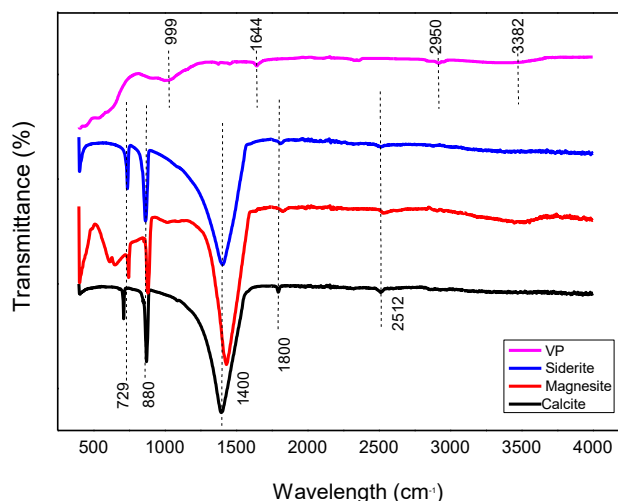


Figure 2.6: FTIR spectra of precipitation around the reactor (VP) showing different peak positions as compared to characteristic peaks of carbonate minerals (calcite, magnesite and siderite)

The measured cation concentrations from dissolved SM and RP phases were converted to their respective molar ratios with respect to Si and presented as stoichiometric formula (Table 2.6). It is observed that the mass of Fe is relatively high in both fractions, which suggests Fe-oxides were formed concurrently with other minerals. FTIR peaks of RP already confirmed the formation of smectite and zeolite. The spectrum of SM (Fig.A1.5) confirmed the presence of chabazite (zeolite). The total mass of cations consumed through the formation of the SM and RP fractions is 7.0×10^{-5} mole.

Table 2.6: Stoichiometry and calculated mass of suspended (SM) and rinsed (RP) solid phase fractions.

Solid phase		Mass (mole)
SM	Ca (0.22) Mg (0.06) Fe (3.07) Na (0.16) Al (1.76) K (0.42) Si	3.71×10^{-5}
RP	Ca (0.30) Mg (0.24) Fe (2.36) Na (0.96) Al (0.66) K (0.45) Si	3.23×10^{-5}

The precipitation products found at the surface of the basalt wafers have a different chemical composition compared to the suspended matter. The orange precipitate on wafer W5 is predominantly Fe-oxide. It is believed that even after purging the reactor with CO₂, the reactor was not completely devoid of oxygen (Luhmann et al. 2017, Menefee et al. 2018). The EDS mapping also showed abundant Al and Si along with Fe and O, which suggests a coprecipitation of kaolinite and Fe-oxides (Fig. 2.7).

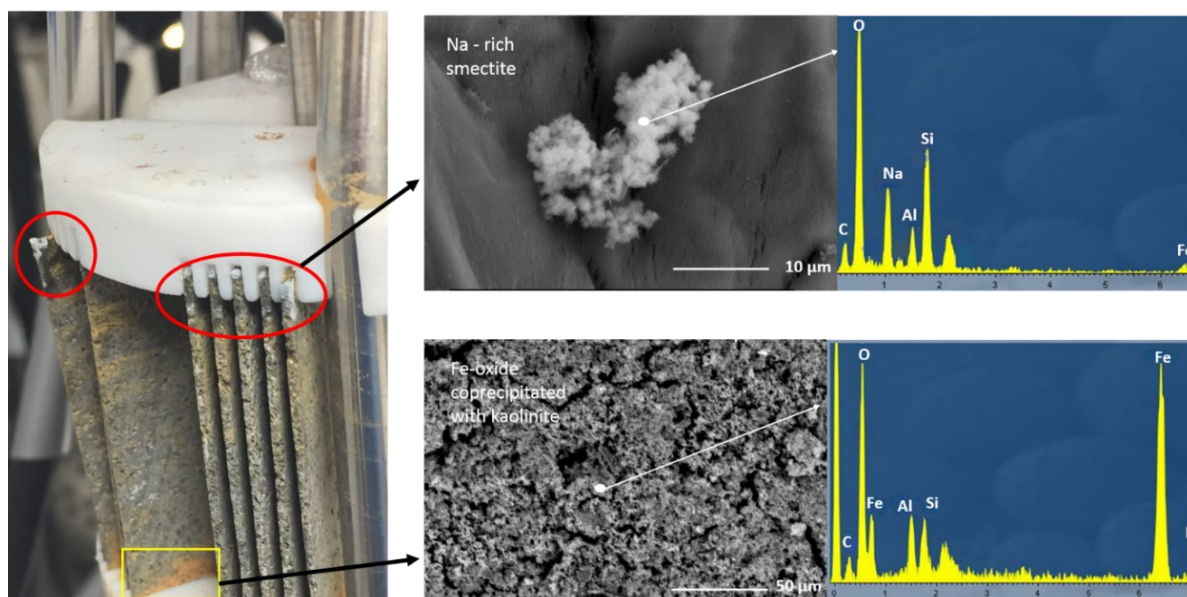


Figure 2.7: SEM image and EDS map of precipitate on basalt wafers

A minor carbon peak was also observed, suggesting precipitation of siderite (Fe-carbonate mineral). White precipitates were observed on the edges of the multiple wafers. Minerals rich in Na, Si, Al with trace amounts of Fe and Mg were also observed and it is believed to be Na-rich smectite based on observations at natural analogue sites (Goldberg et al. 2008, Flaathen et al. 2009).

Pores and vugs at the surface of the pristine basalt wafer W10 were filled and coated with secondary mineral phases of three different morphologies (Fig. 2.8). The morphologies of L1 and L3 were observed to be fine-grained and tightly spaced, while L2 showed elongated nanowire-like structure. At the surface of L2, flaky material was observed and was interpreted as poorly crystalline hydroxide carbonate phase based on its EDS spectrum (Fig. 2.8b).

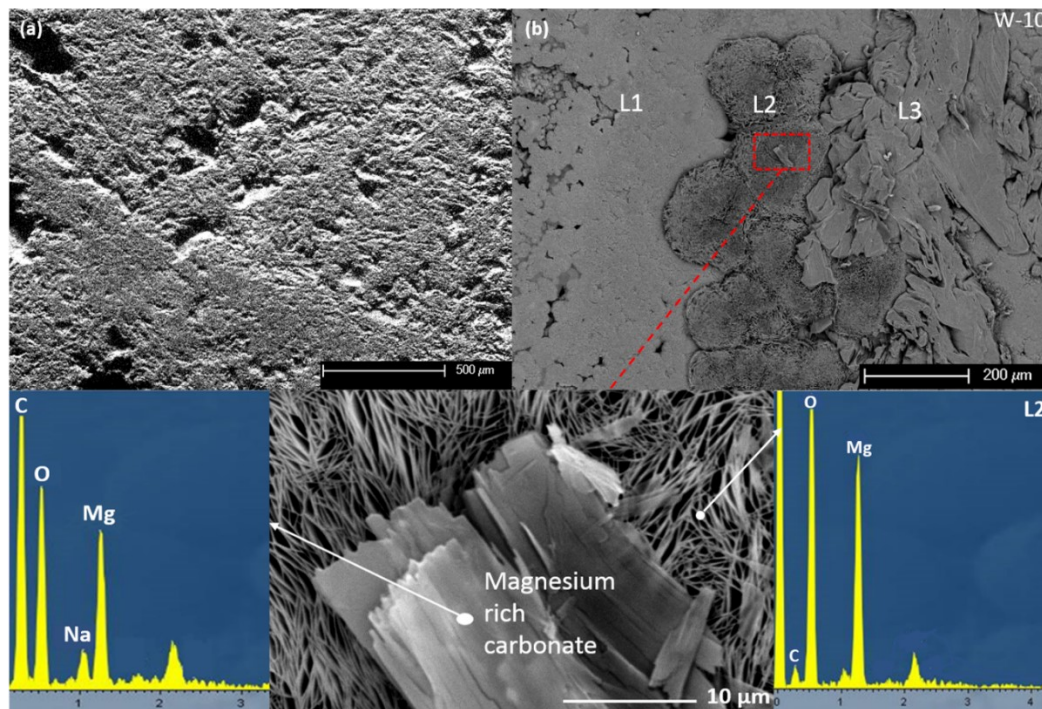


Figure 2.8: SEM images of (a) pristine basalt wafer with primary pores and vugs (b) post experimental W-10 wafer covered with three different layers. Red box indicates flaky Mg-rich carbonate on top of Mg-rich carbonate fibrous layer L2.

2.3.3 Water composition

The cation concentration of the synthetic formation water was comparable with the water composition in Columbia River Basalt (Newcomb 1972) but showed elevated concentrations of Mg, Fe, and HCO_3^- ions with an initial pH of 8.1 (Table 2.7).

Table 2.7: Composition of initial formation water.

Component (mg/L)	pH	Si	Mg	Ca	Fe	Na	Al	K	SO4	Cl	HCO_3^-
Incubation water ^a	8.1	56.26	52.12	9.14	70.46	14.67	0.13	3.87	-	-	489
CRB water ^b	8.2	55	12	24	0.09	17	-	2.5	6.2	5.5	154

^aLaboratory prepared; ^b (Newcomb 1972)

The water composition of the fluid samples showed a rapid increase in dissolved Si, Mg and Na for the first 6 days suggesting mineral dissolution, followed by a concurrent drop in major ions (Si , Ca^{2+} , Mg^{2+} , K^+ , Al^{3+} , and Na^+) and alkalinity concentrations by more than 30 % of their maximum concentrations for the remaining incubation period of 38 days suggesting

secondary mineral precipitation (Fig. 2.9). The initial concentration of Fe in the formation water was 70.46 mg/L. However, the concentration was only 0.23 mg/L in the sample taken on day one of the incubation presumably caused by the formation of Fe-oxides in the initial synthetic formation water before subjecting it into the reactor (Table 2.8). The given cause for the very low dissolved Fe concentration is supported by previous experiments where the reactor was not oxygen-free after purging the reactor with CO₂ (Luhmann et al. 2017).

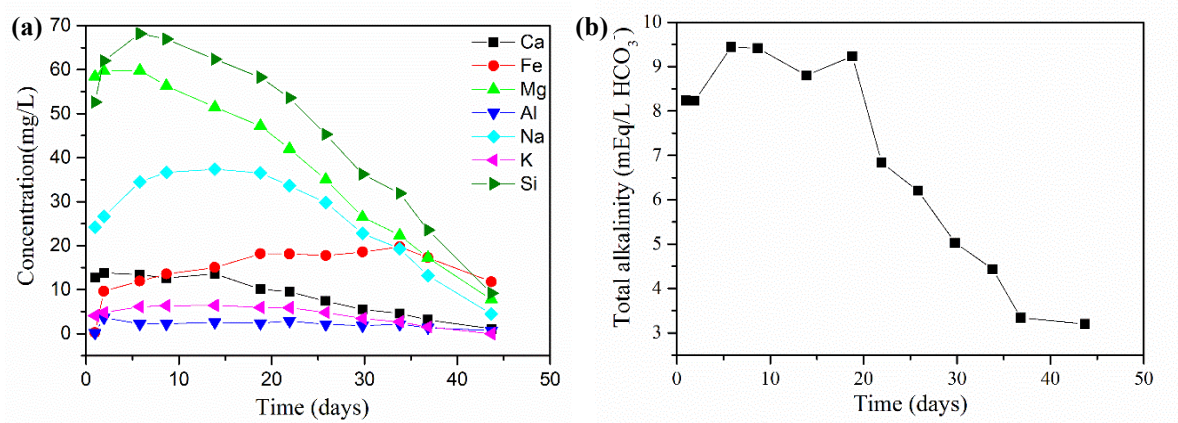


Figure 2.9: (a) Major cation and Si concentration in the fluid and (b) total alkalinity over a period of 44 day

However, dissolved Fe gradually increased after day 1 until it started to decline after 34 days. Relatively high concentrations of Mg and Fe indicate the dissolution of olivine while high Na and K suggest the congruent dissolution of Na-rich matrix minerals.

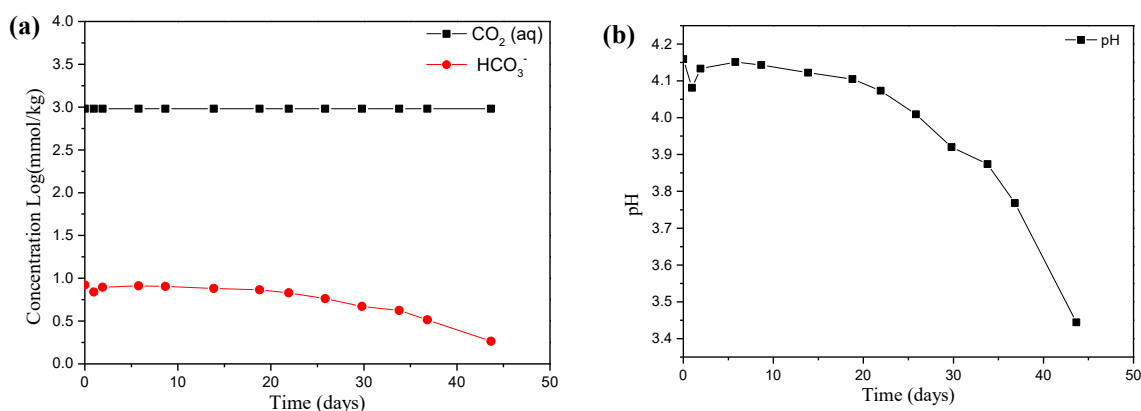


Figure 2.10: (a) Calculated pH of the effluent (b) concentrations of aqueous CO₂ and HCO₃⁻ in the fluid over a period of 44 day

The decrease of Mg and Si ions suggests that they are involved in concurrent precipitation. Similarly, total alkalinity shows a decreasing trend over a period of 44 days. Initially, the alkalinity of the fluid decreased from 8 meq/L to 6.6 meq/L on the 1st day (Fig. 2.9b). Subsequently, it decreased until the end of the experiment after increasing slightly from day 2 to day 6. The pH of the fluid also follows the same decreasing trend (Fig. 2.10a). The CO₂ solubility at 60°C and 80 bars is 0.91 mol/kg (Duan and Sun 2003).

Table 2.8: Outlet fluid concentration over the experimental duration

Time (days)	pH ^a	Ca (mg/L)	Fe (mg/L)	Mg (mg/L)	Al (mg/L)	Na (mg/L)	K (mg/L)	Si (mg/L)	Total Alkalinity HCO ₃ ⁻ (mg/L)
0	8.1	9.14	70.46	52.12	0.13	14.67	3.87	56.26	498
1	4.08	12.71	0.23	58.46	0.18	24.19	4.09	52.62	403
2	4.13	13.80	9.64	59.71	3.63	26.65	4.79	62.02	459
6	4.15	13.42	11.96	59.85	2.24	34.49	6.16	68.20	478.5
9	4.14	12.66	13.59	56.34	2.22	36.67	6.38	66.95	469
14	4.12	13.57	15.03	51.47	2.57	37.39	6.45	62.36	446.3
19	4.10	10.12	18.15	47.23	2.36	36.50	5.98	58.28	427.8
22	4.07	9.50	18.10	42.00	2.90	33.60	5.90	53.60	396.3
26	4.00	7.40	17.76	35.02	2.13	29.78	4.80	45.29	339.2
30	3.92	5.53	18.57	26.53	1.81	22.78	3.45	36.25	274.3
34	3.87	4.57	19.74	22.35	2.13	19.33	2.68	31.90	245.9
37	3.76	3.15	17.30	17.27	1.36	13.19	1.52	23.56	190.9
44	3.44	1.10	11.80	7.80	0.70	4.50	0.00	9.20	107.5

^a Calculated pH

Modeling the aqueous speciation accounted for the measured total alkalinity and cation concentrations as well as CO₂ solubility suggests HCO₃⁻ is about three orders of magnitude lower compared to dissolved CO₂ (Fig. 2.9b). This is the result of equilibrium constants of those species, the given pressure and temperature conditions and the low pH of the fluid throughout the experimental duration.

2.3.4 Mineral Saturation

The secondary mineral saturation state showed an interesting trend (Fig. 2.11). Smectites were initially supersaturated and became less saturated or undersaturated with the progress of time. Nontronite remains highly supersaturated until the end of the reaction time. Beideillite was

initially supersaturated but became undersaturated after 40 days. Montmorillonite closely followed the trend and became undersaturated after 35 days of reaction. Stilbite which belongs to the zeolite group remains supersaturated for 35 days. Fe-oxides and hydroxides show supersaturation throughout the experimental duration. Among the group of carbonate minerals, siderite was observed to be close to saturation followed by magnesite and ankerite. Kaolinite was initially supersaturated but became less saturated and was close to equilibrium at the end. Chalcedony was consistently supersaturated. Nontronite, montmorillonite, stilbite was identified as secondary minerals in the batch experiment through solid phase analysis.

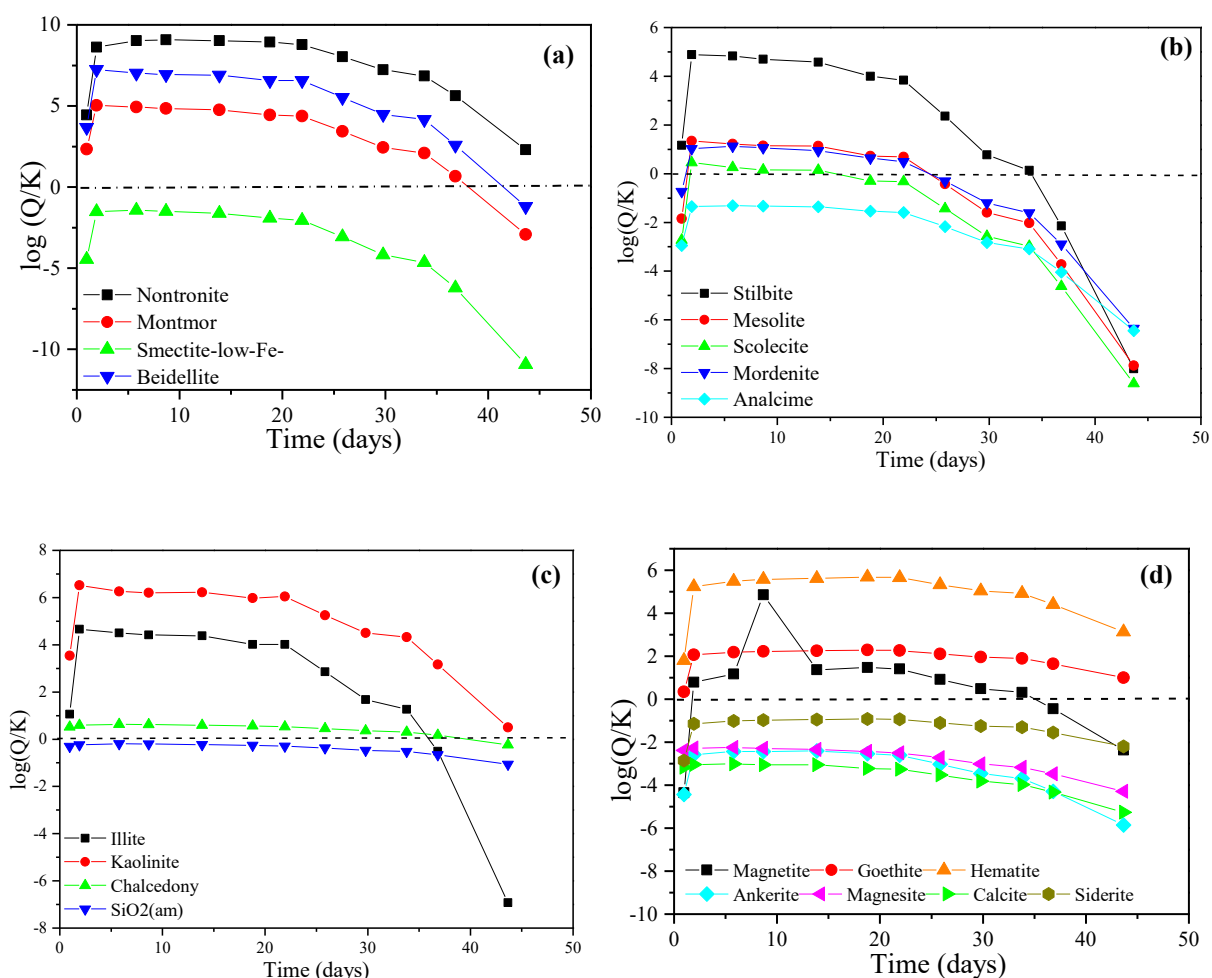


Figure 2.11: The saturation state of potential secondary minerals over time (a) smectites (b) zeolites (c) simple Si-Al and SiO₂ minerals (d) Fe-oxides, hydroxides and carbonate minerals

Kaolinite and Fe-oxides were also formed as secondary minerals on the wafers. The observed supersaturated minerals from the aqueous speciation modeling matched closely with the secondary minerals in the experiment. Major secondary minerals formed from basalt alteration

are phyllosilicates, zeolites, chalcedony, calcite (Sukheswala and Avasia 1974, Rogers et al. 2006, Luhmann et al. 2017, Srivastava et al. 2018).

2.4 Discussion

2.4.1 Nature of mineral precipitation

Fe-oxide, kaolinite, Mg-rich carbonate, Na-rich smectite and zeolite formed on the wafer surface as a coating on top of the primary minerals. The observed minerals were consistent with modeling results as they were supersaturated except for magnesite.

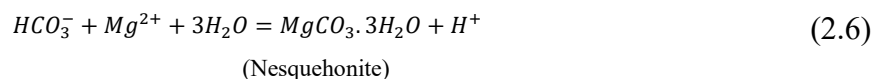
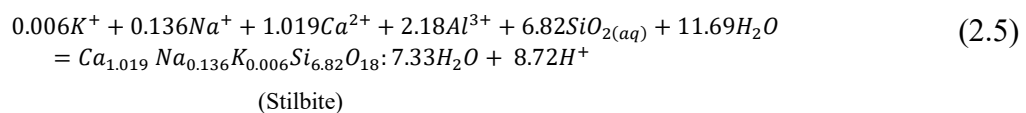
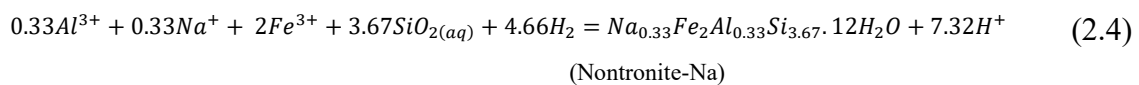
The surface layers L1 and L2 could be any form of hydrous Mg-carbonate ($\text{MgCO}_3 \cdot x\text{H}_2\text{O}$), a phase commonly known to form as a precursor to magnesite (MgCO_3). Nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) was observed to form at elevated $p\text{CO}_2$ and lower pH compared to dypingite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) in previous experiments (Harrison et al. 2013, Harrison et al. 2015). Hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) may form as a secondary intermediate hydrous Mg-carbonate (Power et al. 2007). Hydromagnesite may then transform into magnesite at higher temperature and pressure and over a longer experimental time (Hänchen et al. 2008). Elevated dissolved Fe(II) concentrations (10-20 mg/L) in the experimental study experiment may have accelerated the nucleation and precipitation of hydrous Mg-carbonate (Saldi et al. 2013, Sissmann et al. 2013, Sissmann et al. 2014).

Smectite in the form of montmorillonite and nontronite, and zeolite in the form of stilbite were observed to form in the residual fluid (SP fraction), and at the surface of the internal part of the vessel (RP). Additionally, smectite was observed at the wafer surface and nontronite was the most supersaturated mineral in the system followed by kaolinite. The formation of Si-Al minerals belonging to the groups of smectites and zeolites have been observed in other experimental studies with comparable conditions and at natural analogue sites as well. Ca-Mg-Fe smectites formed in experiments with variable temperature and pressure together with Fe-oxides (Gysi et al. 2011, Gysi and Stefánsson 2012b, Sissmann et al. 2014, Hellevang et al. 2017) and iron-rich saponite, nontronite, goethite were found in the joints of basalt located at Geelong, Australia (Shayan et al. 1988). Interaction of fluid with low concentration of CO_2 at low temperature $< 100^\circ\text{C}$ formed amorphous or poorly crystalline hydroxides, allophane, imogolite, kaolinite and clay minerals such as Mg-, Ca-, and Fe-rich smectites (Arnalds 1990,

Crovisier et al. 1992, Stefánsson and Gíslason 2001, Aradóttir et al. 2012) while formation of zeolite-facies mineral assemblages, consisting of mixed-layer chlorite/smectite clays, thomsonite, natrolite, gonnardite, analcime and chabazite were observed under elevated CO₂ (Rogers et al. 2006).

Precipitation of carbonate minerals either in form of calcite or mixed Ca-Mg-Fe minerals was not detected despite the Ca-rich composition and the abundance of Ca-rich plagioclase and pyroxene minerals in the PF basalt sample (9 wt.% CaO). This result disagrees with most experimental studies, but differences in the pressure, temperature, initial water composition and pCO₂ conditions compared to this study can be used to explain those differences. At low temperature (20-50 °C), low partial pressure of CO₂ (< 10⁻² bar) and high pH (> 9) calcite was observed as a pre-existing carbonate at the Carbfix site, Iceland (Matter et al. 2016). Similarly, ankerite precipitation was found in CRB at a temperatures of 36-44 °C and a pressure of 77 bars at Big Sky Carbon Sequestration Project site (McGrail et al. 2016). Several studies at elevated pressure and temperatures (> 100°C and > 100 bars) and with a longer experimental duration reported the higher saturation indices of Ca-carbonate such as aragonite, ankerite and calcite (Menefee et al. 2018, Snæbjörnsdóttir et al. 2018, Xiong et al. 2018). However, in this study, the Ca²⁺ was consumed by the precipitation of smectite and zeolite.

Interestingly, the formation of Fe-oxide, hydrous Mg-carbonate, smectite and zeolite lead to the concurrent formation of H⁺ and consequently lead to further acidification during the experiment.



The gradual decrease in pH with respect to reaction progress is observed in Fig. 2.10b. Even though the decrease in pH and cation concentrations means primary minerals such as olivine, pyroxene and plagioclase become even more undersaturated, the dissolution of those minerals

is not indicated by means of an increase in respective cation concentrations after several days of incubation. This is interpreted as evidence for the passivation of wafer surfaces together with the observed formation of secondary mineral coatings (as shown in Fig.2.8).

2.4.2 Net release and uptake rate of elements

The release rate of elements (cations and Si) from primary minerals is important to determine as it could limit secondary mineral formation. The element release rate from primary minerals with potential concurrent uptake rate by secondary minerals, r , was calculated as

$$r = \frac{\Delta n_i(\text{elements})}{SA \cdot \Delta t} \quad (2.7)$$

where r is the net release rate of elements in the reactor (mol/cm²/sec); ($\Delta n_i(\text{elements})/\Delta t$) is the change in amount of cations and Si over time (mol/sec) due to dissolution and precipitation; SA is the total surface area the wafers (cm²). Release rates of cations and Si are presented in Fig. 2.12. Most of the cations were released into the fluid for the first 2-5 days, ($r > 0$). On day 5, the rate of cations and Si mobilisation and uptake were similar ($r \approx 0$) and a net cation uptake ($r < 0$) was observed between day 5 and the end of the incubation (day 44) for Ca²⁺, Al³⁺, Na⁺ and K⁺ while Mg²⁺ uptake rate is observed as early as day 2. An initial rapid release of cations was observed in the form of an early spike in the net mobilisation rate except for Si and Fe. The initial drop of Si and Fe depicts the rapid uptake rate of Si and Fe ions. This could be due to the formation of amorphous silica and Fe-oxides just after the preparation of the formation water and before subjecting it into to the reactor.

The dissolution of crystalline basalt is dominated by the release of Fe and Mg at low pH (3-5) due to the high dissolution rate of olivine and pyroxene while plagioclase has a higher dissolution rate at higher pH (Oelkers, 2001, Gudbrandsson et al. 2011). The rapid dissolution of olivine and pyroxene and the Na-rich matrix can also be seen by the initial high release rate of Mg, Na, and Si in this study, while the increase in dissolved Fe is very small presumably due to Fe oxidation (Fig. 2.12). Even though potential secondary minerals were supersaturated from the beginning of the incubation (Fig. 2.11), mineral dissolution initially exceeded precipitation based on cation concentration changes.

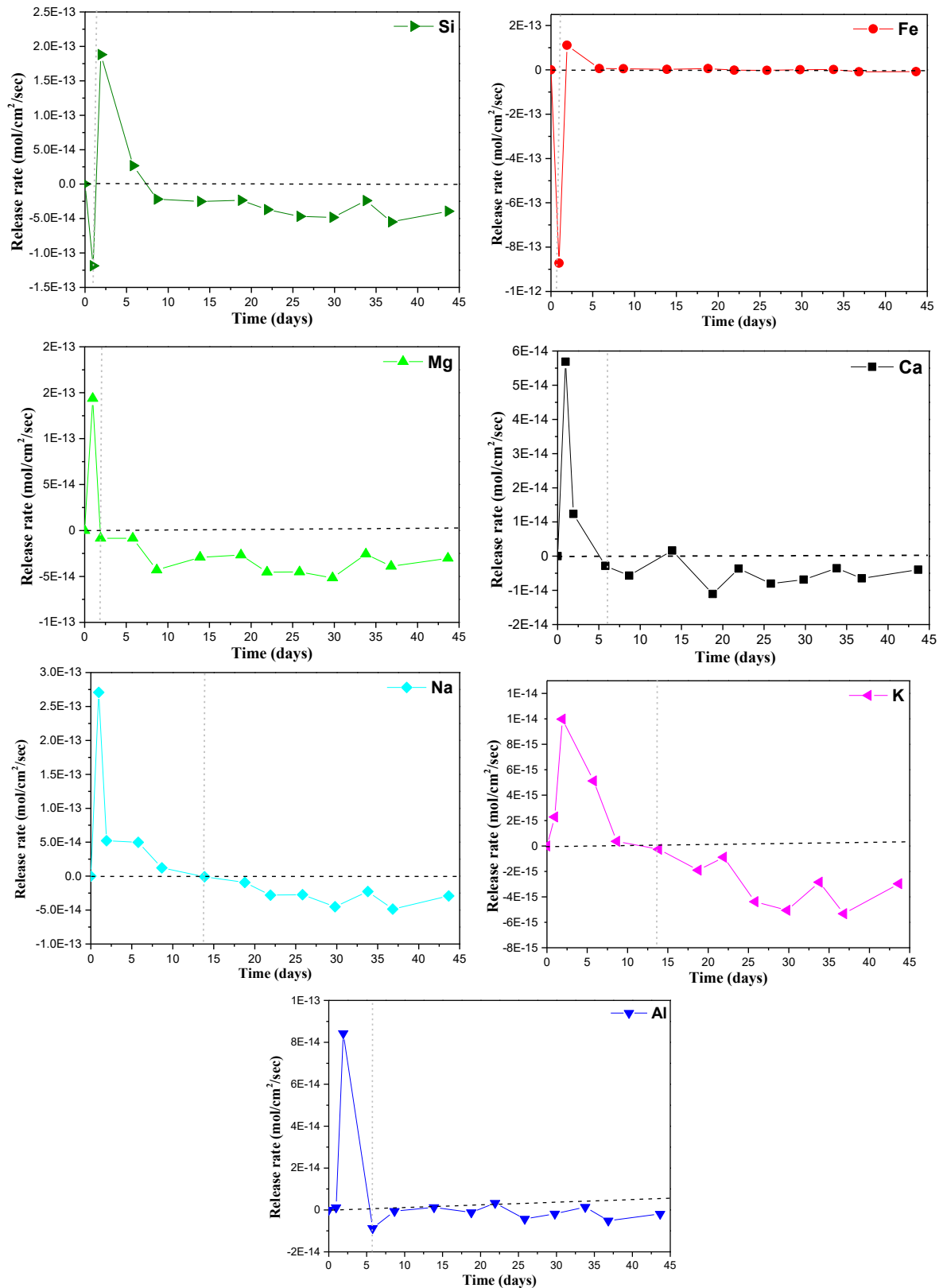


Figure 2.12: Element release rates and uptake rates over the period of 44 days. The dashed line indicates the first drop under ($r < 0$), and thus the initiation of cation uptake secondary phases.

However, within a few days the precipitation rate exceeded cation and Si release rate and dissolution rate of the primary minerals. Overall, the changes in dissolved cation concentrations are dominated by the cation uptake throughout most of the experiment and cation concentrations decreased to about 10 mg/L or less towards the end of the experiment.

The total mass of cations precipitated inside the reactor was calculated from the concentration gradients over time and is equivalent to $2.81 \cdot 10^{-3}$ mole. For comparison, the total mass of cations consumed by the suspended (SP) and rinsed (RP) fractions is $7.0 \cdot 10^{-5}$ moles (Section 3.2), which is only 2.5 % of the total precipitation. This suggests that over 95 % of cations precipitated onto the wafer surface. Assuming all Si and Mg precipitated onto the wafer surface the averaged Si and Mg precipitation rates are $4.17 \cdot 10^{-14}$ mol/cm²/sec and $3.9 \cdot 10^{-14}$ mol/cm²/sec, respectively. Assuming all Mg is precipitated as hydrous Mg-carbonate (nesquehonite) and using the respective mineral density the volume of precipitated hydrous Mg-carbonate is estimated with 0.05 cm³. Assuming all Si is precipitated as stilbite or nontronite, the precipitated mineral volume is 0.14 cm³ or 0.25 cm³, respectively. When those mineral volumes are normalised to one litre of water, a total of 0.13 cm³ of hydrous Mg-carbonate mineral and a total of 0.36-0.66 cm³ of Si-Al mineral are estimated to have precipitated. These mass balance calculations reflect a very large capacity of authigenic mineral formation almost exclusively as a coating on the basalt surface. This process has led to surface passivation of the primary minerals and the amount of H⁺ ions in the system increased due to mineral formation. Several studies have been performed to understand the effect of surface coating on primary mineral dissolution rates (Cubillas et al. 2005, Stockmann et al. 2011, Stockmann et al. 2013, Sissmann et al. 2014, Harrison et al. 2015). Stockmann and group reported that calcite precipitation on diopside and basaltic glass did not inhibit the dissolution rate (Stockmann et al. 2011, Stockmann et al. 2013) while other studies suggested the formation of silica-rich layers inhibited dissolution rates of olivine and serpentine (Stockmann et al. 2013, Sissmann et al. 2014). Precipitation of magnesite clogged the pores and limited the reaction during olivine carbonation (Hövelmann et al. 2012). The dissolution of the primary mineral is not hindered if the secondary mineral has a (1) porous crystalline structure or (2) dissimilar crystalline structure avoiding epitaxial growth. The porous structure allows the underlying cations to diffuse into the fluid (Daval et al. 2009, Stockmann et al. 2013). Thus, the transformation of the porous structure to denser impermeable layers over reaction progress leads to surface passivation (Harrison et al. 2015).

2.5 Conclusion

An experimental study was carried out to study mineral dissolution and precipitation involving basalt and CO₂-saturated formation water at a pressure of 80 bars and a temperature of 60 °C. Those conditions were chosen as they reflect a depth of approximately 800 m within a continental flood basalt sequence where CO₂-rich fluid may react with fractured basalt. This study tested the hypothesis of mineral precipitation at those conditions potentially leading to the self-sealing of CO₂ migration pathways.

Synthetic formation water was prepared from powdered basalt, where primary minerals (olivine, pyroxene, plagioclase) were undersaturated and potential secondary minerals (zeolite, smectite) were supersaturated. Following an initial phase of 5 days of net dissolution and potentially crystal seed formation, the cation and HCO₃⁻ concentrations show a linear decline during the following incubation period of 39 days. The latter trend suggests the precipitation of secondary minerals exceeds the dissolution of primary minerals. The authigenic minerals zeolite, smectite, kaolinite and Fe-oxide in solid phase samples, which is in agreement with aqueous speciation modeling. Carbonate minerals other than hydrous Mg-rich-carbonate mineral were not observed. Surface passivation of the primary minerals favoured precipitation even at low pH. The estimated Si precipitation rate onto basalt surface is $4.17 \cdot 10^{-14}$ mol/cm²/sec equivalent to a total Si-Al mineral precipitation between 0.36 and 0.66 cm³/L. These results argue against significant mineral carbonation in basalt under the given pressure and temperature conditions. However, the high net precipitation rate of Si-Al-minerals suggests its formation on the fracture surface at an early stage of reaction progress. The observed minerals could likely self-seal the potential CO₂ leakage pathways at a depth of approximately 800 m. This circumstance contributes to the containment of a potential CO₂ storage reservoir in continental flood basalts. This result is also in agreement with natural analogue sites showing zeolite and smectite mineralisation in basalt fractures exposed to hydrothermal fluids in the past.

Chapter 3: A study on elemental release rate from massive and vesicular basalts at variable P/T and far-from-equilibrium conditions

Abstract

When basalt reacts with CO₂-enriched mildly acidic water, the dissolution of minerals leads to the release of elements such as Ca, Mg, Fe, Na, K, Al and Si. These cations may precipitate as secondary mineral phases in the pores space and fractures. The release rate of elements is considered as the rate-limiting condition for secondary mineral formation. The net release rate of major cations and Si from massive and vesicular basalt in CO₂-saturated water was studied under conditions mimicking deep subsurface and near-surface environment. Dissolution experiments were performed at three different pressure and temperature sets: (1) 100°C and 120 bars (2) 60°C and 80 bars, (3) 25°C and 5 bars with powdered basalts in a batch reactor for 7 days. The net Si release rate was found to be lower at 100°C;120 bars than at 60°C;80 bars and was very similar same in experiments at different rock:water ratios. Both observations suggest higher mineral precipitation at higher temperature and at a higher rock:water ratio possibly leading to surface passivation and lowering the net release rate of elements. Aqueous speciation modeling showed olivine was the most undersaturated primary mineral, and smectites, kaolinite and zeolites were the most supersaturated secondary minerals. Siderite was the only supersaturated carbonate mineral. Carbonate minerals and zeolites were undersaturated at 25°C and 5 bars. Reaction path modeling confirmed the extensive precipitation of secondary minerals (mostly kaolinite and siderite) at 100°C and 120 bars for MB, reaffirming the impact of surface passivation on cation and Si release rate at the higher temperature.

3.1 Introduction

Basalts are mafic rocks containing abundant divalent cation rich minerals such as olivine, plagioclase, and pyroxene. The dissolution rate of individual basalt forming minerals has been studied extensively (Stillings and Brantley 1995, White and Brantley 1995, Chen and Brantley. 2000, Pokrovsky and Schott 2000, Rosso et al. 2000, Oelkers, 2001). Olivine and pyroxene contain Mg and Fe and can dissolve at a relatively high rate at low pH but slows down at higher pH. Plagioclase mainly contains Ca, which dissolves at a higher rate in very acidic and basic conditions, having a U-shaped rate variation with pH (Palandri and Kharaka 2004, Gudbrandsson et al. 2011).

The element release rate at far-from-equilibrium conditions in fluid mineral systems reflects the balance between dissolution and precipitation rate of minerals. When primary minerals are highly undersaturated, but the element release rate is low, then the rate of secondary mineral precipitation is expected to be high. In this case, secondary mineral precipitation could lead to sealing of leakage pathways that would contain the remaining undissolved buoyant CO₂ from escaping. Several studies have been conducted at far-from-equilibrium conditions in pH buffered and flow-through experiments to determine the dissolution rate of minerals and glass in basalts and the nature of secondary mineral formation as a function of pH and temperature (Gislason et al. 2003, Wolff-Boenisch et al. 2006, Gysi and Stefánsson 2008, Gysi et al. 2011, Gysi and Stefánsson 2012a, Gysi and Stefánsson 2012b, Gysi and Stefánsson 2012c). The dissolution rate of crystalline basalt at far-from-equilibrium condition is less well understood. The dissolution rate of Columbian River basalt (U.S.A) and Stapafell basalt (Iceland) has been observed over a range of temperature (25°C -150°C) and pH conditions (2-11) in flow-through experiments. The rate of the basalt dissolution was derived based on the steady state Si release rate. An increased rate was observed with increasing temperature and decreasing pH (Gislason and Hans 1987, Gudbrandsson et al. 2008, Schaefer et al. 2009, Gudbrandsson et al. 2011). Si showed the highest release rate from basalt in any of those previous studies mentioned above and hence is considered as the rate-determining ion of basalt. Moreover, the Si release rate from basaltic glass at low pH is comparable to Si release rate from crystalline basalt of similar chemical composition at temperatures > 25°C, but lower at alkaline pH and temperatures > 50°C (Gudbrandsson et al. 2011). The dissolution of basalt increases the pH of the solution until secondary mineral phases precipitates (McGrail et al. 2006), but the release of Ca²⁺, Mg²⁺,

Fe^{2+} and Si at far-from-equilibrium conditions at variable P/T (pressure and temperature) conditions for short experimental durations is not well reported for crystalline basalt.

This study aims to understand the availability of potential secondary mineral forming major cations such as Ca^{2+} , Mg^{2+} , Fe^{2+} , and Si from crystalline basalt at the far-from-equilibrium conditions. The net-element (major cations and Si) release rate under variable P/T conditions was determined in response to the dissolution of primary minerals and precipitation of secondary minerals. Reactions between CO_2 -enriched water with massive (MB) and with vesicular basalts (VB) were studied at three different P/T conditions in a stirred batch reactor. The release of elements from basalts was investigated as a function of reaction time for both VB and MB to assess and compare the reactivity of the minerals of both basalts. Additionally, an experiment was performed for MB with different rock:water (r:w) ratios, but the same P/T conditions to understand the impact of total rock surface area on element release rate. The fluid composition during the incubation was used to calculate the saturation indices of the primary and secondary minerals from geochemical modeling. Reaction path modeling was undertaken for MB by matching the end cation concentration and pH to the experiments to estimate the amount of dissolved and precipitated minerals.

3.2 Materials and Methods

3.2.1 Sample characterization

Pristine MB and VB samples were collected from a quarry at Port Fairy, Victoria. Port Fairy is located within one of the main lava flows from Mount Rouse in the Newer Volcanic Province. The VB and the MB samples were retrieved from a single block of rock. (Fig.3.1), showing subsequent vesicular flow top and a dense massive interior. The methods used for rock sample characterizations are reported in Chapter 2 (Sections 2.2.2 and 2.3.1) where only the description of massive basalt is presented. Additional data on vesicular basalt can be found in the appendix 1. The bulk chemical compositions of the MB and VB basalt samples were analysed by XRF (X-ray fluorescence) and are presented in Table 3.1.

Table 3.1: Bulk chemical composition of massive basalt (MB) and vesicular basalt (VB) rocks obtained by XRF analysis

Component (wt. %)	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Cl	LOI	Sum
MB	49.2	2.0	13.7	12.1	0.2	10.0	9.0	3.3	1.1	0.4	< 50	-0.88	100.88
VB	50.3	3.6	14.0	13.5	0.2	4.1	7.8	4.5	2.0	0.7	< 240	-0.70	100.70

LOI: loss of ignition



Figure 3.1: Block of basalt sample showing layers of vesicular (VB) and massive basalt (MB)

The major difference between the MB and VB in their bulk composition is the higher wt. % of MgO and CaO in the MB which is 10.0 and 9.0 wt. % and only 4.1 and 7.8 wt. % in VB respectively. However, VB has a comparatively higher composition of all the other oxides (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, Na₂O, and K₂O). The mineral composition was determined by X-ray Powder Diffraction (XRD). Plagioclase, clinopyroxene, and olivine were detected as major minerals with small amount of ilmenite and apatite as opaque minerals in both MB and VB samples. An amorphous phase was detected with a concentration of 16.6 wt. % and 23.4 wt. % in MB and VB, respectively. Anorthoclase, a K-feldspar (alkali feldspar) was detected to be 21.3 wt. % in MB and 17.3 wt. % in VB.

Thin section analysis showed no presence of any volcanic glass, and no K-feldspar was observed. However, a fine-grained Na-rich matrix with a small amount of K was detected in the MB by probe analysis and a few patches of devitrified glass were present in the VB mostly around the olivine minerals which is only 4.3 wt. % of the bulk rock. This could be due to the

presence of very fine grains that were not detected by XRD analysis and was classified as the amorphous phase. The electron microprobe analysis was performed to understand the specific chemical mineral composition. The mineral formula obtained from electron microprobe analysis is presented in Table 3.2. The wt. % of Na-matrix in MB and the devitrified glass in the VB in Table 3.2 is the combination wt. % of amorphous phase and anorthoclase detected through XRD.

Table 3.2: Mineral composition of basalt samples obtained by XRD (wt. %) and electron microprobe analysis

Mineral	Massive basalt (MB) composition	Vesicular basalt (VB) Composition
Plagioclase	23.3 wt. % $Ca_{0.54}Na_{0.46}Fe_{0.04}Al_{1.55}Si_{2.43}O_8$	27 wt. % $Na_{0.54}Ca_{0.46}Fe_{0.04}Al_{1.46}Si_{2.52}O_8$
Pyroxene	21.2 wt. % $Ca_{0.86}Mg_{0.74}Fe_{0.30}Mn_{0.01}Ti_{0.07}Na_{0.04}Al_{0.36}Si_{1.87}O_6$	26.9 wt. % $Ca_{0.84}Mg_{0.68}Fe_{0.39}Mn_{0.01}Ti_{0.07}Na_{0.045}Al_{0.37}Si_{1.83}O_6$
Olivine	16.6 wt. % $Mg_{1.54}Fe_{0.47}Mn_{0.01}Si_{0.9}O_4$	4.3 wt. % $Mg_{1.10}Fe_{0.90}Mn_{0.01}SiO_4$
Ilmenite	1.2 wt. % $Fe_{1.60}Ti_{0.93}Mg_{0.07}Mn_{0.01}O_3$	1 wt. % $FeTi_{0.96}Mg_{0.06}Mn_{0.02}O_3$
Devitrified glass ^b and rest	-	40.8 wt. % ^a $Si_{0.68}Na_{0.25}K_{0.17}Fe_{0.22}Mg_{0.01}Al_{0.20}O_2$
Na- matrix ^a and rest	37.7 wt. % $Na_{0.68}K_{0.039}Ca_{0.08}Fe_{0.08}Al_{1.10}Si_{2.46}O_8$	-

a (Na-rich plagioclase matrix,) normalised to K-feldspar formula

b less than 4 % consist of devitrified glass as it is only observed around olivine mine

3.2.2 Experimental method

The MB and VB samples used in the dissolution experiment were crushed to powders with jaw crusher and agate ring mills at the School of Earth Science, University of Melbourne. The powdered samples were sieved, and the grain size of the sieved samples ranged from 45-106 µm. The sieved samples were then sonicated in deionised (DI) water followed by acetone to remove ultra-fine particles and then oven-dried at 40°C for 48 hours. The specific surface area of cleaned and dried MB and VB samples was measured by BET method using 3-Flex (Micromeritics) and were determined to be 1.2936 and 3.0882 m²/g respectively. The relative pressure range (p/p⁰) for both MB and VB is 0.08 - 0.29. The surface area of the VB is 2.3 times higher than the MB. This agrees with the measured BET surface area of VB of crushed Grande Rhonde basalt Formation which is 2.6 times higher than the massive basalt (Schaefer et al. 2009). The high BET surface area of VB might be due to the presence of micropores (nm

range). The isotherm BET plots of MB and VB are presented in Fig. A2. Surface area is one of the major factors controlling the dissolution rate.

Dissolution experiments were performed for 7 days in a high-pressure 450 mL Parr[®] reactor. The internal parts of the reactor consist of titanium fittings and valves and equipped with external temperature and stirring controller. Experiments were conducted by incubating 5-20g of basalt samples with 271-380 mL deionised water (DI). Deionised water was used as a starting solution to ensure far-from-equilibrium conditions. The reactor was then sealed, and the temperature was set. The reactor was purged with CO₂ at 2 to 5 bars for 30 minutes to remove any existing oxygen. The purging process was followed by the addition of CO₂ to the reactor from a CO₂ cylinder via a syringe pump. The rock and fluid mixture was stirred continuously at 300 rpm. Table 3.3 summarises the experimental conditions which includes temperature, pressure, mass of reacted basalt and volume of DI water, initial rock:water ratio and experimental run time. Experiments conducted at 100°C and 120 bars were run with 5 g of basalt powder to provide enough headspace for CO₂, but same rock:water ratio (r:w) was maintained.

To study the impact of higher surface area (higher r:w ratio) on element release rates, an experiment was conducted with 20g basalt sample at 60°C and 80 bars.

Table 3.3: Experimental conditions of the massive and basalt powder experiments

Sample	T (°C)	pCO ₂ (bar)	Basalt (g)	DI water (mL)	Total rock surface area (m ²)	r:w ^a ratio	Run Time (hrs)
MB _(100, 120)	100	120	5	271	6.46	0.01	151
MB _(60,80)	60	80	7	380	9.05	0.01	142
MB _(25,5)	25	5	7	380	9.08	0.01	143
MB _(60,80,0.05)	60	80	20	380	25.8	0.05	143
VB _(100,120)	100	120	5	271	15.44	0.01	146
VB _(60,80)	60	80	7	380	21.6	0.01	142
VB _(25,5)	25	5	7	380	21.6	0.01	144

^abased-on mass

Fluid at the outlet was regularly sampled using the built-in deep sample tube and then filtered through 0.45 μm diameter pore size and acidified with 2 % HNO_3 prior to Si, Ca^{2+} , Mg^{2+} , Fe^{2+} , Na^+ , Al^{3+} and K^+ analysis by ICP-OES. Total alkalinity of the fluid was also analysed.

3.2.3 Geochemical modeling

Aqueous speciation was modeled using Geochemist's Workbench 11.0 (GWB). Mineral saturation states and pH were calculated using the sampled fluid compositions. The $\text{CO}_2(\text{aq})$ concentration in the speciation model was calculated from the CO_2 solubility at the temperature and pCO_2 using Duan and Sun model (Duan and Sun 2003). The standard thermo.com V8. R6+ database was used for all calculations after updating the primary mineral compositions based on microprobe analysis. The thermodynamic data of the solid solutions of the primary minerals (augite and andesine) and secondary Ca-Mg-Fe carbonate minerals (ankerites) were updated based on ideal mixing using different ratios of the end members (Kerrick et al. 1975). The equilibrium constants (Log K's) for the Na-rich matrix were considered the same as for K-feldspar. The likely dissolution reactions of the primary minerals and potential secondary minerals are presented in Table 3.4. The equilibrium constants of minerals at 25°C, 60°C and 100°C from V8. R6+ database are presented in Table 3.5 (GWB11 2016).

Reaction path modeling was carried out in conjunction with experimental results from MB experiments. The net dissolution of the primary minerals and the net precipitation of the secondary minerals was estimated. The fluid concentrations of the first measured sample and CO_2 -solubility at the given pressure and temperature conditions were entered into the model as starting conditions. 1 kg of CO_2 -saturated water was reacted with 5-7 g of basalt. The mass (g) and the surface area (cm^2/g) of each of the primary minerals were calculated from the total mass and BET surface area respectively considering the wt. % of each mineral from XRD data. For example, calculating the total surface area of plagioclase (andesine) in powdered MB. If 7 g of MB powdered is used with a specific surface area of 1.29 m^2/g , then its total surface area become (7 g * 1.29 m^2/g) 9 m^2 . Therefore, the total surface area of plagioclase in MB (23 % according to XRD analysis) is 2.1 m^2 . The initial mass and surface area of each primary mineral are reported under MB_(25,5) in Table 3.6. The initial mass was varied with rate constants for MB_(60,80) and MB_(100,120)

Table 3.4: The dissolution reactions for the primary, saturated and close to saturation secondary minerals

Mineral	Reactions
Primary	
Forsterite	$Mg_{1.54}Fe_{0.46}SiO_4 + 4H^+ = SiO_{2(aq)} + 2H_2O + 1.54Mg^{2+} + 0.46Fe^{2+}$
Augite	$Ca_{0.45}Mg_{0.4}Fe_{0.15}SiO_3 + 2H^+ = SiO_{2(aq)} + H_2O + 0.15Fe^{2+} + 0.45Ca^{2+}$
Andesine	$Ca_{0.54}Na_{0.46}Al_{1.5}Si_{2.5}O_8 + 6.04H^+ = 2.5SiO_{2(aq)} + 3.02H_2O + 0.54Ca^{2+} + 0.46Na^+ + 1.5Al^{3+}$
Na-rich matrix	$Na_{0.60}K_{0.40}AlSi_3O_8 + 4H^+ = 3SiO_{2(aq)} + 2H_2O + 0.4K^+ + 0.6Na^+ + Al^{3+}$
Secondary	
Beideillite-Mg	$Mg_{0.16}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 4H^+ = 3.67SiO_{2(aq)} + 4.66H_2O + 0.165Mg^{2+} + 2.33Al^{3+}$
Montmor-Mg	$Mg_{0.49}Al_{1.67}Si_4O_{10}(OH)_2 + 6H^+ = 4SiO_{2(aq)} + 4H_2O + 0.165Mg^{2+} + 1.67Al^{3+}$
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ = 2SiO_{2(aq)} + 5H_2O + 2Al^{3+}$
Siderite	$FeCO_3 + H^+ = Fe^{2+} + HCO_3^-$
Calcite	$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$
Magnesite	$MgCO_3 + H^+ = Mg^{2+} + HCO_3^-$
Ankerite CaFe(CO ₃) ₂	$CaFe(CO_3^{2-}) + 2H^+ = Ca^{2+} + Fe^{2+} + 2HCO_3^-$
Ankerite Ca _{0.6} Mg _{0.2} Fe _{0.2} CO ₃	$Ca_{0.6}Mg_{0.2}Fe_{0.2}CO_3 + H^+ = 0.6Ca^{2+} + 0.2Mg^{2+} + 0.2Fe^{2+} + HCO_3^-$
Ankerite CaMg _{0.3} Fe _{0.7} (CO ₃) ₂	$CaMg_{0.3}Fe_{0.7}(CO_3)_2 + 2H^+ = Ca^{2+} + 0.3Mg^{2+} + 0.7Fe^{2+} + 2HCO_3^-$
Ankerite CaMg _{0.5} Fe _{0.5} (CO ₃) ₂	$CaMg_{0.5}Fe_{0.5}(CO_3)_2 + 2H^+ = Ca^{2+} + 0.5Mg^{2+} + 0.5Fe^{2+} + 2HCO_3^-$
Mordenite	$Ca_{0.28}Na_{0.36}Al_{0.94}Si_{5.0}O_{12} \cdot 3.468H_2O + 3.76H^+ = 5SiO_{2(aq)} + 5.348H_2O + 0.28Ca^{2+} + 0.36Na^+ + 0.94Al^{3+}$
Mesolite	$Ca_{0.65}Na_{0.67}Al_{1.99}Si_{3.01}O_{10} \cdot 2.647H_2O + 7.96H^+ = 3.01SiO_{2(aq)} + 6.627H_2O + 0.657Ca^{2+} + 0.676Na^+ + 1.99Al^{3+}$
Stilbite	$Ca_{1.019}Na_{0.136}K_{0.006}Al_{2.18}Si_{6.82}O_{18} \cdot 7.33H_2O + 8.72H^+ = 6.82SiO_{2(aq)} + 11.69H_2O + 1.019Ca^{2+} + 0.136Na^+ + 2.18Al^{3+} + 0.006K^+$

Table 3.5: Mineral equilibrium constants ($\log K_{eq}$) for the primary, and potential secondary minerals at the three experimental temperatures

Mineral	$\log K_{eq}$ 25°C	$\log K_{eq}$ 60°C	$\log K_{eq}$ 100°C
Forsterite	25.6156	21.9895	18.6264
Augite	11.378	9.9	8.473
Andesine	15.3242	11.6584	8.0718
Na-rich matrix	-0.2753	-0.961	-1.8555
Beideillite-Mg	5.5537	2.1824	-1.2549
Montmor-Mg	2.3879	0.1598	-2.2354
Kaolinite	6.8101	3.8468	0.9541
Siderite	-0.192	-0.8309	-1.4967
Calcite	1.8487	1.333	0.7743
Magnesite	2.2936	1.4383	0.5875
Ankerite $\text{CaFe}(\text{CO}_3)_2$	-0.196	-1.096	-2.084
Ankerite $\text{Ca}_{0.6}\text{Mg}_{0.2}\text{Fe}_{0.2}\text{CO}_3$	1.9069	1.1535	0.3616
Ankerite $\text{CaMg}_{0.3}\text{Fe}_{0.7}(\text{CO}_3)_2$	1.532	0.425	-0.757
Ankerite $\text{CaMg}_{0.5}\text{Fe}_{0.5}(\text{CO}_3)_2$	1.1659	0.0926	-1.0493
Mordenite	-5.1969	-5.2927	-5.7869
Mesolite	13.6191	10.0728	6.6121
Stilbite	1.0545	-1.0105	-3.4291

(GWB11 2016)

The kinetic dissolution data of the primary minerals were taken from the literature (Palandri et al. 2004). The kinetic data of K-feldspar was used for the Na-rich matrix. The rate constants and the surface areas were altered following trial and error to match the end experimental concentrations of the major cations and the final pH. Andesine (plagioclase) was assigned the lowest rate constant as it is less reactive compared to the other basalt forming minerals (Gudbrandsson et al. 2011). The kinetic expressions for the precipitation of the potential secondary minerals were also entered. Three different rate laws were used to match the experimental results with the model. Non-linear rate law was coupled with cross-affinity rate law for the dissolution of some of the primary minerals. However, simple rate law was used for potential secondary mineral precipitation. The rate constants were increased for higher P/T conditions.

Table 3.6: Kinetic parameters of the primary and secondary minerals used in the reactive path model

Mineral	Rate constant k_i (mol/cm ² /sec ⁻¹)	Mass (g)	Surface area (cm ² /g)	cross affinity mineral	Order α	Order β
MB_(25,5)						
<i>Primary minerals</i>						
Forsterite	1.5e-11	1.162	15	Montmor-Mg	0.01	0.05
Augite	1.0e-11	1.484	11.0	Beidellite-Ca	0.1	2.0
Andesine	1.0e-13	1.63	2.1		1	1
Na-rich matrix	5.0e-11	2.59	5.0	Beidellite-Na	0.01	0.5
React Fe (mol/l)	5.0e-05					
Slide Na ⁺ (activity)	0.00014					
<i>Secondary minerals</i>						
Beideillite-Mg	1.0e-15	0.01	10.0			
Beidellite-Ca	1.0e-15	0.01	15.0			
Kaolinite	2.0e-12	0.05	20.0			
Mineral	Rate constant k_i (mol/cm ² /sec ⁻¹)	Mass (g)	Surface area (cm ² /g)	cross affinity mineral	Order α	Order β
MB_(60, 80)						
<i>Primary minerals</i>						
Forsterite	1.5e-09	1.11	15.0	Ankerite ^a	0.1	3.1
Augite	8.0e-10	1.3	1.0		2	1
Andesine	1.38e-13	1.6	21.0		1	1
Na-rich matrix	2.0e-11	1.5	13		1	3
React Fe (mol/l)	0.00053					
<i>Secondary minerals</i>						
Beideillite-Mg	1.0e-16	0.01	20.0			
Stilbite	1.0e-15	0.1	20			
Kaolinite	1.0e-15	0.001	5			
Mineral	Rate constant k_i (mol/cm ² /sec ⁻¹)	Mass (g)	Surface area (cm ² /g)	cross affinity mineral	Order α	Order β
MB_(100,120)						
<i>Primary minerals</i>						
Forsterite	2.0e-08	0.83	10.0	Montmor-Mg	0.017	1.5
Augite	2.0e-09	1	13	Ankerite	0.008	1
Andesine	1.38e-13	1.165	15.0		0.2	0.8
Na-rich matrix	1.0e-10	1.2	15	Montmor-Na	0.006	1.0
React Fe (mol/l)	0.0003					
Slide activity Na ⁺	0.0004					
Slide activity Ca ²⁺	0.0001					
<i>Secondary minerals</i>						
Beideillite-Mg	1.0e-10	0.085	20.0			
Stilbite	1.0e-12	0.05	2.0			

^aCaMg_{0.5}Fe_{0.5}(CO₃)₂

The following non-linear rate law was used for primary mineral dissolution to match the exponential trend of the experimental cation concentrations (GWB11 2016).

$$r_k = \text{sgn} \left(1 - \frac{Q}{K} \right) S.A k_+ \prod_j (a_j | m_j)^{P_j} \left| 1 - \left(\frac{Q}{K} \right)^\alpha \right|^\beta \quad (3.1)$$

where r_k is the reaction rate (positive for dissolution), sgn is a function returning -1 or +1, depending on the signs of the argument, $S.A$ is the mineral surface area (cm^2), k_+ is the rate constant ($\text{mol}/\text{cm}^2/\text{sec}$), $\prod$ is the product function, $(a_j | m_j)$ signifies the activity or molality of the promoting or inhibiting species, P_j is the species power in the rate law, Q and K are the activity product and equilibrium constant for the dissolution reaction, α and β are the orders of the rate law which defines the nonlinearity.

Furthermore, the cross-affinity rate law was used in combination with non-linear rate law for the dissolution of the some of the primary minerals. In this rate law (in the same Eq 3.1), the saturation state (Q/K) of one mineral calculates the reaction rate of the primary dissolving mineral. The reaction of an altered surface layer controls the overall dissolution rate (Grambow and Müller 2001, GWB11 2016). This altered surface layer is due to secondary mineral precipitation and in this case is termed as “cross-affinity” mineral. A variety of supersaturated and undersaturated secondary minerals observed in the speciation model were assigned and tried out in the cross-affinity rate law until it produced the best match of the experimental trend. However, the use of highly supersaturated minerals observed in the speciation in the cross-affinity rate law did not provide a good match. For example, beidellite-Mg is highly supersaturated at MB_(100,120), but when used for the forsterite dissolution rate, it lowered the concentration to Mg, Fe, and Si to a great extent and the trend failed to match with the experiment. Instead, the use of a comparatively less supersaturated mineral like Mg montmorillonite provided a better match. Ankerite, a carbonate solid solution which is close to saturation was used as a cross-affinity mineral for forsterite and augite dissolution in experiment MB_(60,80) and MB_(100,120), respectively. Nevertheless, smectites were mostly considered as cross-affinity minerals for the dissolution of most of the primary minerals due to its high saturation state at all temperatures and its potential to form under acidic conditions (Gysi et al. 2011, Gysi and Stefánsson 2012a, Hellevang et al. 2017). The sliding activities of Na^+ and Ca^{2+} were used to change the values and match the end concentration. The Fe^{2+}

concentrations in the models were not as high as in the experiments, thereby free Fe^{2+} was also allowed to react which brought it close to the experimental Fe^{2+} concentration trend. An inbuilt simple rate law was used for mineral precipitation reactions (GWB11 2016)

$$r_k^{\rightarrow} = S.Ak_+ \left(1 - \frac{Q}{K}\right) \quad (3.2)$$

Here, $r_k^{\rightarrow}$ is the reaction rate (mol/s) (negative for precipitation), $S.A$ is the mineral's surface area (cm^2), k_+ is the rate constant ($\text{mol}/\text{cm}^2 \text{ sec}$), Q and K are the activity product and equilibrium constant. By this equation a mineral precipitate when it is supersaturated.

3.3 Results

3.3.1 Element release over time

The element release trends are plotted in Fig. 3.2 based on the aqueous concentrations normalised to the total surface area of the basalt powder and the volume of fluid left in the reactor and is calculated using the Eq.3.4

$$\text{Element release} = \frac{C_i * V_i}{S.A} \quad (3.2)$$

Element release (Si, Mg, Fe, Na, K and Al) is (mol m^{-2}), C_i ($\frac{\text{mol}}{\text{L}}$) and V_i (L) are the element concentrations and the volume left in the reactor at each time step; $S.A$ is the total surface area (m^2). The dissolved mass is calculated by converting the aqueous concentration of the cations (mg/L) in the fluid samples into mol/L and then normalising it to the remaining volume of the fluid in the reactor at every time step. Sample volumes and the remaining volume in the reactor at every time step were recorded accurately.

The release of Si, Mg, Fe, Na, K and Al (mol m^{-2}) were compared as a function of time at three different temperatures and pressures for MB and VB. The solubility of CO_2 varies at these different experimental conditions with 0.9 mol/kg at $60^\circ\text{C}; 80 \text{ bars}$; $> 0.8 \text{ mol/kg}$ at $100^\circ\text{C}; 120 \text{ bars}$; and 0.2 mol/kg at $25^\circ\text{C}; 5 \text{ bars}$.

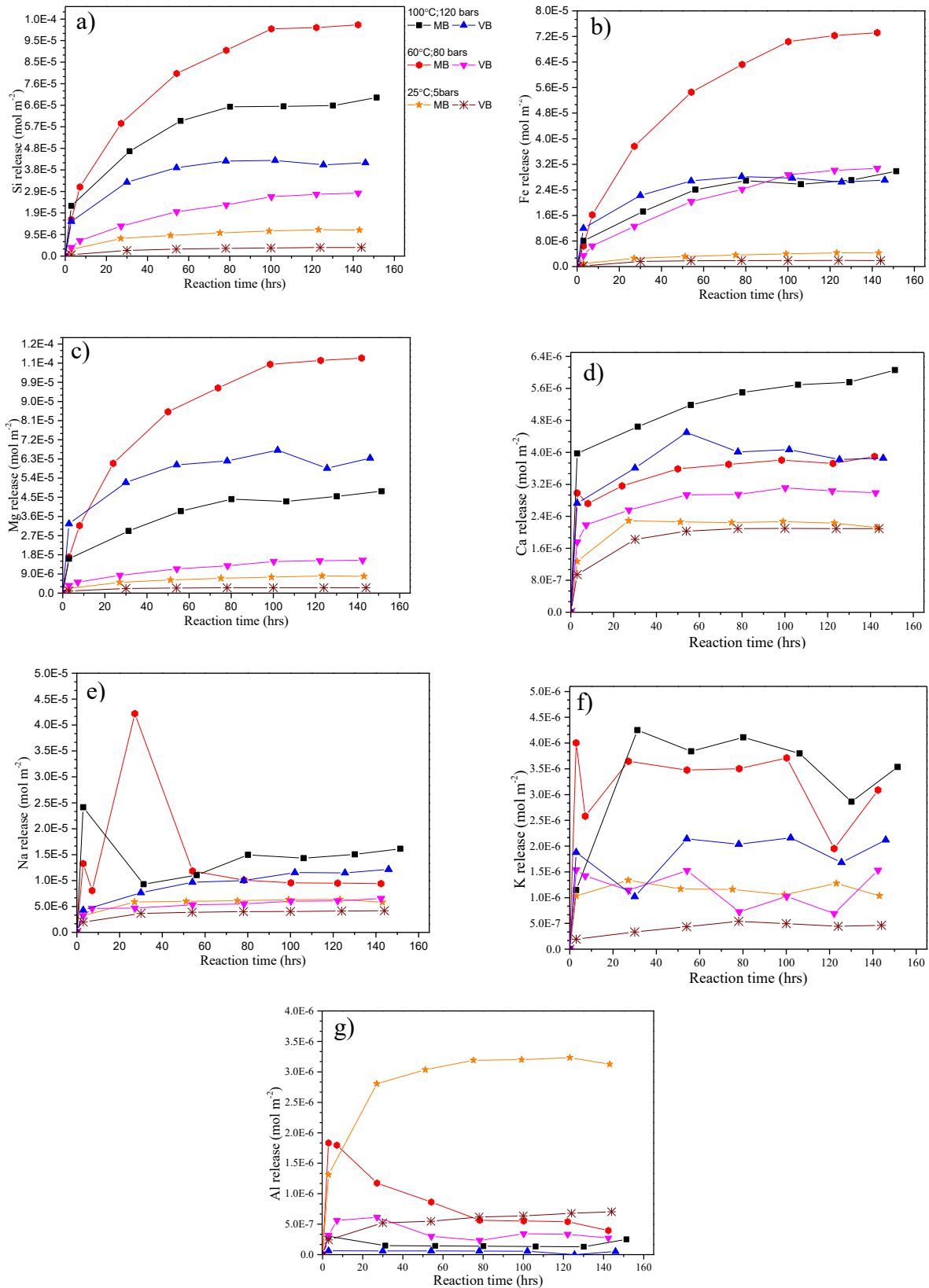


Figure 3.2: Massive (MB) and vesicular (VB) basalt dissolution trend over time in a batch reactor showing the effect of temperature and pressure on individual element release

The release of Si, Mg, Fe and Ca shows an increasing trend before it plateaus after 100 hours. It is interesting to observe that maximum steady state concentrations of Si, Mg and Fe in MB_(60,80) (Fig. 3.2a, b, and c) , while Ca shows the highest steady state concentration in MB_(100,120) (Fig. 3.2d). The release of all the major cations from VB is observed to be lower than MB for all experimental runs. The higher release of Mg, Fe, and Si in the MB compared to VB could be due to the higher wt. % of olivine content in MB. The dissolution of olivine under acidic conditions is comparatively higher than pyroxene and plagioclase (Gudbrandsson et al. 2011).

The Na concentration in the MB_(60,80) experiment showed a rapid increase in the first 24 hours before the concentration dropped rapidly again. The K release shows an uneven trend but remained high in MB_(100,120) compared to VB. The highest increase in Al is observed for MB_(25,5). The low release of Al at 100°C;120 bars and 60°C;80 bars suggests absorption or concurrent precipitation of the ion in both MB and VB experiments. From a thermodynamic point of view, the release of Si, Mg, Fe, and Na at 100°C;120 bars should be higher than at 60°C;80 bars, but this is not true in the case of MB. If those concentration trends were solely regarded as a reflection of dissolution, then Si, Mg, Fe and Na should increase more rapidly at 100°C;120 bars compared to 60°C;80 bars. An unexpected low cation release is also observed in the experiment conducted at 5 times (0.05) higher r:w ratio except for Ca. The release of the elements in the experiment with a larger surface area (20g) of MB showed a linear increase for the first 40 hours and then it flattened out (Fig.3.3).

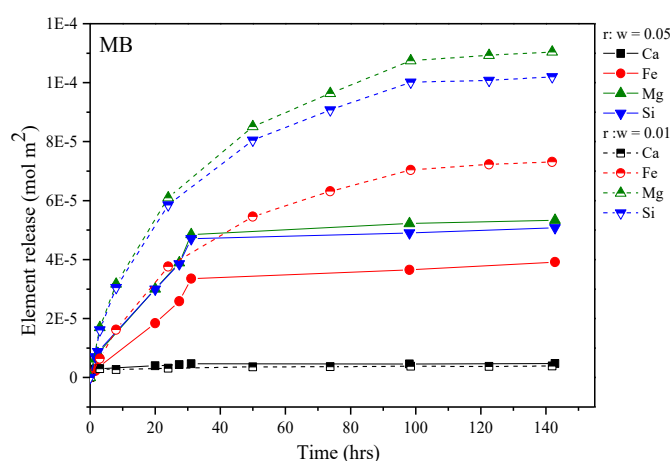


Figure 3.3: Comparison of element release from MB at 60°C and 80 bars at two different rock water ratios of 0.05 and 0.01

This could be due to the instantaneous precipitation and incorporation of Si, Mg, Fe into secondary mineral phases concurrent with the dissolution of the primary minerals.

The calculated pH and measured HCO_3^- concentration showed an increasing trend over the experimental duration (Fig. 3.4a and Fig. 3.4b). The pH depends on CO_2 solubility and alkalinity of the fluid and it remained < 4.3 towards the end of the experiment and comparatively high throughout the $\text{VB}_{(100,120)}$ experiment.

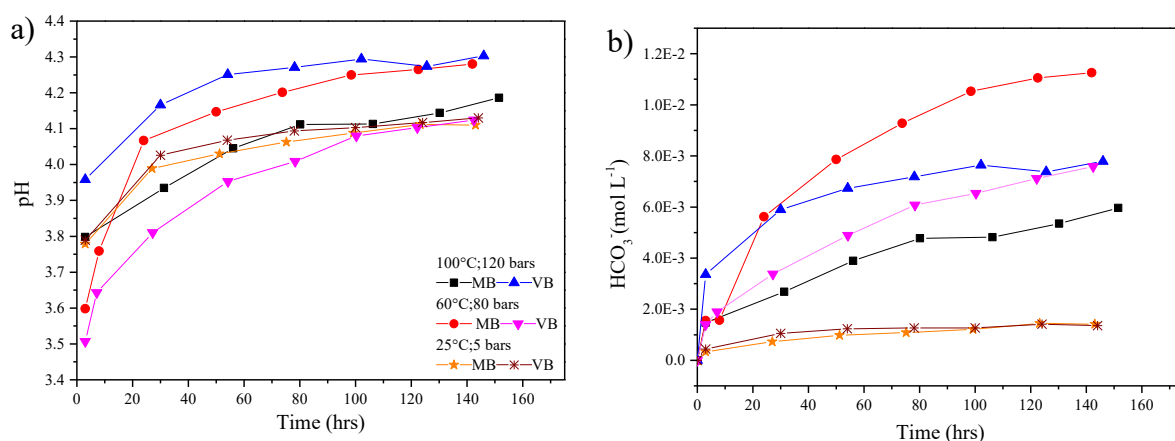


Figure 3.4: (a) Calculated pH and (b) measured HCO_3^- concentration over time

The final pH after 7 days was not much higher compared to the initial pH even after reacting with basalts with the higher surface area. The experiment performed at 60°C and 80 bars showed the highest pH range for both MB and VB. Moreover, $\text{MB}_{(60,80)}$ has the highest HCO_3^- concentration. The pH of $\text{MB}_{(100,120)}$ is lower than $\text{VB}_{(100,120)}$ at every time step. Despite the lowest CO_2 solubility, the lowest pH range was observed (3.8-4.1) at 25°C suggesting only a minor dissolution of basalt.

3.3.2 Calculated net-element release rate per time step

The release rate of elements was calculated for each time step to understand how quickly the system approaches equilibrium in an acidic environment.

The release rate of elements from basalt dissolution in a batch experiments was calculated as

$$r = \frac{\Delta n_i(\text{elements})}{SA \cdot \Delta t} \quad (3.3)$$

where r is release rate of elements ($\text{moles m}^2 \text{ sec}^{-1}$), $(\Delta n_i(\text{elements})/\Delta t)$ is the change in dissolved elemental mass over time (mol/sec) due to dissolution $((C_{i+1} * V_{i+1}) - (C_i * V_i))$; SA is the total surface area of the initial basalt sample (m^2).

Fig. 3.5 presents the calculated release rate of Si-based on Eq.3.4 against calculated pH. The release rate dropped by an order of magnitude in experiments at $100^\circ\text{C}; 120$ bars for both MB and VB, whereas the rates of the other experimental runs showed a gradual decrease. The experiment performed for $\text{MB}_{(100,120)}$ and $\text{MB}_{(60,80)}$ (for both ratios) showed high release rate of Si before approaching pH 4 presented in the Appendix 2 (A.2.9 and A.2.14). The release rate in most of the experimental conditions approached steady state after pH 4. However, the release rates at $\text{MB}_{(60,80)}$ for both the rock:water ratios reached steady state at a pH between 4.25 and 4.45. The Si release rate remained comparatively high for $\text{MB}_{(60,80)}$ suggesting the primary minerals are still undersaturated and are in a dissolving state.

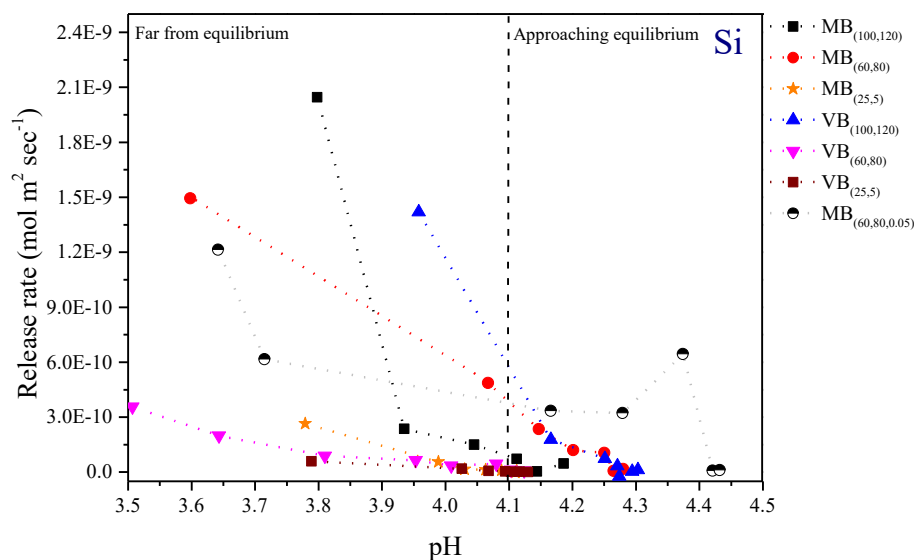


Figure 3.5: Calculated release rate of Si based on (Eq.3.4) against pH change of individual experimental runs. The dashed line at pH 4.1 indicates the difference in rate of far-from-equilibrium and approaching equilibrium conditions.

3.3.3 Net-element release rates at far-from-equilibrium conditions

A representative net release rate was determined at far-from-equilibrium conditions (until pH 4) for the Si, Mg, Fe and Ca. The net release rate of element from MB and VB under far-from-equilibrium conditions are determined as the slope of a weighted linear fit to the data in Fig. 3.2. The linear slope and concentration changes are used to calculate the element release rate. The initial 60 hours are considered to calculate the rate from the slope of the linear fit. The data beyond 60 hours may be affected by the changing saturation state of the primary minerals and supersaturation of secondary minerals. In a batch experiment, the system might reach equilibrium condition at an early stage as the remaining volume decreases over time and the possibility of secondary mineral saturation could be higher. The secondary mineral saturation could lead to early precipitation which could affect the release rate of cations from the primary minerals, and overall dissolution rate of the minerals. Studies from flow-through experiments were conducted to avoid the continuous growth of reaction products that would affect element release rates (Gudbrandsson et al. 2008, Schaef et al. 2009, Gudbrandsson et al. 2011).

The release rate of Mg, Si, and Fe are observed to be the highest for most of the experimental condition, indicating the important role of olivine dissolution. The release rate under far-from-equilibrium conditions in experiment MB_(60,80,0.05) was derived from the first 48 hours as the data points show steady state conditions hence after. The results of the net release rates of Si, Mg, Fe and Ca are presented in Table 3.7.

Table 3.7: Calculated pH, primary mineral end saturation state and calculated far-from-equilibrium release rates of elements

Sample	pH initial ^a	pH final ^a	log(Q/K) Forsterite ^a	log(Q/K) Augite ^a	log(Q/K) Andesine ^a	log(Q/K) Na-rich matrix	Release rate log (mol m ² sec ⁻¹)			
							Si	Mg	Fe	Ca
MB _(100,120)	3.7	4.1	-10.69	-6.22	-3.57	0.03	-9.70	-9.93	-9.97	-11.19
MB _(60,80)	3.6	4.2	-12.94	-7.29	-4.73	0.89	-9.47	-9.40	-9.56	-11.35
MB _(25,5)	3.7	4.1	-20.29	-10.68	-9.64	-2.09	-10.44	-10.64	-10.79	-11.24
VB _(100,120)	3.9	4.3	-10.23	-6.22	-3.57	0.60	-9.88	-9.81	-9.92	-11.01
VB _(60,80)	3.5	4.1	-14.39	-7.80	-5.29	0.06	-10.08	-10.39	-10.01	-11.24
VB _(25,5)	3.7	4.1	-20.48	-10.62	-9.86	-2.42	-10.86	-11.11	-11.01	-11.22
MB _(60,80,0.05)	3.6	4.4	-12.0	-6.57	-3.12	2.03	-9.42	-9.40	-9.55	-10.56

^acalculated pH and saturation states of primary minerals from GWB calculations of sample speciation at the end of the experiments.

The net release rate of Ca^{2+} for all experimental conditions was an order of magnitude lower compared to the other cations. Although, the Ca^{2+} release rate in $\text{MB}_{(60,80,0.05)}$ was higher than in $\text{MB}_{(60,80,0.01)}$, it was still lower than the release rates of Si , Mg^{2+} , and Fe^{2+} at higher rock:water ratio. Interestingly, the element release rate for Si , Mg^{2+} , Fe^{2+} and Ca^{2+} showed the following trend: $\text{MB}_{(60,80)} > \text{MB}_{(100,120)} > \text{MB}_{(25,5)}$. For example, the release rate of Si at $\text{MB}_{(60,80)}$ is $\log(r_{\text{MB}}) = -9.47 \text{ mol m}^2 \text{ sec}^{-1}$ and at $\text{MB}_{(100,120)}$ $\log(r_{\text{MB}}) = -9.70 \text{ mol m}^2 \text{ sec}^{-1}$. The release rate at the higher r:w ratio $\text{MB}_{(60,80,0.05)}$ is very close to the rate at the lower ratio. It has been shown that high rock mass (with larger surface area) corresponds to higher dissolution rate (Wolff-Boenisch et al. 2006). However, in this case it appears the higher dissolution rate is compensated by a higher precipitation rate resulting in a similar net release rate for the two samples with different rock to water ratio. This unusual behaviour of the lower release rate at highest temperature and higher r:w ratio may be due to the immediate precipitation of secondary mineral phases even under acidic conditions affecting the overall dissolution of the primary minerals. It seems like the Ca release rate remained high at r:w ratio (0.05) and was not affected by mineral precipitation. This suggests mineral precipitation and respective surface passivation was limited to Ca -poor primary minerals such as olivine. The $\text{VB}_{(100, 120)}$ experiment has the highest release rate and the $\text{VB}_{(25,5)}$ has the lowest with a minor difference in the rate between $\text{VB}_{(60, 80)}$ and $\text{VB}_{(100, 120)}$. The trend in the VB release rates also suggests commencement of precipitation at the higher temperature.

3.3.4 State of mineral saturation

The saturation states of primary and secondary minerals at the end of the experiments were calculated in GWB based on the aqueous concentration and presented in the Fig. 3.6.

Olivine was highly undersaturated while plagioclase and pyroxene were moderately undersaturated. The release rate of Na was high but Na -rich matrix as represented by the thermodynamic data of K -feldspar which showed supersaturation and is not presented in Fig. 3.6. This could be due to (1) preferential release of Na due to incongruent dissolution (2) Na desorption. Clay minerals (beideillite and kaolinite) was most supersaturated followed by stilbite (a zeolite) at $60^\circ\text{C}; 80 \text{ bars}$ and $100^\circ\text{C}; 120 \text{ bars}$ for both MB and VB . However, additional zeolites like mesolite and mordenite were supersaturated at $\text{VB}_{(100,120)}$ and $\text{MB}_{(60, 80)}$ respectively. Chalcedony and SiO_2 were close to equilibrium at all experimental conditions.

Siderite is the only carbonate mineral that was moderately supersaturated except at 25°C;5 bars for both VB and MB.

It was observed that the primary minerals in the experiment MB_(100,120) were closer to equilibrium than in experiment MB_(60,80) (Table 3.7), and clays, zeolites, and chalcedony were comparatively more supersaturated at MB_(60,80). This trend suggests that at 100°C and 120 bars, the cations concentration was high enough to trigger the precipitation of secondary minerals. The saturation state of olivine, plagioclase, and pyroxene for different r:w ratio shows a similar state of undersaturation.

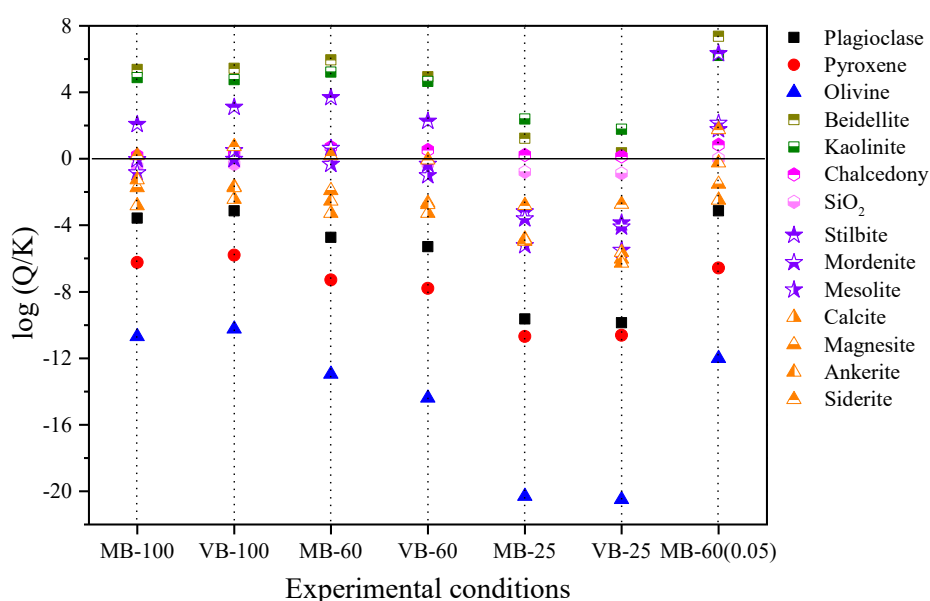


Figure 3.6: State of saturation of primary and secondary minerals based on aqueous speciation at the end of the experiment

However, the secondary minerals with a higher r:w ratio (0.05) showed comparatively higher supersaturation states and additional secondary minerals such as mesolite and mordenite (a zeolite) and amorphous SiO₂ were became supersaturated.

3.3.5 Reaction path modeling

Reaction path modeling was carried out to estimate the balance between mineral dissolution and precipitation leading to the observed net release rate of elements. The observed major

cation concentrations and the calculated pH for each time step in MB experiments were attempted to match with the model results.

The modelled pH and concentrations computed for experiment MB_(25,5) were lower compared to the experiment and followed a linear trend (Fig. 3.7a). In contrast the pH and the Ca, Si and Mg concentrations in MB_(60, 80) and MB_(100,120) showed a good match between experimental and modeling results (Fig. 3.8a and 3.9a). The Fe²⁺ is comparatively lower in all the models (Fig. 3.7b, 3.8b, and 3.9b) even after introducing additional aqueous Fe²⁺ into the model. This is due to the conversion of more soluble Fe²⁺ to less soluble Fe³⁺ or other forms of the secondary phase. It was unsuccessful to match the Na⁺ results as the experimental data showed a fluctuating trend and thus Na⁺ was not presented in the figure.

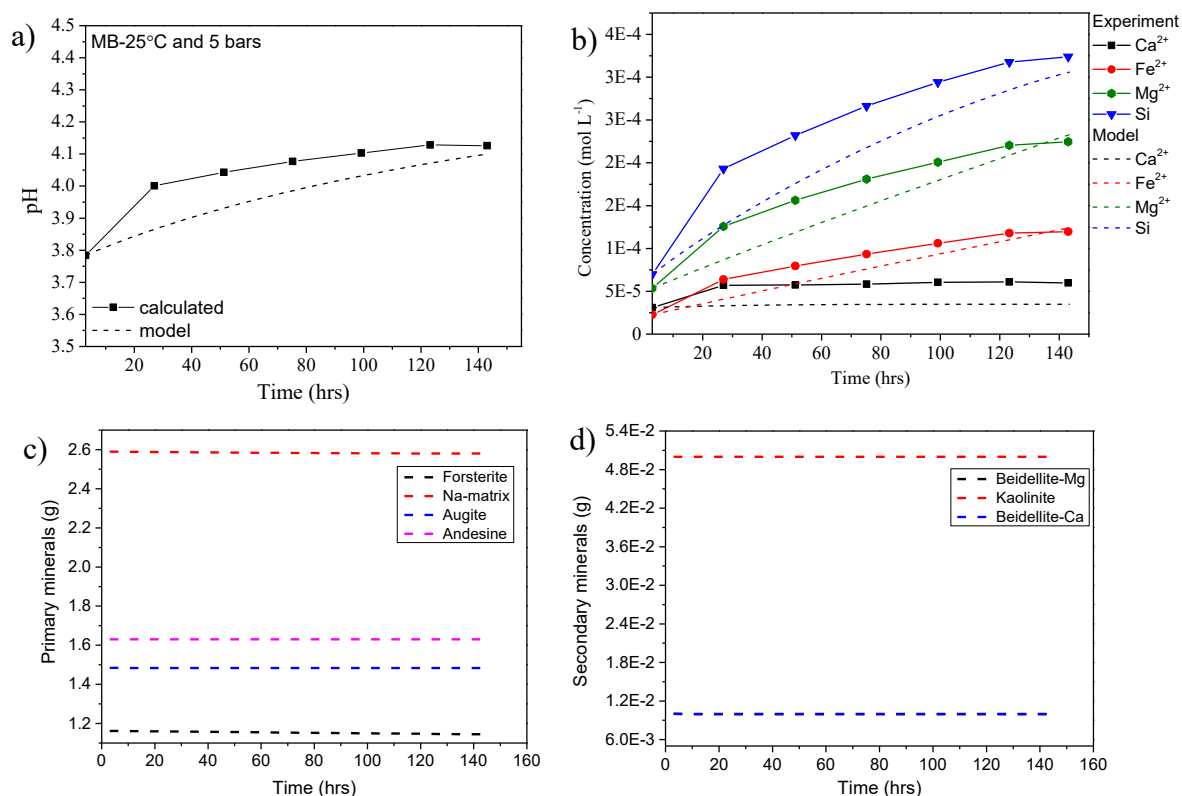


Figure 3.7: Comparison between experimental and modelled results after fine tuning at 25°C and 5 bars (a) calculated and modelled pH, (b) concentrations of major cations and Si (c) reacted mass of the primary minerals and (d) mass of secondary/forming minerals

The reacted mass of primary minerals in experiment MB_(25,5) was relatively low with about 0.4 its of initial mass was consumed compared to 7.7 % and 5.5 % in MB_(60, 80) and MB_(100,120), respectively. The model predicted that only 1.5 % of initial forsterite was consumed in experiment MB_(25,5) compared to 23.3 % in MB_(60, 80) and 10.5 % in MB_(100,120). The reacted mass of primary minerals follows in the following order: forsterite > Na-matrix > augite > andesine in experiment MB_(25,5) (Fig. 3.7c) The order at MB_(60, 80) and MB_(100,120) follows an order: forsterite > augite > Na-matrix > andesine (Fig. 3.8c and 3.9c).

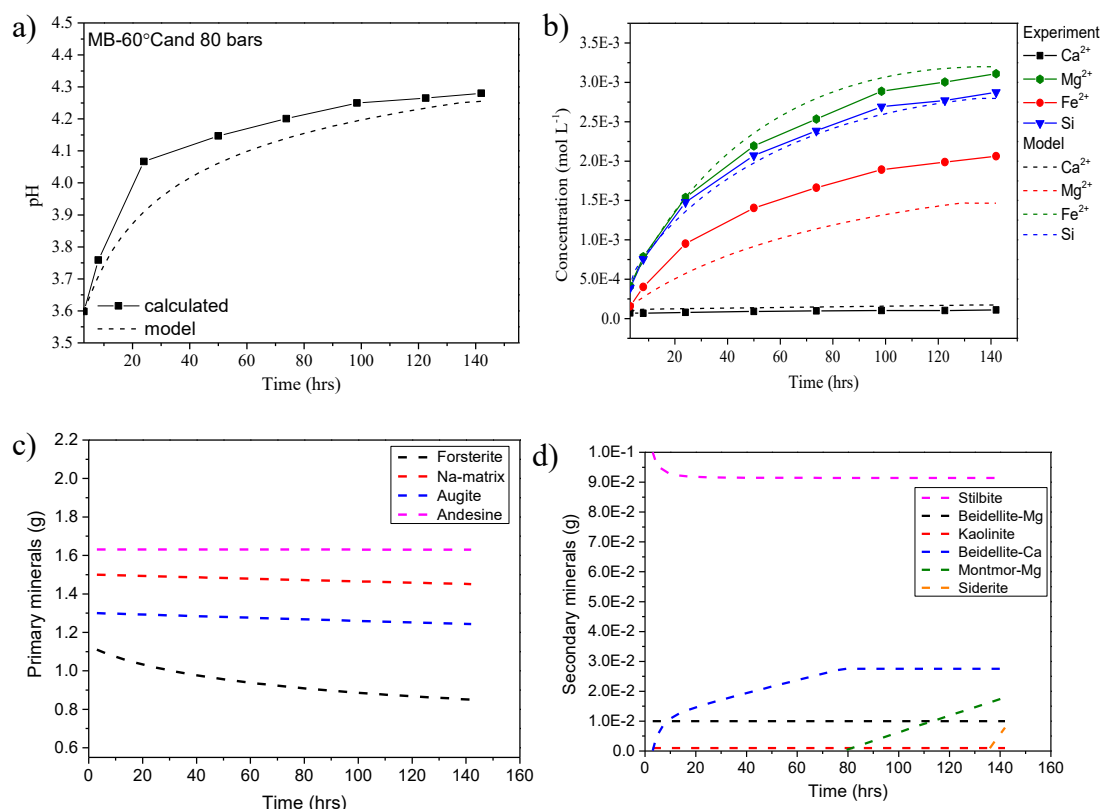


Figure 3.8: Comparison between experimental and modelled results after fine tuning at 60°C and 80 bars (a) calculated and modelled pH, (b) concentrations of major cations and Si (c) reacted mass of the primary minerals and (d) mass of secondary/forming minerals

This sequence is reflecting the same order of the rate constants. The consumption of Na-rich matrix and augite is similar in experiment MB_(60, 80) corresponding to 3.26 % and 4.39 % respectively. It is clear from the model that forsterite dissolution is controlling the release of Mg, Fe and to a lesser extent Si as well. Lowering the rate of forsterite dissolution would lower the concentration of Mg²⁺, and Fe²⁺. The precipitation of kaolinite and Mg-beideillite were controlled by using a simple rate law in MB_(25,5), but the formation of Ca-beideillite was favoured under the experimental conditions (Fig. 3.7d). The secondary mineral precipitation in experiment MB_(25,5) is in the following order: Mg-beideillite > kaolinite > Ca-beideillite.

A wide variety of minerals were observed in the model simulated for experiment MB_(60, 80) (Fig. 3.8d). In this case, formation of siderite (a carbonate mineral) and montmorillonite (a smectite mineral) were also favoured by the system along with beidellite-Ca. On the other hand, kaolinite and siderite formation was favoured in experiment MB_(100,120) where considerable amount of kaolinite formed (Fig. 3.9d). The formation of kaolinite in experiment MB_(100,120) could not be regulated by using simple rate law as the convergence of the model was affected, nevertheless, it formed as its precipitation was not suppressed in the system. Stilbite (a zeolite) was controlled by using simple rate law for mineral precipitation at both the high temperature and pressure condition, but it only showed dissolution trend until the end of the experiment.

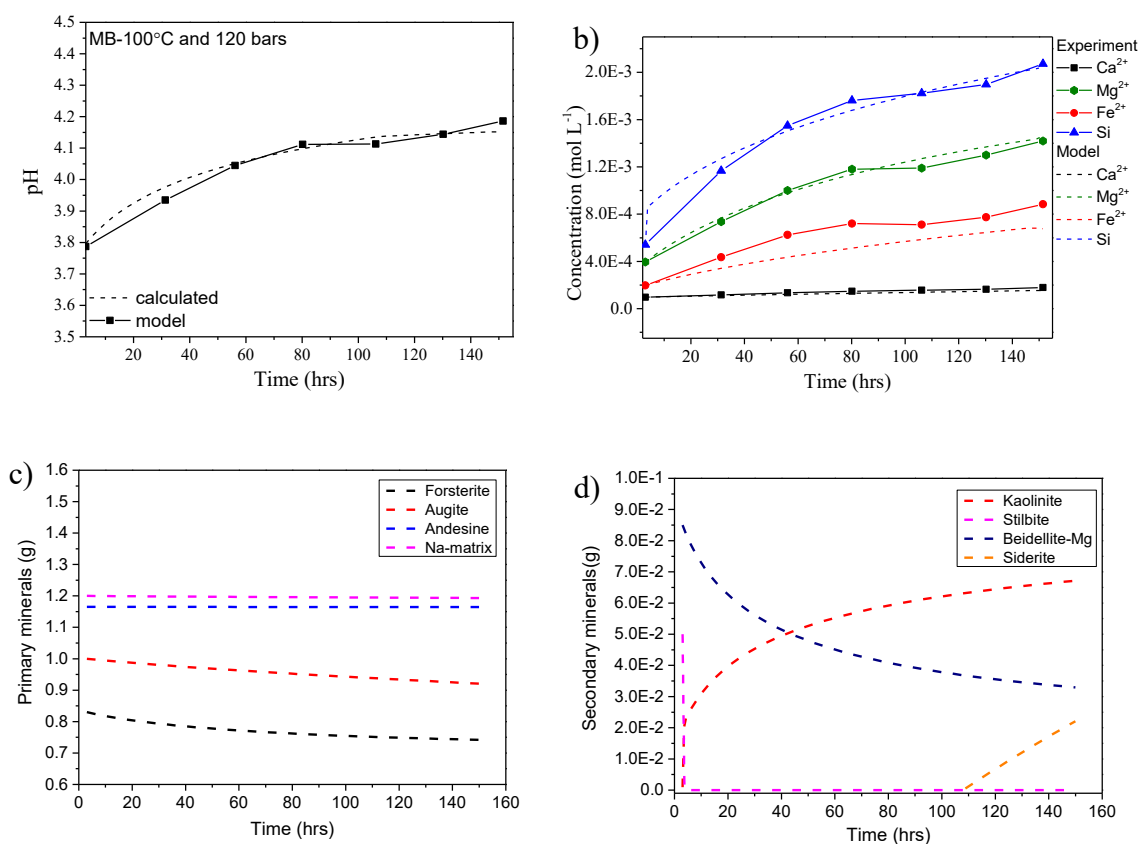


Figure 3.9: Comparison between experimental and modelled results after fine tuning at 100°C and 120 bars (a) calculated and modelled pH, (b) concentrations of major cations and Si (c) reacted mass of the primary minerals and (d) mass of secondary/forming minerals

The mass precipitated over 7 days in experiment MB_(25,5) is only 0.14 % of the mass reacted (precipitation to dissolution ratio), whereas 8 % and 34 % mass precipitated at MB_(60, 80) and MB_(100,120), respectively. According to the model based on the MB_(100,120) experiment a substantial amount of the kaolinite formed leading to limited availability of Si and Al³⁺ to form amorphous SiO₂, smectite and zeolite formation. Additionally, a good match was only possible

using the cross-affinity rate law which suggest that the concentration of elements in the fluid is primarily affected by the saturation state of the secondary minerals.

Siderite (Fe-carbonate mineral) precipitation was an order of magnitude higher in experiment MB_(100,120) compared to MB_(60, 80) suggesting immediate incorporation of Fe²⁺ into carbonate mineral at higher P/T conditions.

3.4 Discussion

3.4.1 Constraining mineral dissolution and precipitation rates at variable P/T conditions

The surface area of VB is 2.3 times higher than MB, but the release rate of elements were an order of magnitude lower in experiments VB_(25,5) and VB_(60, 80) and similar in VB_(100,120) compared to experiments involving MB under the same experimental conditions. Fig. 3.5 confirmed the initial lower Si release rate from VB_(100,120) compared to MB_(100,120), suggesting slow reactions. It seems like this distinct rate behaviour is controlled by the presence of a higher amount of (Mg-Fe) olivine in the MB. The olivine composition in both MB and VB is comparatively lower than pyroxene and plagioclase, but its dissolution rate leads to release of Mg, Fe and Si into the fluid. This could provide favourable conditions for Mg or Fe rich carbonate or silicate mineral precipitation, thus limiting the rate for Ca²⁺ rich mineral formation. At low pH (2-4), the divalent metal flux from the crystalline basalt dissolution is dominated by Mg, Fe and Si release, while Ca release is dominated at high pH (9-11) (Gudbrandsson et al. 2011). Thereby, carbonate minerals formed at low pH, are Fe- and Mg-rich (Rogers et al. 2006). Moreover, the surface area measurement by the BET method may not necessarily be always appropriate to calculate dissolution rates of many silicates as it could have less reactive internal surface and highly reactive external surfaces (Brantley and Mellot 2000). However, in this study high release of Ca was observed at 100°C and 120 bars, which implies mobility of Ca is higher at high temperature and high pH. This behaviour could delay in Ca-mineral precipitation as it takes time for the fluid to shift from acidic to alkaline conditions as a result of mineral dissolution.

The low cation release rate at 100°C and 120 bars compared to 60°C and 80 bars could be explained by enhanced precipitation of Mg-Fe rich mineral phases in case of MB due high olivine content and potential to form Mg- or Fe- carbonates minerals in an acidic regime.

Reaction path modeling suggests the formation of the secondary mineral is ≈ 4 times higher in experiment MB_(100,120) than in MB_(60,80). This behaviour seems to agree also with the experiment conducted with 0.05 r:w ratio. Thus, a higher release rate of Mg²⁺ and Fe²⁺ at different depth conditions from MB could lead to early precipitation of secondary minerals compared to VB. The speciation model also shows siderite as the only carbonate mineral saturated in the experiments performed above 25°C and 5 bars. There is a potential for magnesite and ankerite to form at a higher temperature and over longer times as it is slightly undersaturated at the end of the current experimental period. The formation of Mg-Fe carbonate solid solutions could be possible at higher temperatures, however, the current thermodynamic databases in GWB need to be updated for the (Mg-Fe) mixed carbonate minerals.

The theoretical dissolution rate (R_i) of major primary minerals was calculated using Eq 3.6 after the standard rate constant was corrected for temperature (Eq 3.5) and was compared with the actual net dissolution rate of MB and VB at different P/T conditions. The latter is based on the net Si release rate and accounts for the molar abundance of Si in the whole rock. The comparison of theoretical mineral dissolution rates and the actual net dissolution of MB and VB is shown in Fig. 3.10. This comparison allows to estimate the reduction in whole rock dissolution due to concurrent precipitation as compared to theoretical dissolution of major minerals. Eq. 3.5 and Eq. 3.6 shows the stepwise calculation of rate constant and dissolution rate at 25°C, 60°C and 100°C and at pH 4.

The kinetic parameters from the literature (Palandri and Kharaka 2004) (Table 3.5) were used for forsterite (olivine), augite (pyroxene) and andesine (plagioclase) rate calculation (Table 3.8). Most of the rate constant data are reported at 25°C and can be calculated for higher temperature using the Arrhenius equation.

$$k_i = k_{25} \cdot \exp \left[\frac{Ea}{R} \left(\frac{1}{T_2} - \frac{1}{298.15} \right) \right] \quad (3.4)$$

$$R_i = S.A [k_i \cdot (aH^+)^n] \quad (3.5)$$

where k_i (mol m² sec⁻¹) is the rate constant at a temperature T_2 (K), Ea is the activation energy (kJ mol⁻¹); R is the molar gas constant (J mol⁻¹ K⁻¹); 298.15 K is the reference temperature; r_i is the specific mineral dissolution rate (mol/sec); $S.A$ is the total BET surface area of the

specific mineral in the basalt sample; a is the activity of the H^+ ; n is the reaction order w.r.t H^+ .

Fig. 3.10 shows the mineral specific dissolution rates at 25°C, 60°C, and 100°C at a pH 4 and dissolution rates of MB and VB based on net Si release rate at far-from-equilibrium condition. The dissolution rate for forsterite and augite is similar, while the rate of andesine is several magnitudes lower and the specific dissolution rates increased with increase in temperatures. As the MB and VB is comprised mostly of these three specific minerals, it is expected that the net release rate of Si should be close to the theoretical specific mineral dissolution rates. However, the theoretical specific dissolution rate of forsterite and augite is > 2 orders at 25°C and 60°C and > 3 orders at 100°C compared to the net Si release rate from MB and VB. The rate of andesine dissolution is similar to MB at 25°C and 60°C but the difference becomes larger towards higher temperature.

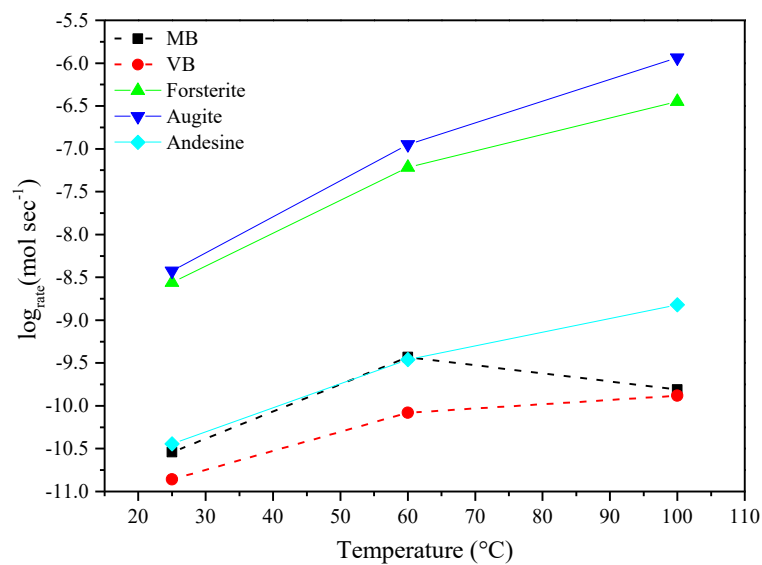


Figure 3.10: Comparison of dissolution rate of MB and VB based on experimental Si release at 25°C, 60°C and 100°C at far-from equilibrium condition to the dissolution rate of the specific minerals calculated at pH 4 using Eq (3.5) and (3.6)

This large difference in the theoretical mineral specific dissolution rate and the net Si release rate of the basaltic rock is very significant and can only be explained by co-precipitation of secondary mineral phases.

Crystalline basalt dissolution at acidic pH is dominated by the dissolution of olivine given its dissolution rate is at least one order of magnitude higher than plagioclase (Gudbrandsson et al. 2011). Olivine is high in Mg and Fe content but low in Ca. In this study, we observed the net release rate of Si at far-from-equilibrium condition is congruent to the net Mg and Fe release rate from MB and VB at all the P/T experimental conditions which suggest primarily olivine dissolution and presumably followed by pyroxene dissolution (Table 3.8).

Table 3.8: Dissolution kinetics data of forsterite, augite and andesine and its theoretical calculated rates at pH 4 at temperature 25°C, 60°C and 100°C

Mineral	Forsterite	Augite	Andesine
$T_1(K)$	298.15	298.15	298.15
$T_2 (K)$	333.15	333.15	333.15
$T_3(K)$	373.15	373.15	373.15
$E_a(kJ\ mol^{-1})$	67.2	78.0	53.5
n	0.470	0.700	0.541
k_0 at pH = 0; 25°C	1.41E0-7	1.51E-7	1.31E-9
SA at 25°C and 60°C	1.503	1.91	2.10
SA at 100°C	0.83	1.06	1.165
pH	4	4	4
$k_{(25)}$	1.41E0-7	1.51E-7	1.31E-9
R_{25}	2.754E-9	1.96E-09	3.59E-11
$k_{(60)}$	2.43E-6	4.103E-6	1.26E-8
R_{60}	4.74E-8	5.33E-08	3.47E-10
$k_{(100)}$	3.24E-5	8.41E-5	9.90E-8
R_{100}	3.55E-7	1.16E-06	1.51E-09

k_0 (mol m² sec⁻¹); R_i (mol/sec) SA (m²), the kinetic data to calculate the dissolution rates were taken from (Palandri and Kharaka 2004) at acidic mechanism.

Similar batch experiments performed at temperatures > 100°C have shown that 56 wt. % of initial MgO reacted in basalt compared to only 5 wt. % in case of pure olivine mineral. The study observed the formation of Fe-bearing magnesite (Mg_{0.8}Fe_{0.2}CO₃) was 40 times higher in the basalt experiment relative to pure olivine (Sissmann et al. 2014). Moreover, porous Si-rich layers presumably clay were also observed on the surface of the primary silicate minerals. (Sissmann et al. 2014, Hellevang et al. 2017, Luhmann et al. 2017, Wolff-Boenisch and

Galeczka 2018). Another factor that could inhibit the dissolution rate at high temperature is the formation of secondary minerals in form of layers on top of the primary minerals.

3.4.2 Instantaneous precipitation at higher temperature

It was observed that the element release rate from MB_(100,120) based on linear fit are lower compared to MB_(60,80). This trend is not in agreement with the previous dissolution rate studies of minerals at varying temperatures. There could be two possibilities for this kind of observation (1) The released major cations and Si instantaneously precipitated at higher temperature even at a far-from-equilibrium conditions. (2) The element release from the primary minerals were restrained by the precipitated layer. Fig. 3.11 compares the stepwise experimental Si release rate based on Eq. 3.4 for MB at different P/T and provides a magnified view for the first 24 hours.

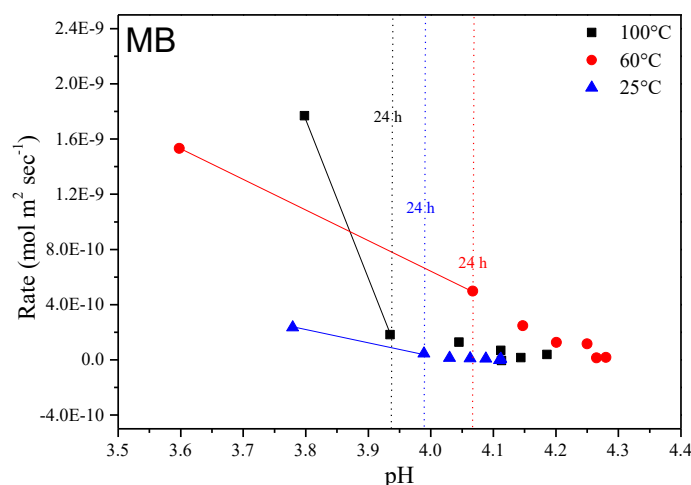


Figure 3.11: Comparison of calculated Si release rate of MB at 25°C;5bars 60°C;80bars and 100°C;120 bars vs pH for the initial 24 hours (dotted line). The data points in the initial 24 hrs are connected to show the trend of rate for different experimental run.

It is observed that in experiment MB_(100,120) there was a steep drop, while in MB_(60,80) the drop is more gradual. The release rate at MB_(25,5) is low from the beginning. It is clear that the pH is different for each experimental condition at 24 hours. It is observed that the Si release rate in experiment MB_(100,120) is slightly higher than MB_(60,80) in the beginning and then almost coincides with the rates at 25°C and 5 bars. Thereby, the release rate for MB_(100,120) drops by one order of magnitude over a pH range of only 0.5 before it reaches pH 4 and becomes steady

at pH 4.1, while in experiment MB_(60,80) the rate remained comparatively higher but showed a gradual decreasing trend until pH 4.3.

This initial sharp rate drops in the Si release rate at far-from-equilibrium condition in experiment MB_(100,120) clearly suggests concurrent mineral precipitation.

The discrepancy between similar rates (Table 3.7) in experiments MB_(25,5) and MB_(100,120) and a higher rate in MB_(60,80) from the weighted linear fit for the first 60 hours is clearly explained by the dissolution trends in Fig. 3.11. This shows that even if the system is far-from-equilibrium with respect to the major primary minerals at the higher temperature, the precipitation of the secondary phases begins immediately leading to surface passivation of primary minerals. This conclusion is similar to the one derived from our previous wafer experiment (Chapter 2) where a low dissolution rate of the underlying primary minerals was observed. Previous studies have shown favourable conditions for the formation of mineral groups such as smectites, zeolites, and Fe-oxides, based on secondary mineral saturation state in the speciation model (Schaefer et al. 2009, Luhmann et al. 2017). It appears that minor secondary mineral phases may form during dissolution experiments significantly reducing mineral dissolution rates in experiment MB_(100,120) and to a smaller degree in MB_(60,80).

Reaction path modeling showed instantaneous precipitation of kaolinite at low pH at all P/T conditions (Fig. 3.7d, 3.8d, and 3.9d). However, the mineral saturation of beidellite, and stilbite decreased over time in experiments MB_(60,80) and MB_(100,120) even after implementing a simple rate law (Eq. 3.2) for the two minerals. This is due to the incorporation of maximum Al and Si into kaolinite, which became rate-limiting for the formation of smectites and zeolite. Stilbite comprises Na⁺ cation, but modelled Na concentrations were difficult to match with the experimental data possibly due to incongruent dissolution of Na-rich matrix. This could be the reason not to observe stilbite precipitation in the model. Moreover, the good match between the modelled results when using the cross-affinity rate law and the experimental data suggests that the dissolution rate of the primary minerals is affected by the saturation state of the secondary minerals. The impact is observed in the individual release of the major cations and Si. The large amount of kaolinite formation as predicted for experiment MB_(100,120) is likely a factor controlling the dissolution rate and should not be neglected. Secondary Si-Al-rich minerals were observed to form as a layer on top of the primary minerals in basalt within the

wafer experiment in Chapter 2 and elsewhere (Sissmann et al. 2013, Sissmann et al. 2014, Hellevang et al. 2017, Menefee et al. 2018, Wolff-Boenisch and Galeczka 2018). This implies that the rate of mineral dissolution in basalt under CO₂ storage at depth > 800 meters may cause early saturation of some secondary minerals and lead to instantaneous mineral precipitation mostly in the form of smectites, zeolites, and other Si-rich phases.

3.5 Conclusion

In this study, we observe that element release rates of MB are up to 5 times higher at three sets of P/T conditions compared to VB, mostly likely due to a higher olivine content in MB. Olivine is the major mineral which controls the overall dissolution rate of basalts at a far-from-equilibrium conditions in an acidic regime. The initial release rate decreased in MB_(60,80,0.5) in experiments with larger surface area even at a far-from-equilibrium conditions, suggesting mineral precipitation causing surface passivation. Siderite may form as early as 7 days and only at higher P/T conditions. Fe and Mg carbonate minerals or mixed carbonate solid solutions have the potential to form at far-from-equilibrium conditions at about pH 4 due to the high content of dissolved Mg and Fe from olivine dissolution.

Reaction path modeling estimated that 5.5 % of the initial rock mass dissolved in experiment MB_(100,120) and 34 % of dissolved rock precipitated as secondary minerals, whereas only 0.4 % and 8 % mass precipitated in experiment MB_(25,5) and MB_(60,80) respectively. This implies that the precipitation rates of secondary minerals in basalt are higher at a depth of 800 m and beyond, even under acidic conditions and these secondary phases control the whole rock dissolution rate over time. The initial release of divalent cations, and Si was high, but the release rate dropped quickly particularly at higher P/T conditions.

Chapter 4: The impact of mineral dissolution and precipitation on the pore network adjacent to the fractures

Abstract

Pores connected to fractures provide an increased surface area for fluid-rock interaction when a reactive fluid migrates along fractures. In case of a CO₂ leakage scenario, buoyant CO₂ together with fluid is expected to migrate along the fractures. Predominantly, diffusion-controlled transport of ions including Ca²⁺, Mg²⁺, Fe²⁺ and Si into the adjacent connected pores lead to local mineral saturation causing precipitation of secondary minerals and potentially can seal leakage pathways. In this experimental study, changes to the pore network geometry in a fractured basalt was studied under subsurface condition (60°C and 80 bar). CO₂-saturated water with a supply of ions from the dissolution of basalt powder reacted with the pore network connected to an artificially fractured basalt sample over 12 weeks. Solid solution carbonate minerals as well as Si-Al rich phases were observed in the fractures. X-ray micro-CT analysis was used to determine changes to the pore network.

The net pore volume reduced by 7.7 %, which is equivalent to a 1 % increase in the grain volume. A total of 237.8 mm³ secondary minerals precipitated and 95.2 mm³ of primary minerals dissolved in the whole artificially fractured core with a total volume of 17824 mm³. The connected pore network (CPN) changed its structure during the experiment, a volume of 13.4 mm³ new fluid pathways opened after mineral dissolution, and previously isolated pores became connected. A net volume of 17.8 mm³ blocked after precipitation with a net reduction of 4 mm³ (< 1 %) of the CPN. The pore network model showed a decrease in 15 % and 4.4 % of connected pores and throats in the post-experimental un-grooved half core, depicting the importance of mineral precipitation in pores rather than in pore throats. The presence of fractures increases the CO₂-rock-fluid reaction and enhances mineral dissolution and precipitation under diffusion-controlled reactions.

4.1 Introduction

Basalt formations are often fractured, posing a leakage risk during CO₂ storage. Despite their fractured nature, they are favoured for long term storage of CO₂, due to their high mineral trapping capacity, exclusive structural feature, and large potential storage capacities (Matter et al. 2016, McGrail et al. 2016, Xiong et al. 2018). The advantage of fractures is their connection to the pores, which contributes to the reactive surface area of the rock and plays a dominant role in providing fluid pathways in low permeability rocks. If, however, mineral precipitation occurs along the CO₂ leakage pathways within fractures, risks of long-term leakage are less severe. Mineral precipitation in basalt fractures has been observed where hydrothermal fluids migrated upwards over geological time (Eggleton et al. 1987, Rogers et al. 2006, Goldberg et al. 2008). However, a range of factors including the flow velocity of the CO₂-enriched plume, fluid chemistry, pressure and temperature conditions and the fracture aperture size need to be considered in order to predict the rate and extend of self-sealing of fractures (Brunet et al. 2016).

Several laboratory studies were performed to understand the influence of transport limitations on the extent of mineral formation and pore network alterations in natural basalt cores when exposed to acidic CO₂ rich fluid under relevant geologic storage conditions (Adeoye et al. 2017, Xiong et al. 2017a, Xiong et al. 2017b, Menefee et al. 2018, Xiong et al. 2018). Experimental flow studies conducted by Luhmann and colleagues (2017) at 150°C; 15 MPa pCO₂ and Adeoye and colleagues (2017) at 45 and 100°C; 10 MPa pCO₂ observed no carbonate mineral precipitation. The former study observed Si- and Al-rich phases leading to permeability reduction while net mineral dissolution was detected in the latter case due to a short residence time. Experiments involving artificially fractured basalt core samples at 100°C and 150°C; 10 MPa pCO₂ observed formation and uneven distribution of carbonate mineral in the areas where the solute transport was diffusion-controlled (Xiong et al. 2017, Xiong et al. 2018). Menefee and colleagues (2018) studied the extent of carbonation under different flow regimes at 100°C and 150°C; 10 MPa and using NaHCO₃ as a buffer and carbonate ions source. This study showed that mineralization predominantly occurred at higher temperature in the diffusion-limited zones adjacent to the bulk flow path. The CO₂-enriched acidic fluid reacted with the fracture and lead to the mobilization of cations. The cations diffused into the pores connected to the fracture due to the concentration gradient. The fluid within the pores became

supersaturated with respect to certain minerals and local mineral precipitation occurred. Therefore, these studies demonstrated mineral dissolution occurs where advection controls solute transport, while diffusion-controlled zones within the pore network play an important role in mineral carbonation in the context of geological carbon storage in basalts. Studies showed the ability of enhanced mineral precipitation in fractured basalt in diffusion-controlled zones, nonetheless, were associated with longer experimental duration, carbonate supply (NaHCO_3), shallow fracture depth (100 μm) and unrealistic reservoir P/T conditions (Luhmann et al. 2017, Luhmann et al. 2017, Xiong et al. 2017, Menefee et al. 2018, Xiong et al. 2018). Therefore, the above-mentioned studies have focused on secondary mineral precipitation in fractured cores, the spatial location, and quantification. However, the concurrent and potentially coupled processes of dissolution and precipitation need to be considered in order to fully assess the changes to the connected fracture network. Coupled dissolution and precipitation processes can significantly modify the connected fracture network. For example, Singurindy and Berkowitz (2005) investigated the influence of fractures on the evolution of hydraulic conductivity structure caused by the dissolution of calcium carbonate and precipitation of gypsum in carbonate rocks. The cores with rough fracture surfaces, isolated and multiple fractures clogged more rapidly, causing a change in the overall conductivity and porosity (Singurindy and Berkowitz 2005, Huerta et al. 2012).

The objective of this study is to evaluate the changes in the pore network and the influence of coupled dissolution and precipitation processes in fractured massive basalt rock under diffusion-controlled condition at micrometer scale. A static experiment (M-core) was conducted at a P/T conditions representing a depth of 800 m in the subsurface, using an artificially fractured core with multiple mm deep fractures. A continuous supply of ions into the reactive fluid was maintained representing a key condition in a fluid flow system. Prior to the M-core experiments two short baseline static experiments were conducted (B-1 and B-2) with to determine the optimum rock:water. Changes in the pore network were analyzed using non-destructive imaging techniques (SEM and X-ray micro CT), which would assist in understanding the impact of coupled dissolution and precipitation processes in a connected pore network, mainly changes in the pore and solid phase volume; and the surface area. Pore and throat size distribution of the pre- and post-experimental basalt were mapped and compared. Most importantly, the total volume of mineral dissolution and precipitation was calculated and changes in connected pore network were estimated. This study thus gives new

insight into the processes and conditions important for the consideration of geological CO₂ storage in fractured basalt reservoirs, especially on the self-sealing capacity of fractures and associated pore network on interaction with CO₂-saturated fluid.

4.2 Materials and Methods

4.2.1 Fractured core preparation

Massive basalt was sourced from the Bamstone Bluestone quarry in Port Fairy, Australia. The chemical and mineral compositions are listed in Chapter 2. A core of 1-inch diameter and 6 cm length was drilled out from a sample block by using the automated plugging machine (Vinci Technologies). The core is cut into half with a rock saw diamond blade. On the surface of the one-half core, four grooves representing fractures were drilled with a diameter of 2 mm and a depth between 1-2 mm using a mini drill (Dremel 3000) with a 2 mm diamond bur (Fig. 4.1a). A hand-drawn stencil was fixed on top of the flat surface of the half core as a guide when grooves were milled. The core surfaces were first wiped with ethanol to remove any stains and then sonicated in water before oven dried at a temperature of 40°C for 2 days. The half core samples were glued together by applying Master Bond EP42HT-2 on the clean dried outer edges along the length of the core. The thickness of the bond layer should be around 0.10-0.15 mm to achieve optimum adhesion. Pore surfaces were filled in with more adhesive on the edges. The glued core sample was left to cure for 12 hours at room temperature and 3-5 hours at oven under 65°C. The outer core surface was also covered by a bond layer to avoid any reaction, and similar curing procedures were followed. Longer curing period gives higher bond strength. After the curing process, PTFE tape was wrapped around the core as an additional protective layer.

4.2.2 Core holder design

A core holder was designed to accommodate the assembled core inside the reactor. Due to the corrosive nature of the reacting fluid, the holder was made of high-grade stainless steel (T316 SS). The holder has two thick circular disks. The core was fit in between the disks and fixed together with six long stainless-steel screws. The dip tube was shortened and fitted to the inlet of the core holder (Fig. 4.1b). The dip tube is the common line for CO₂ injection and fluid sampling.

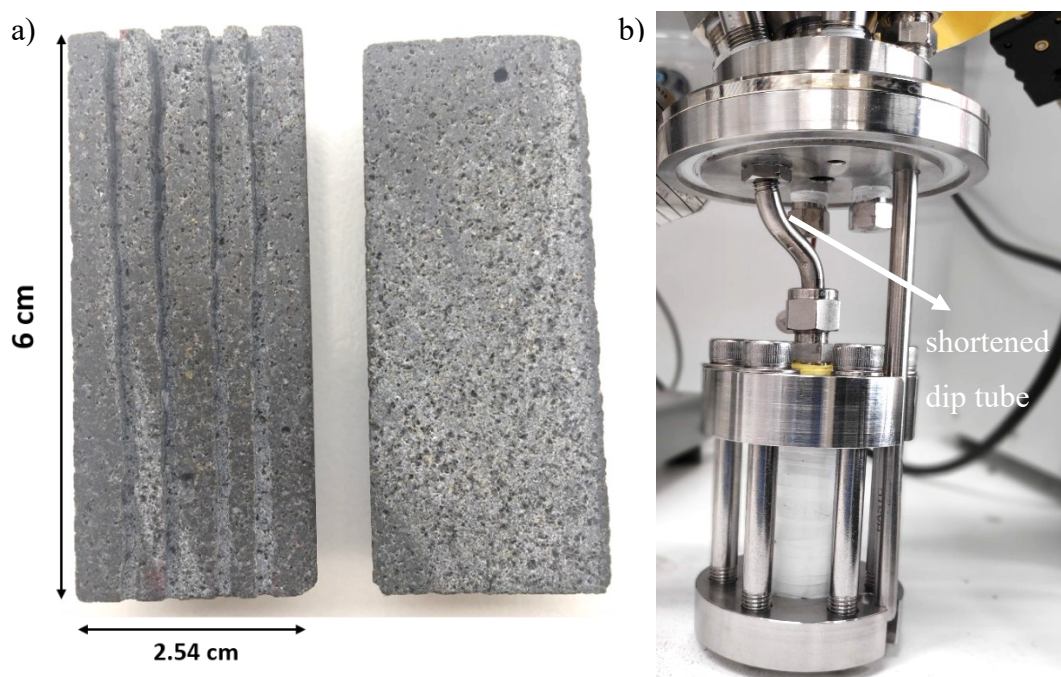


Figure 4.1: (a) Artificially engraved massive basalt core; with four grooves to increase the reactive surface area (b) Assembled core with the core holder, with modified short dip tube connected to the assembled core top

4.2.3 Diffusion-controlled experiments

Baseline Experiments

Prior to the main fractured experiment, two baseline experiments (B-1 and B-2) were performed in a high-pressure 450 mL Parr[®] Reactor at 60°C and 80 bars to (a) observe the change in concentration of cations, Si and total alkalinity of the solution over time and (b) estimate the optimal rock:water (r:w) mass ratio for the main fracture experiment that would enhance the supply of cation concentrations and lead to early supersaturation of secondary minerals in the fluid leading to favourable mineral precipitation.

In both baseline experiments (B-1 and B-2), different amounts of basalt powder were used. The initial r:w mass ratios were 0.015 for B-1 and 0.043 for B-2; the r:w ratio in B-2 was about 3 times higher than in B-1 (Table 4.1). This was done by packing basalt powder with a grain size of 90~125 μm fraction inside a single nylon bag and immersing it in 300 mL of deionised water (DI). The solid basalt sample were crushed and powdered, as described in section 2.2.1. The mesh size of the nylon diffuser bag was 90 microns, i.e. the grain size of the basalt powder was kept larger than the mesh size of the nylon diffuser bag. As there was no fluid advection in the

reactor, mineral dissolution was diffusion-controlled except for the first half hour when the fluid was purged with CO₂ gas at 4 bars for 30 minutes with CO₂ gas to remove residual oxygen. The purging process was followed by the addition of CO₂ to the reactor from the CO₂ cylinder by the syringe pump. Fluid samples were collected sequentially, as shown in Table 4.1. The experimental system is shown in Fig. 4.2.

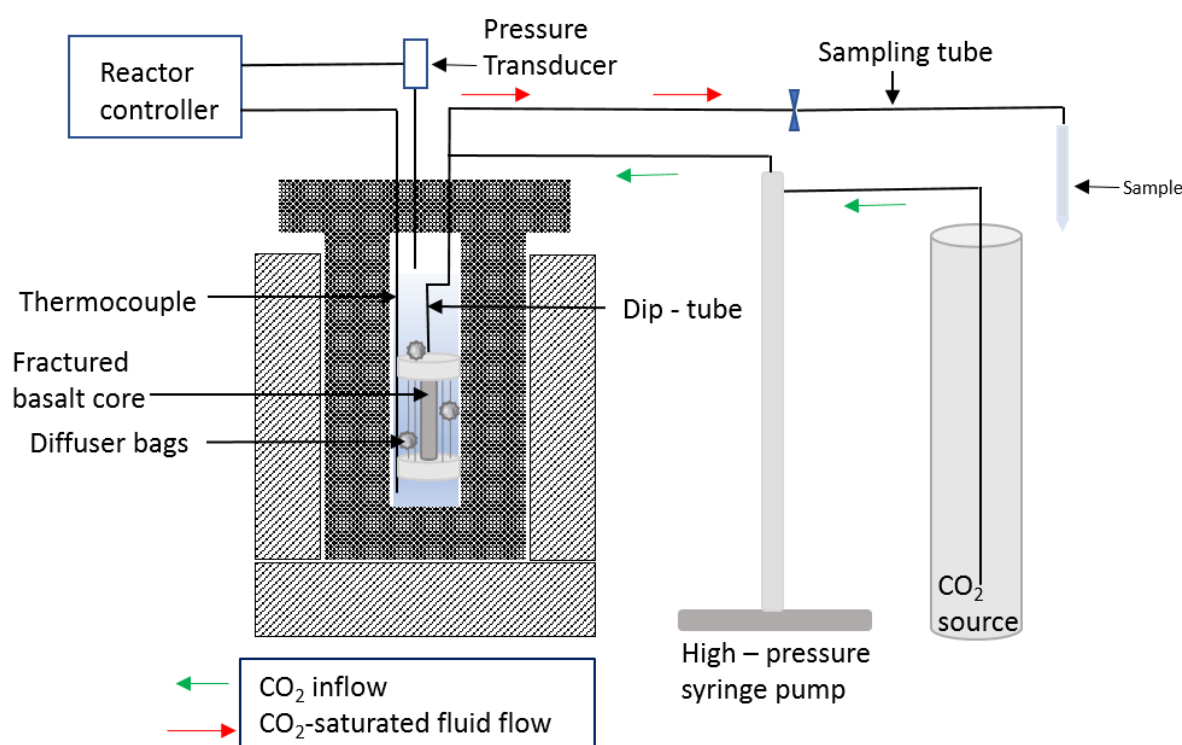


Figure 4.2: Schematic of static core experimental set up

The main static core (M-core) experiment was incubated with 250 mL of DI water, so that the core and the core holder assembly were fully immersed, and a headspace of 80 mL was maintained. In order to reach mineral supersaturation in the fluid quickly, 38 grams of powdered massive basalt (90~125 μm size fraction) was introduced in the reactor by inserting basalt powders in 3 nylon bags (Fig.4.2). The r:w ratio is 0.152 excluding the exposed core fracture. The core was held in the core holder and the diffuser bags (nylon bags) were placed on the either sides and one on the top of the holder. This was done to avoid the effect of local concentration gradient outside the core. This was also the maximum number of bags that could be accommodated inside the reactor.

Previous studies have introduced analytical grade chemicals to supply carbonate forming cations in the reactive fluid to speed up the reaction time (Hellevang et al. 2017, Luhmann et al. 2017, Menefee et al. 2018). Allowing ions to diffuse from the powdered basalt in the nylon bags into the fluid as implemented here is considered to be closer to natural conditions.

The temperature of the reactor was set to 60°C and was purged with CO₂ gas at 2 bars for 30 minutes to remove the residual oxygen from the fluid. Once the CO₂ line was opened, CO₂ flowed through the grooves of the core before encountering the surrounding fluid at top of the core. The reactor vessel was pressurized to 85 bars. Fluid samples were collected from the high-pressure sampling valve of the Parr reactor after 1, 4, 14, 50 and 86 days. After the long incubation period of 12 weeks, the reactor was cooled down and was slowly depressurized before it was opened. The core was air dried for 10 days.

Fluid samples from the baseline and the main core experiment were filtered with a mesh size of 0.45 µm and acidified with 2 % HNO₃ acid before major and minor cations, and Si were analysed.

4.2.4 Analytical methods

4.2.4.1 Fluid analysis and solid-phase analysis

Aqueous samples from the baseline and the main core experiments were analysed by inductively coupled plasma optical emission spectrophotometer (ICP-OES) to measure the major ion concentrations (Ca²⁺, Mg²⁺, Fe²⁺, Na⁺, K⁺, Si, and Al³⁺). Total alkalinity analysis was performed using a potentiometric titration method (916 Ti- Touch titrator, Metrohm) on unfiltered aqueous samples. Solid-phase analysis was performed by an optical microscope on each groove to detect any form of mineral precipitation in the grooved half core. Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDX) was performed on the gold-coated grooved half core to identify secondary mineral phases.

4.2.4.2 Micro-CT analysis of the core

The pre- and post-experimental core was imaged using the GE Nanotom Micro-CT scanner. The analysis of high-resolution core images by micro-CT would help in determining the physical changes of the core post-reaction. Micro-CT scanning is a non-destructive technology

and generates a digitized 3D image of the sample. The working principle is based on differences in X-ray attenuation by different materials. The absorption of X-rays by the pores (air) is different from the solid matrix. A typical micro-CT set-up consists of a sample holder, an X-ray source and a detector (Fig. 4.3). The sample is placed on a rotating sample holder between the X-ray source, and the detector. A series of 2D radiographs, also called slices, are acquired during the scan, which represents maps of x-ray attenuation of materials in the sample. The 2D radiographs are reconstructed and stitched together using the Phoenix datos software from GE to achieve a 3D representation of the sample consisting of voxels. A voxel or a 3D pixel is a representation of a volume of one element in the 3D dataset. A stack of the 2D image generates a 3D volume, and this 3D dataset is called a 3D image.

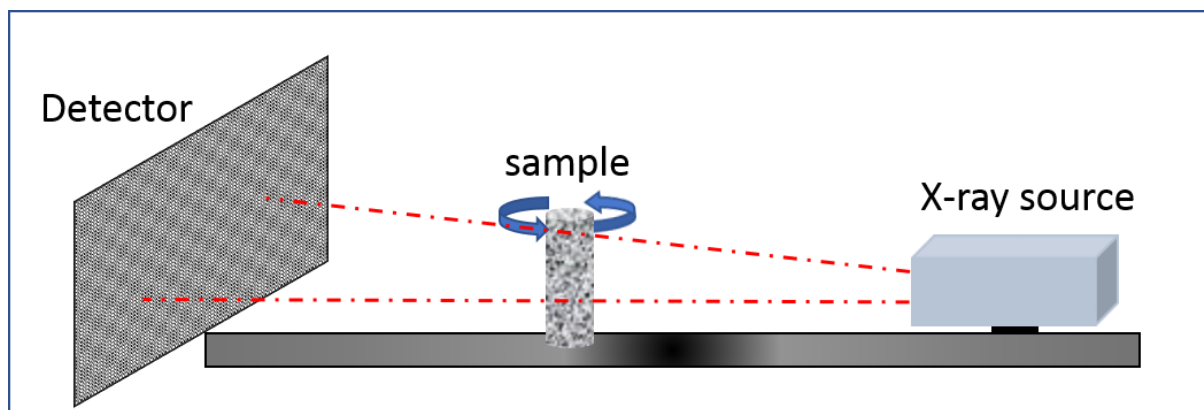


Figure 4.3: Schematic diagram of a micro-computer tomography (micro-CT) imaging of a core sample. X-rays from the source are propagated through the rotating sample, acquired by the detector.

The resolution of a scan is an important factor as it defines the size of the voxel. Features (such as pores, pore throats and solid grains) below the scanned resolution are not detected. In this study, the cores were scanned at a resolution of $14.99\ \mu\text{m}$. The scan was acquired using a voltage of 55 kV, current of $270\ \mu\text{A}$, and power of 14.9 W. The reconstructed data was imported, and processed in the AVIZO[®] software (Thermo Fisher Scientific)

Segmentation

The basalt core consists of only two phases, the basalt rock (solid grains) and the pore space (voids). These two phases have very different attenuation of the x-rays, which make them distinguishable in the acquired image. The images are represented using greyscales, with the colour black representing no attenuation of x-rays and shades of grey representing different

minerals in the rock phase. This clear distinction between the two phases allows for a straightforward binarisation of the image. Binarisation means the transformation of a greyscale image into a binary image. Binarization is a simple segmentation method that puts a range of greyscale values of interest into a single bit value. An interactive thresholding was used to obtain a binary image. In this method, an initial value is defined by dividing the peaks representing the two phases at their minima in the greyscale histogram. The threshold value was further optimised using visual feedback on the output dataset until a clear boundary between the two phases was achieved. The segmented images are also validated using the porosity values measured from the physical analysis (saturation and buoyancy technique) and compared to two regions of interest in the reacted and the unreacted cores away from the grooves. The greyscale intensity threshold for void space was 0-16500 for reacted core image and 0-17500 for the unreacted core image. As these are two different images captured by the micro-CT, a difference in their greyscale histograms is expected. Once a single slice had been segmented, the same segmentation is iterated to all the slices of the 3D dataset.

Voxel size below 3 μm was masked and filtered to avoid minor errors from segmentation and noise (Luhmann et al. 2017). In the post-experimental CT image, microfractures were observed at the inlet and outlet of the core; this could be due to excessive pressure of the core holder on the core while setting up. Another reason could be the high CO_2 pressure that flushed through the grooves during CO_2 pressurization. Due to the observed microfractures in the post-experimental core, the analysis and registration of the pre-and post-experimental images of the whole core was not viable. Therefore, the half cores (grooved and the un-grooved sides) were registered and analysed separately and only the mid-section (4 cm) of the core was considered for CT analysis. The connected pore network of the initial 6 cm core is shown in the result section. The grooved half of the core contains pore network connected in the z-direction due to the presence of the artificial fractures. Due to the absence of the fractures on the un-grooved other half of the core it did have a connected pore network in the z-direction. Therefore, the CPN analysis could only be performed on the grooved side of the core.

Porosity, total surface area and grain volume analysis

Numerical algorithms were used to quantify physical changes of the pre- and post-experimental samples from the segmented dataset. Porosity, grain volume, and surface area of the core halves were extracted individually from the segmented scanned images.

Porosity is the ratio of the pore voxels to the total numbers of voxels, and it can be estimated as:

$$\emptyset = \frac{n_{pore}}{n_{pore} + n_{mineral}} \quad (4.1)$$

where, $\emptyset$ is the porosity, n_{pore} is the number of voxels assigned to the pores space, and $n_{mineral}$ is the number of voxels assigned to the mineral phases of the dataset. The total surface area of the mineral phases is calculated as the product of the number of pixels exposed to the fluid ($pixel_i$) and surface area of each of those pixels (SA_{pixel_i}), n is the number of pixel (Scientific 2018). Note: the total surface area is underestimated when the scan resolution is too large.

$$S.A_{total} = \sum_{i=0}^n pixel_i \cdot SA_{pixel_i} \quad (4.2)$$

Similarly, the total volume of the mineral phases is calculated as the product of the number of voxels ($Mineral_{voxel}$) assigned to the mineral phases and the volume of each of these voxels V_{voxel} (Scientific 2018).

$$V_{mineral} = \sum_{i=0}^n Mineral_{voxel} \cdot V_{voxel} \quad (4.3)$$

Pore network model

Pore network models (PNM) are used for the topological equivalent representation of a porous media into pores and throats. A PNM was generated for the un-grooved half core which allows a complex porous rock to be represented using simpler shapes (balls and stick model) but without losing out on the original topological properties of the rock. This is done by computing watershed lines on the binarized image. This method is a high-level combination of the watershed, distance transform, and numerical reconstruction algorithm (Doroszko and Seweryn 2017, Ramos and Matouš 2018, Ahmed and Lebedev 2019). The first step is constructing a chamfer distance map, which represents the minimal distance of a voxel from the pore boundary. The higher intensity represents bigger pores, and the low intensity represents smaller pore. This distance map is used as a priority map input for the watershed process. The most inner areas of the pores, which are the maxima areas in the distance maps

are used as markers in the watershed process. The output from this module is a separated labelled image with a unique label assigned to each object. This map is taken as an input for constructing the pore network model.

When using the watershed method for constructing pore-network models, the watershed fills the pores starting from the higher intensity regions and enlarges it towards the boundary of the pores. The throats of the network are defined by the locations where the fluid from two different pores converge. Subsequently, the volume of the pores and the surface area of the throats are calculated. The ideal pore is a sphere with an equivalent volume of the irregular shaped real pore, and the ideal throat is the cylinder with an equivalent surface area as the irregular shaped real throat.

Pores can be irregular in shape, so the total volume of all the voxels in a pore cluster results in estimating the total volume of the irregular shaped pore clusters. The model considers the volume of the pore clusters of voxels being a perfect sphere, and the equivalent diameter (D_{eq}) is calculated, as the size of the pore and is given as

$$D_{eq} = \sqrt[3]{\frac{6 \cdot N_{Veq}}{\pi}} \quad (4.4)$$

where, N_{Veq} is the equivalent pore volume size of the sphere. The idealised pores are centred according to the actual position of the real pores. The output from the pore-network model consists of the number of pore and throats in the rock and their equivalent radius (Scientific 2018).

Quantification of dissolved and precipitated minerals

To quantify the volume of the dissolved and precipitated minerals in the grooved and the un-grooved half cores, the “AND” arithmetic operator was used on the segmented images. The quantification of dissolved minerals was estimated by using the “AND” arithmetic operator on the unreacted mineral image ($V_{UR}^{minerals}$) and reacted pore image (V_R^{pores}). This generates an output showing the mineral voxels in the unreacted image transformed to pore voxels in the reacted image signifying the formation of new pores due to mineral dissolution after the experiment.

In order to quantify the volume of precipitated mineral the “AND” arithmetic operator was used on reacted mineral image ($V_R^{minerals}$) and unreacted pore image (V_{UR}^{pores}) which outputs the pore voxels in the unreacted image transformed to mineral voxels in the reacted image signifying formation of secondary solid phases due to mineral precipitation after the experiment. This method estimated the total volume of mineral dissolution and precipitation during the experiment. Fig. 4.4 is a visual representation of the “AND” arithmetic operator used to estimate the volume of mineral dissolution and precipitation.

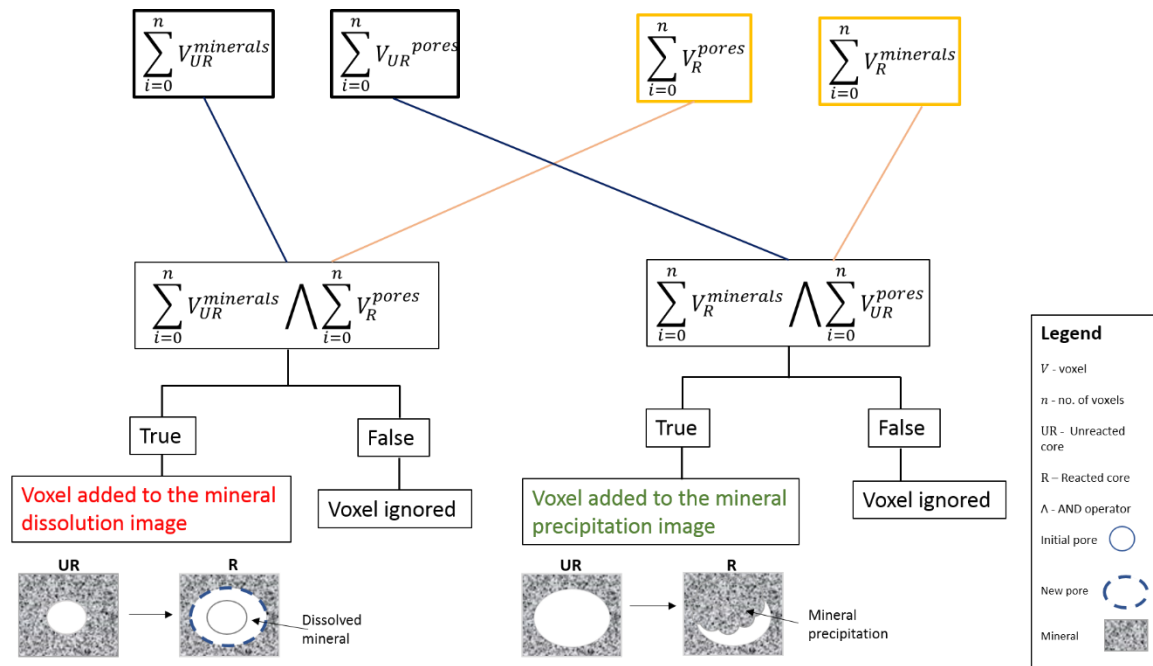


Figure 4.4 Flow chart showing the algorithm and steps used to separately quantify the total volume of dissolved and precipitated minerals in the half cores

When the arithmetic operation is applied to the reacted pore image and the unreacted mineral image, it works like a true/false filter. This allows the voxels which belonged to the reacted pore image but now belong to the unreacted mineral image to form a new voxelised image representing mineral dissolution. Similarly, when the arithmetic operator is applied to the reacted mineral image and the unreacted pore image, the true/false filter only allows the voxels of the unreacted pore image but transformed to mineral in the reacted image. This forms a new voxelised image representing mineral precipitation. The grey images below in Fig. 4.4. give a 2D pictorial representation of the volume of mineral lost by dissolution or formed by secondary precipitation.

Connected pore network structure

As the focus of the experiment was to observe the changes in the fractures and adjacent pore network due to mineral reactions, the connected fracture network was isolated from the images of the grooved half core and analysed separately. The images of the connected pore networks (CPN) in the reacted and the unreacted pore images were extracted. This is also referred to as effective pore network in case of fluid migration. The volumetric changes in the CPN were also calculated.

The unreacted CPN was subtracted from the reacted CPN to estimate the volume of the new pore network connection by grain dissolution. This algorithm does not quantify the net volume of dissolution or precipitation; however, it determines the volume of the previously isolated pore network in the unreacted sample, which is now connected in the post-experimental reacted sample by grain dissolution. In contrast, the reacted CPN was subtracted from unreacted CPN to estimate the volume of the disconnected blocked pathways by mineral precipitation. Similarly, the previously connected part of the pore network in the unreacted sample is now lost due to mineral precipitation by blocking small pores and pore throats.

The initial CPN of the pre-experimental 6 cm core was extracted before the two half cores were analysed separately (Fig.4.9).

4.2.5 Geochemical modeling

Aqueous speciation and the respective state of mineral saturation were calculated for the two baseline and the main core experiments using Geochemist's Workbench 11.0 (GWB) to understand whether certain minerals are under or supersaturated at certain times during the experiment. Mineral saturation indices were computed for each fluid sample as a function of time with the updated thermo.comV8.R6+ database. The detailed description of the minerals in the updated database is presented in chapter 3 in section 3.2.3. The $\text{CO}_2(\text{aq.})$ concentration in the speciation model was calculated from the CO_2 solubility at the temperature and pCO_2 using Duan and Sun model (Duan and Sun 2003). The pH is calculated based on the charge balance. The mineral saturation indices of the final fluid composition of the baseline experiments that cation concentrations are high enough to reach supersaturation of secondary minerals in the system.

4.3 Results

4.3.1 Fluid chemistry

Major cation and alkalinity concentrations of the baseline (B-1 and B-2) and main-core (M-core) experiments are presented in Fig. 4.5 and Fig. 4.6. Table 4.1 presents the experimental conditions of the baseline and the core experiments.

Concentration differences between the two baseline experiments with different rock:water ratios were compared as a function of time. Si, Ca^{2+} , Al^{3+} , and K^{+} concentrations are higher in B-2 which has a higher rock:water ratio. Interestingly, the higher concentration of Mg^{2+} and Fe^{2+} were observed in experiment B-1 with a lower rock:water ratio compared to the B-2 (Fig. 4.5a).

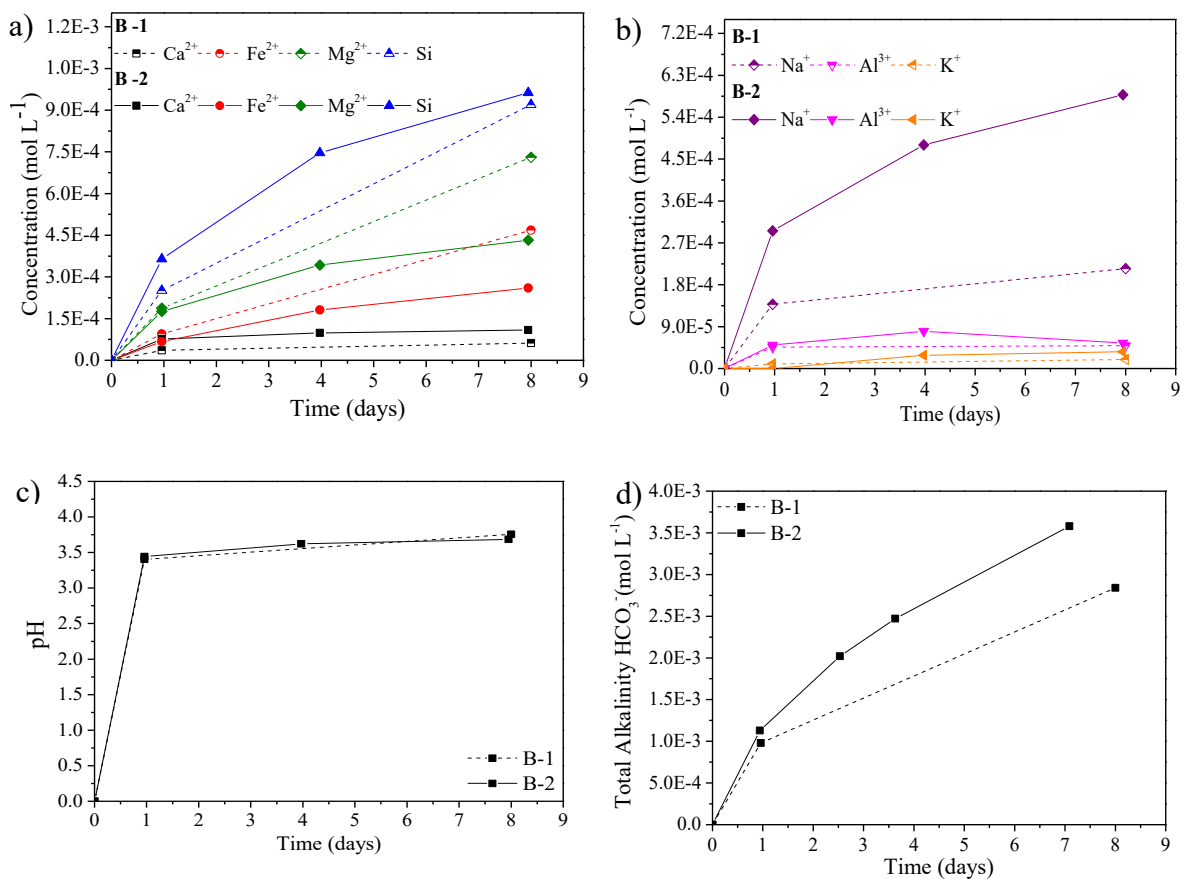


Figure 4.5: Fluid chemistry comparison of baseline experiments (B-1 and B-2) (a) concentrations of divalent cations and Si (mol L^{-1}), (b) concentrations of monovalent and trivalent cations (mol L^{-1}), (c) pH, and (d) total alkalinity (HCO_3^{-}) (mol L^{-1})

Table 4.1: Experimental conditions and concentrations of the baseline and the main core diffusion experiments

Experiment	r/w	Run time (days)	pH	Ca (mol L ⁻¹)	Mg (mol L ⁻¹)	Fe (mol L ⁻¹)	Si (mol L ⁻¹)	Na (mol L ⁻¹)	Al (mol L ⁻¹)	K (mol L ⁻¹)	HCO ₃ ⁻ (mol L ⁻¹)
B-1	0.0152	0.96	3.40	3.59E-05	1.88E-04	9.53E-05	2.51E-04	1.38E-04	4.61E-05	1.02E-05	9.80E-04
		8	3.75	6.19E-05	7.31E-04	4.68E-04	9.20E-04	2.15E-04	4.91E-05	1.94E-05	2.84E-03
B-2	0.043	0.96	3.44	7.69E-05	1.76E-04	6.73E-05	3.65E-04	2.96E-04	5.04E-05	0.00E+00	1.13E-03
		3.97	3.62	9.88E-05	3.42E-04	1.81E-04	7.46E-04	4.80E-04	8.01E-05	2.86E-05	2.02E-03
		7.95	3.68	1.09E-04	4.33E-04	2.60E-04	9.63E-04	5.88E-04	5.49E-05	3.58E-05	2.47E-03
M-core	0.152	1.04	4.03	3.14E-04	7.20E-04	1.79E-04	1.10E-03	3.12E-03	3.71E-05	1.82E-04	4.61E-03
		4.08	3.99	3.39E-04	7.41E-04	2.36E-04	1.82E-03	2.25E-03	5.56E-05	2.40E-04	4.80E-03
		14.08	4.10	4.14E-04	8.60E-04	2.08E-04	2.48E-03	3.62E-03	4.45E-05	3.68E-04	6.60E-03
		50.08	4.20	4.49E-04	9.56E-04	1.78E-04	2.53E-03	5.00E-03	5.10E-05	4.80E-04	7.75E-03
		85.00	4.40	5.16E-04	1.90E-03	8.51E-04	3.01E-03	7.12E-03	3.71E-06	6.24E-04	1.52E-02

^a rock to water ratio; ^b Calculated pH;

The higher rock mass in the B-2 experiment provided higher surface area for fluid-rock interaction, thereby, all cation concentrations were expected to be higher due to a higher mineral dissolution rate.

The Na^+ concentration is almost 3 times higher in B-2 compared to B-1 (Fig. 4.5b). The pH is calculated based on the charge balance between cations and anions, and in this case, the main anion is the HCO_3^- concentration of the fluid. The measurement of pH in the outlet fluid sample would give erroneous value as CO_2 gets depressurized.

The pH shows a similar range over time in both baseline experiments; however, the HCO_3^- concentrations are higher in B-2 than B-1 (Fig. 4.5c and 4.5d). This could be due to the immediate incorporation of Mg^{2+} and Fe^{2+} into secondary silicates such as smectites and zeolites in B-2, maintaining a low pH, and whereas the high HCO_3^- concentration is balanced by the high concentrations of Na^+ , Ca^{2+} , Al^{3+} , and K^+ .

Fig. 4.6 presents the change in cation concentrations, alkalinity, and pH of the core experiment over 85 days. The bulk solution chemistry in the fluid is mostly contributed from the basalt diffuser bags and only a very minor degree from the exposed areas of the top and the bottom and the grooves within the core. The concentrations of Mg^{2+} , Fe^{2+} , and Si increases till day 14, plateaus till day 50, and then again increases until the end of the experiment. However, it is interesting to observe, the subsequent increase in Na^+ over time with a minor drop on the 4th day. This suggests the high dissolution of the primary Na-rich matrix, and its release is more than double of Si. The HCO_3^- concentration also increases by an order of magnitude from its initial concentration. The pH increases from 4 to 4.4.

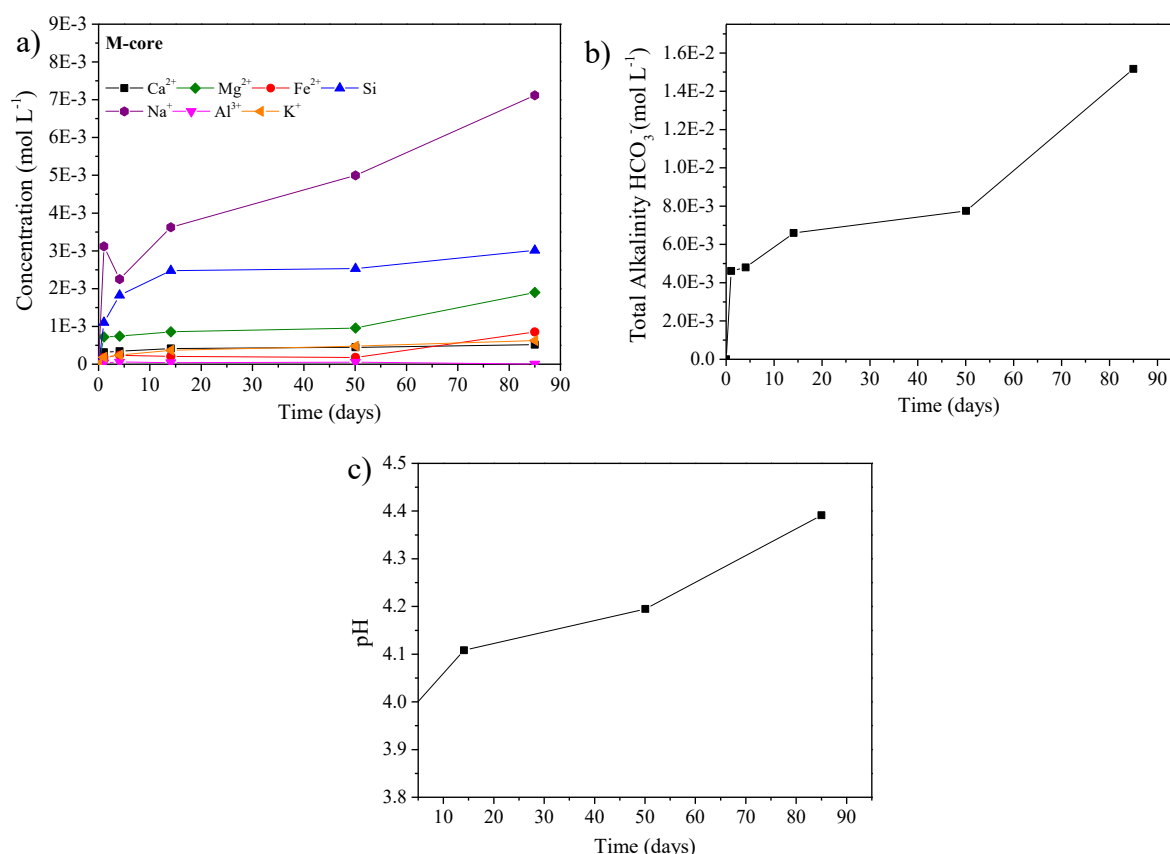


Figure 4.6: Fluid chemistry of the core experiment (a) Major cation concentrations in the fluid, (b) total alkalinity, and (c) calculated pH of the fluid over a period of 86 days

4.3.2 State of mineral saturation

The final outlet fluid concentration was used to compute the mineral saturation index for experiments B1, B2, and M-core. The state of mineral saturation of the primary minerals and secondary minerals at the end of the experiments (7 days) of both the baseline experiments (B-1 and B-2) with different rock:water ratio is compared in Fig. 4.7, and is grouped into (a) primary minerals, (b) secondary carbonate minerals (c) zeolites, and (d) clays minerals, and different form of SiO₂.

The mineral saturation state is very similar in both baseline experiments B-1 and B-2. Among the group of primary minerals, forsterite (olivine) is the most unsaturated mineral, while Na-rich matrix (thermodynamic data taken for K-feldspar) is close to saturation. Siderite (FeCO₃) is the closest to the saturation, followed by magnesite (MgCO₃) and Mg-Fe-Ca carbonate solid solution (ankerite).

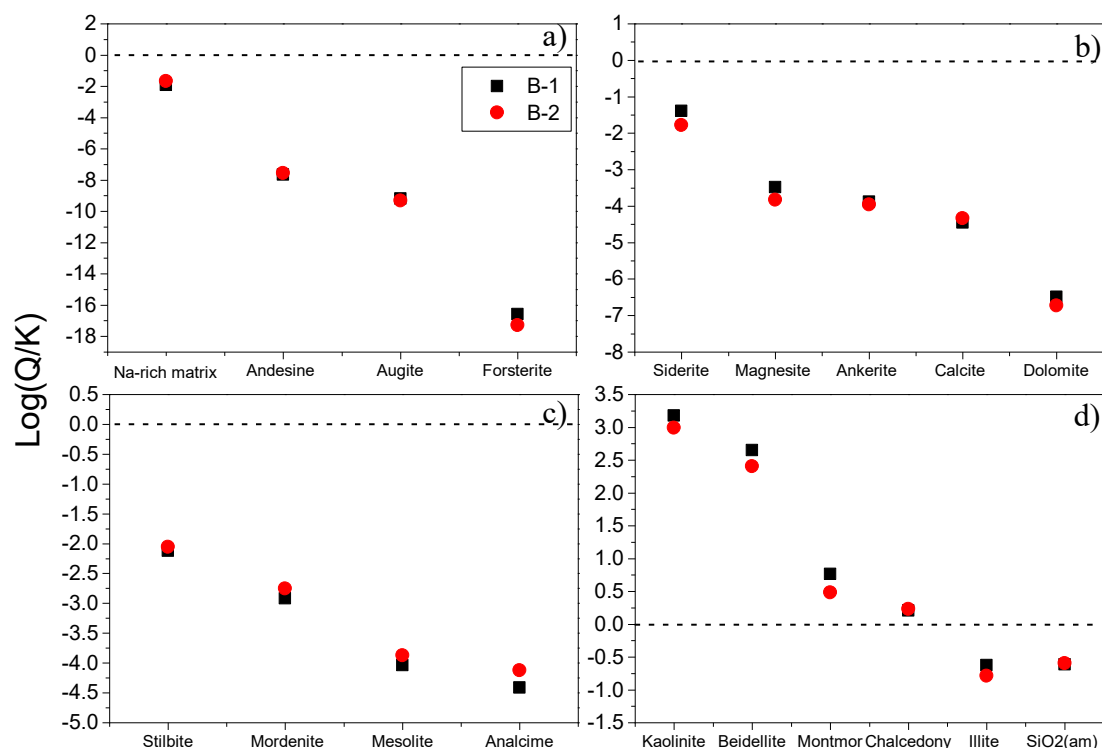


Figure 4.7: Primary and secondary mineral saturation state from GWB calculation of sample speciation at the end of the baseline experiments B-1 and B-2 (a) Primary minerals, (b) carbonate minerals, (c) zeolites, and (d) clay minerals and SiO₂ minerals

Among the group of zeolites, stilbite is closest to saturation followed closely by mordenite. However, several clay minerals such as kaolinite, beidellite, montmorillonite and chalcedony (SiO₂) are already supersaturated at the end of the experiment. The experiments performed with different rock:water ratios show the similar state of mineral saturation, with clay minerals being supersaturated, and carbonate minerals zeolites, and primary minerals being undersaturated. The state of saturation follows the following order: clays > carbonate minerals > zeolites > primary minerals. However, the saturation of siderite, magnesite, and dolomite (carbonate minerals) and of kaolinite, beidellite, montmorillonite, and illite (clays) are relatively higher in experiment B-1 with the lower rock:water ratio. This trend suggests the possibility of concurrent mineral precipitation at higher rock:water ratio (B-2).

Experiment M-core had a rock:water ratio of 0.15 which is 10 times and 3.7 times higher compared to experiment B-1 and B-2 respectively. The undersaturated state of carbonate minerals under these two different rocks: water ratios of the baseline experiments suggest that the cation concentrations and the low pH were insufficient for the formation of carbonate

minerals over 7 days. Therefore, the higher rock surface area should lead to an earlier time when carbonate minerals became supersaturated.

The state of mineral saturation of the main core (M-core) experiment was calculated stepwise over time until the end of the experiment and results are shown in Fig.4.8

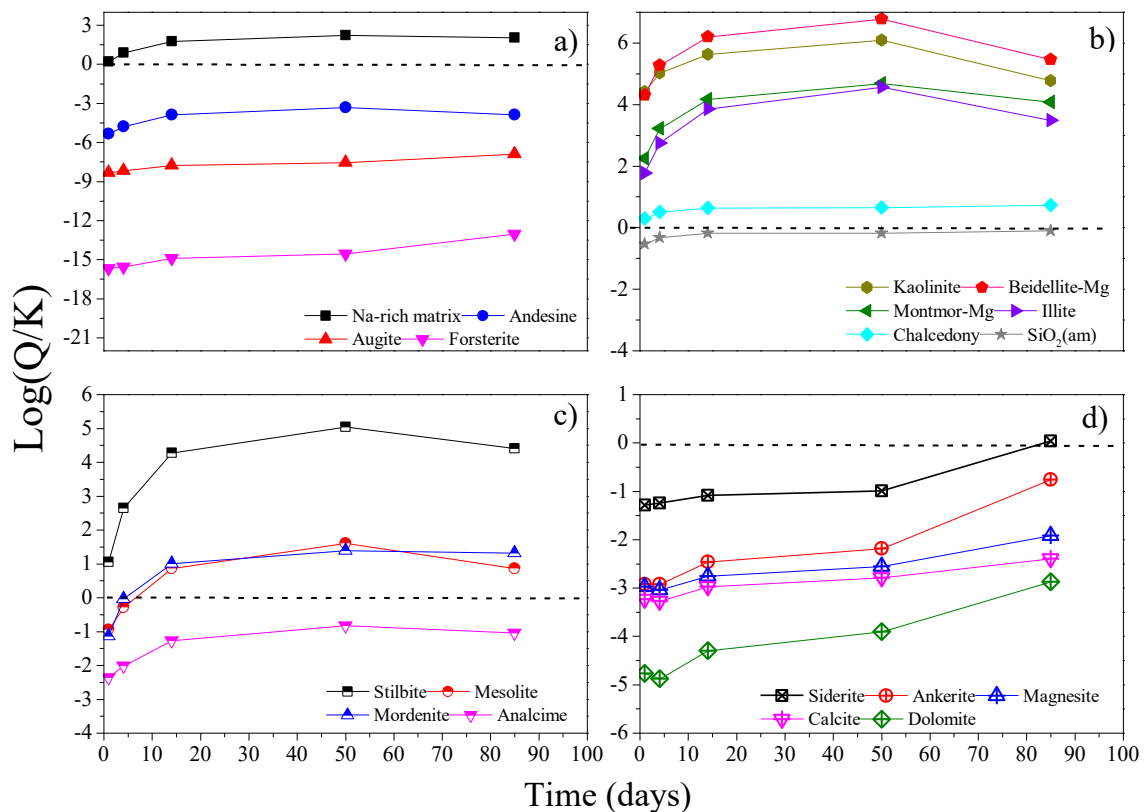


Figure 4.8: Primary and secondary mineral saturation state from GWB calculations at the end of the main diffusion experiment (M-core) (a) primary minerals (b) clay minerals and SiO₂ minerals (c) zeolites, and (d) carbonate minerals

A similar pattern in the state of mineral saturation was observed as in the baseline experiments. However, the Na-rich matrix (a primary mineral), stilbite (a zeolite) and representative clay minerals (smectites) were supersaturated from the beginning to the end of the experiment. Additionally, zeolites such as mesolite and mordenite showed supersaturation after day 4. All the carbonate minerals show a similar trend, but remain undersaturated throughout the experiment, only siderite was in equilibrium at the end of the experiment.

However, the state of saturation of zeolites increased much more over the first 15 days in the M-core experiment compared to carbonate minerals (Fig. 4.8c and 4.8d). This can only be

explained by the precipitation of carbonate minerals, whereas the saturated zeolites are still approaching precipitation. The state of saturation of the highly supersaturated clay minerals, and zeolites showed a declining trend towards the end. The amorphous SiO_2 is in equilibrium throughout the experiment. The saturation index of kaolinite was higher than beideillite in the baseline experiments, but in the main core experiment, the state of saturation of beideillite was higher than kaolinite. This could be due to the higher precipitation rate of kaolinite compared to beideillite. The saturation state of amorphous SiO_2 also could reflect concurrent precipitation. Previous studies observed formation of amorphous SiO_2 (Gysi and Stefánsson 2012a, Menefee et al. 2018).

4.3.3 X-ray micro-CT results

The CT-image of the connected pore network (CPN) of the pre-experimental core is presented in Fig. 4.9 which includes the groves and adjacent connected pores in the grooved and the un-grooved half cores.

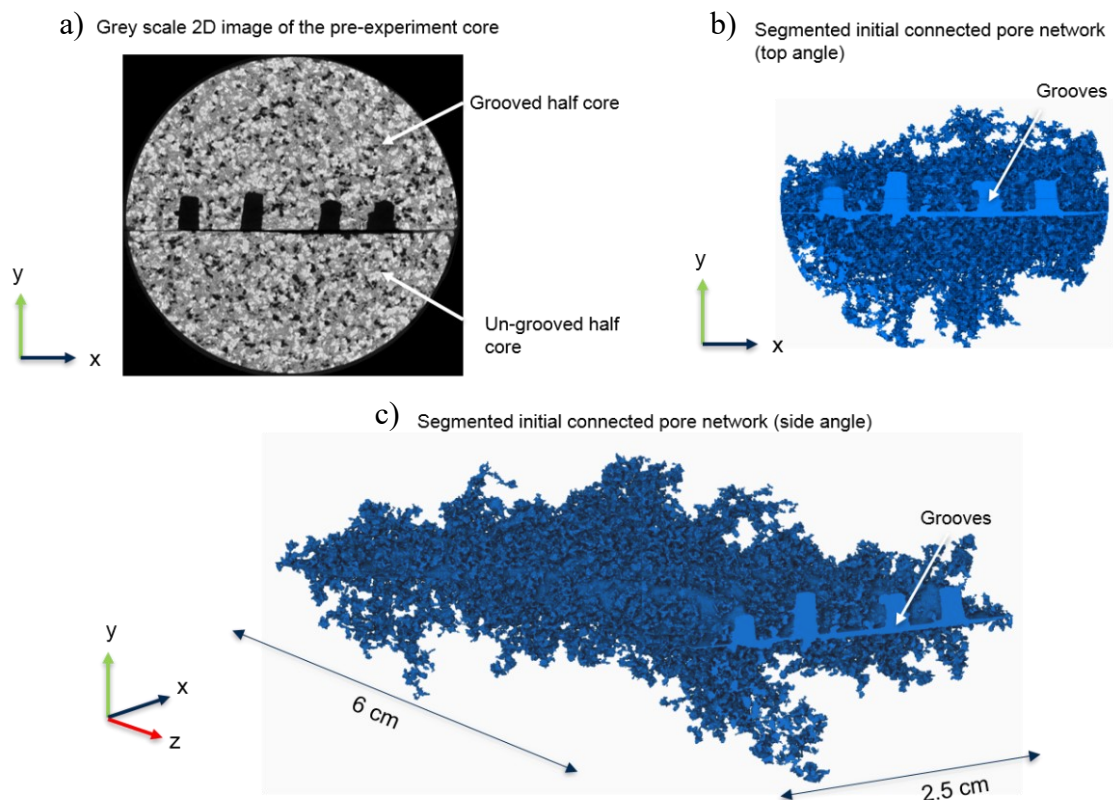


Figure 4.9: CT images of the pre-experimental assembled core with a length of 6 cm (a) grey scale 2D image of the artificially fractured core (b) segmented initial connected pore network from top angle, (c) segmented initial connected pore network from an side angle

As mentioned earlier, due to registration issues, the grooved and the un-grooved halves (Fig. 4.10) were analysed separately, description of both can be seen in the following sections.

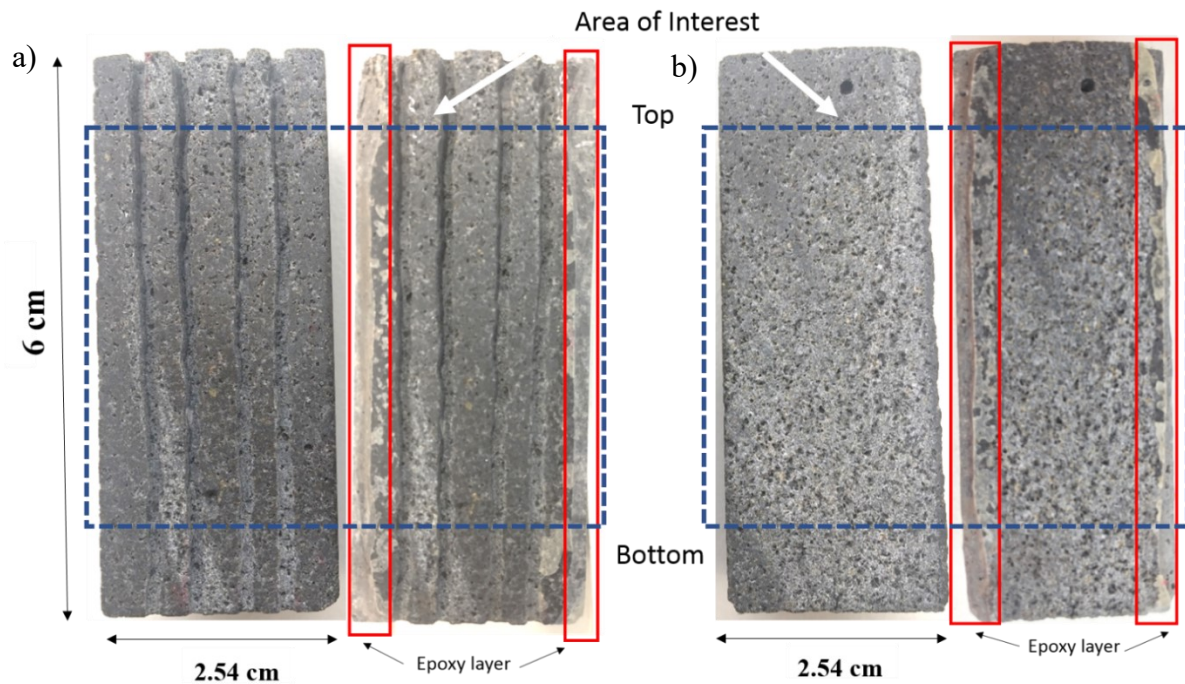


Figure 4.10: Comparison of the pre- and post- experimental grooved and un-grooved half cores

4.3.3.1 Physical changes

It should be noted that the CT results are the analysis on the mid-section (4 cm) of the core, which is the interval from 1.5 cm to 5.5 cm from the top. The actual core size is 6 cm, and a part of the inlet and outlet had to be ignored as it was fractured during the experiment. The grooved and the un-grooved half cores were analysed individually. The pre- and post-CT scan data were used to separately determine the porosity, grain volume, and surface area of the grooved and the un-grooved half cores. The pre- and post-experimental porosity of both the half cores are presented with respect to distance from the inlet (core top) (Fig.4.10). The initial porosity in slices perpendicular to the length of the core ranges from 11% to 15.5 % in the grooved core and 7.5 % to 11.5 % in the un-grooved core. The porosity in the grooved half core shows a decreasing trend due to the uneven depth in the grooves which is deeper at the inlet (core top) compared to the outlet (core bottom). This uneven depth resulted from manual drilling. The porosity range is higher in the grooved core due to the inclusion of the grooves in the porosity. In the post-experimental half cores, porosity per slice in average decreased by 0.5

% and 1 % in the grooved and the un-grooved half cores respectively (Fig. 4.11a and Fig.4.11b).

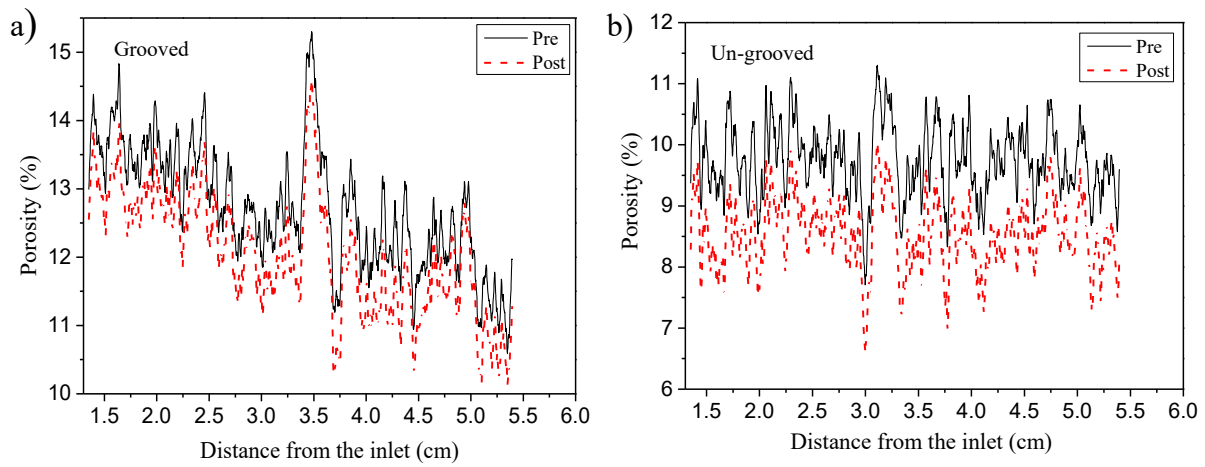


Figure 4.11: Porosity percentage of the pre- and post-experimental half cores CT images

Fig. 4.12a. presents the net change in total grain volume of the grooved and un-grooved half cores. The net total grain volume in the grooved half core increased by 0.7 %, i.e. from an initial value of 8874.9 mm³ to 8941.9 mm³. The grain volume in the un-grooved half core increases by 1.3 %, i.e. from 6909.71 mm³ to 7001.9 mm³. The increase in the net grain volume clearly suggests net precipitation, which is in agreement with described decrease in porosity. The change in total surface area is shown in Fig. 4.12b. The total surface area of the grains in the grooved half core decreased from 24361.1 mm² to 23167.7 mm², a reduction of 4.89 %. The change in grain surface area in the un-grooved half core is more significant than the grooved half core. A reduction by 10.6 % from 20015.3 mm² to 17878.2 mm² was observed.

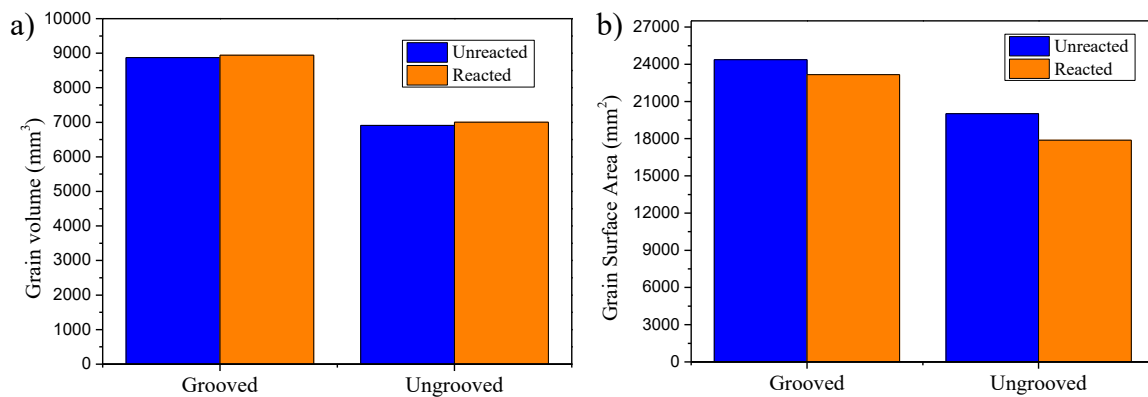


Figure 4.12: (a) Total grain volume and (b) surface area in the grooved and un-grooved half cores

As the two half cores are considered as one entity (a fractured core) in the study, thereby the net total surface area reduces by 7.7 %, and the net grain volume increases by 0.8 %.

4.3.3.2 Mineral quantification and net precipitation

The volumes of dissolved and precipitated minerals were quantified by using AND ($\wedge$) arithmetic operator. A slice in the x-y direction, 2.1 cm from the top of the core is extracted and used for an explicit demonstration of how the AND operator was used to quantify the dissolution and precipitation during the experiment. Fig. 4.13 and Fig. 4.14 shows combination of pre-and post-experimental 2D images to quantify the dissolved and precipitated volumes and the respective workflow is described below.

When the images of rock unreacted (Fig.4.13a) and the image of pores reacted (Fig.4.13b) are processed using the “AND” operator, it generates a new image. This new image (Fig. 4.13c) shows the pixels of the grain in the pre-experimental image that have dissolved and became pore volume in the post-experimental image.

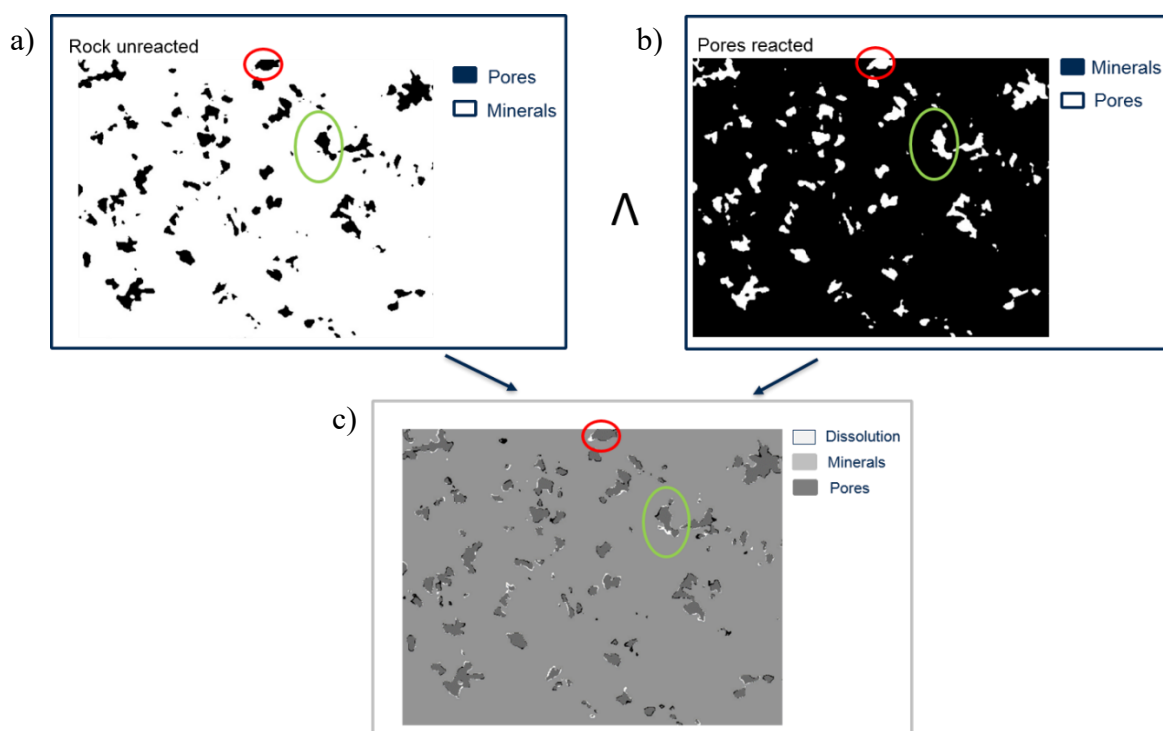


Figure 4.13: 2D images showing use of quantification method of dissolved and precipitated volumes using AND arithmetic operator (a) rock unreacted (b) pores reacted (c) New generated image after using AND operator. Bright white spots are dissolved minerals. The encircled pore points out the mineral dissolved during the experiment.

The pores in the unreacted rock sample image (Fig. 4.13a) encircled in red and green increased in size when compared to the pores in the reacted rock sample image (Fig.4.13b) due to mineral dissolution. The bright white spots in Fig.4.13c are the result of mineral dissolution.

Similarly, when the image of pores unreacted (Fig. 4.14a) and the image of rock reacted (Fig.4.14b) is processed using the “AND” operator, it generates a new image. This new image (Fig. 4.14c), shows the additional pixels of the pores of the pre-experimental image which are filled by rock due to mineral precipitation in the post-experimental image. The circle in red in the unreacted rock sample image shows pores which became two different pores in the reacted rock sample image by mineral precipitation, the pores encircled in yellow is also getting reduced in size, and the pores in green is almost clogged in the reacted rock sample image. These additional voxels in 3D image are quantified as precipitation volume. The bright white spots in Fig.4.14c are the result of mineral precipitation.

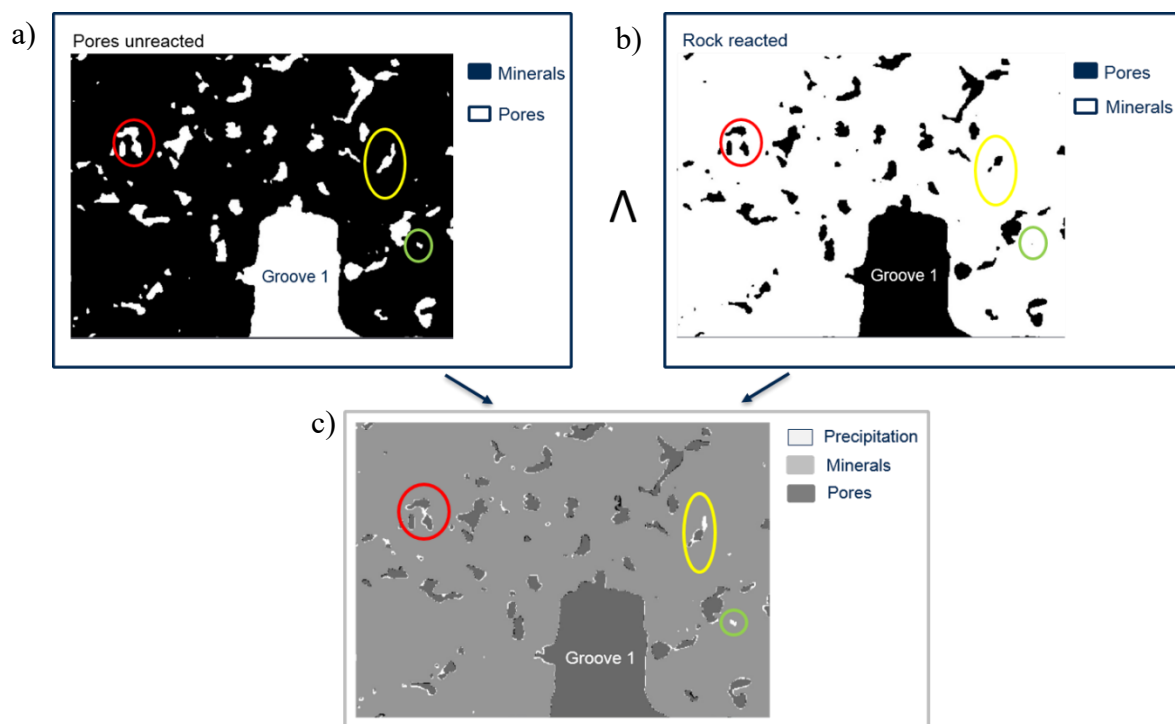


Figure 4.14: 2D images showing the use of quantification methods to determine dissolved and precipitated volumes using the AND arithmetic operator (a) pores unreacted (b) rock reacted (c) generated image after combining the pore unreacted image and rock reacted image. Bright white spots are mineral precipitation. The pores encircled in red in the pore unreacted image are filled with rock in the rock reacted image due to mineral precipitation

As mentioned before, the grooved and un-grooved parts of the core are analysed separately. The CT data was used to create 3D-segmentation of the pre- and post-experimental half cores.

Fig. 4.15 shows the greyscale image of the initial grains, segmented initial pores, and dissolved and precipitated minerals of the grooved half core. The grains (minerals) and the pores are represented by different greyscale values. The high-density grains attenuate more X-rays and appear brighter on the greyscale histogram.

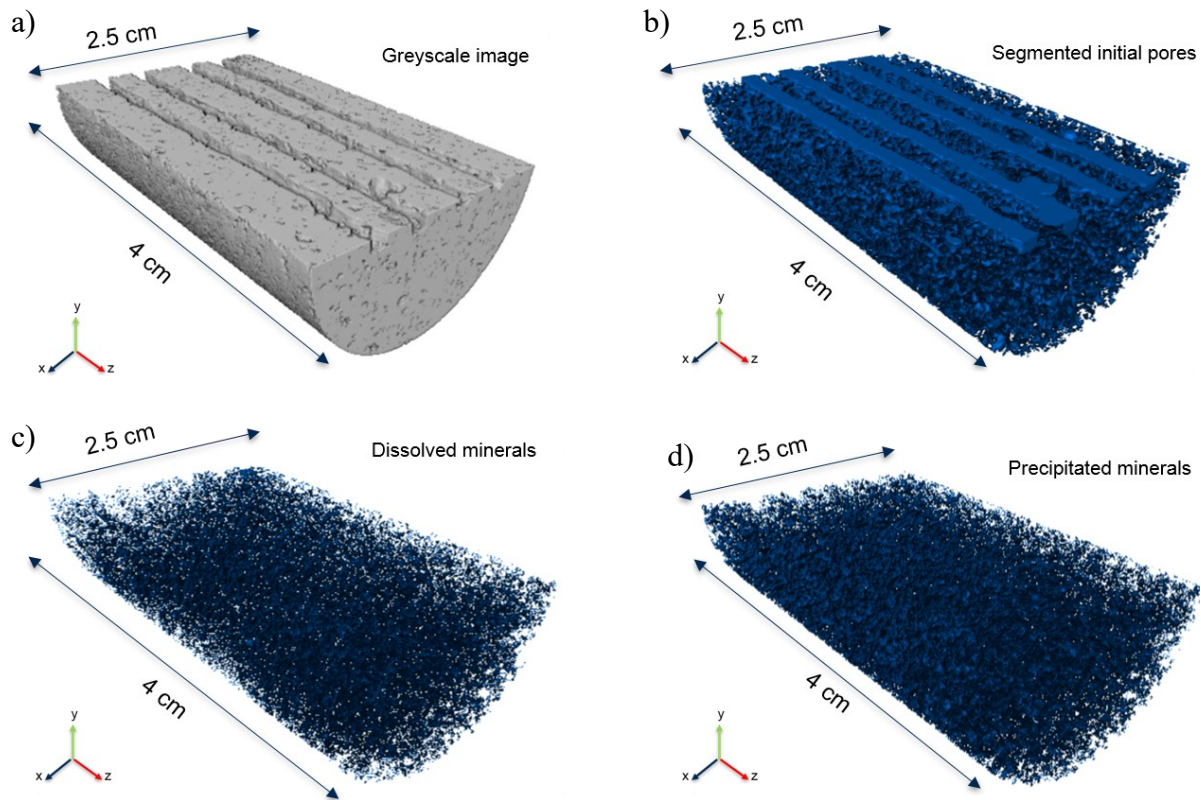


Figure 4.15: CT images of the grooved half core (a) initial greyscale image of the grooved half core, (b) segmented initial pores (c) dissolved minerals and (d) precipitated minerals; Images (c) and (d) were derived using the AND arithmetic operator algorithm (section 4.4.2)

The total volume of primary mineral dissolution and secondary mineral precipitation in the half cores were quantified separately using the AND arithmetic operator between the unreacted and reacted minerals and pores, as shown in the flowchart in Fig. 4.4 (section 4.2.4.2). A volume of 137.16 mm^3 of secondary minerals formed within the initial unreacted pore volume of 1295 mm^3 , whereas a volume of 74.7 mm^3 of the initial primary minerals were dissolved in the grooved half core. A volume of 20.58 mm^3 and 100.67 mm^3 minerals dissolved and precipitated in the un-grooved half core respectively. Thereby, the total volume of mineral dissolution and precipitation in the whole core is 95.28 mm^3 and 237.83 mm^3 respectively. The net precipitation is 142.55 mm^3 which is about ≈ 1.5 times higher than the volume of dissolved minerals. Fig.

4.15c and 4.15d show the segmented 3D image of the dissolved grains and the precipitated minerals, respectively, after the experiment. The initial grains are dissolved, and secondary minerals formed in the initial pores due to fluid-rock interaction.

4.3.3.3 Dynamics of connected pore network (CPN)

The 3-D pore axis connectivity was segmented out from the grooved half core and analysed separately. The initial CPN volume is 40 % of the total porosity (CPN volume + isolated pore volume) which is 518.10 mm^3 . A net reduction of 4 mm^3 of the CPN volume was observed in the post-experimental core which is $< 1 \%$ of the initial CPN volume, suggesting minor blockage of pores by mineral precipitation. In addition, the dimensions of the CPN changed, and a new structure was observed in the post-experiment sample which is presented in Fig. 4.16. For example, the pore clusters connected to the mid-section of the 1st groove (encircled in red in Fig. 4.16), no longer existed in the reacted CPN. However, a new pore cluster was observed connected to the 4th groove (encircled in green) in the reacted core.

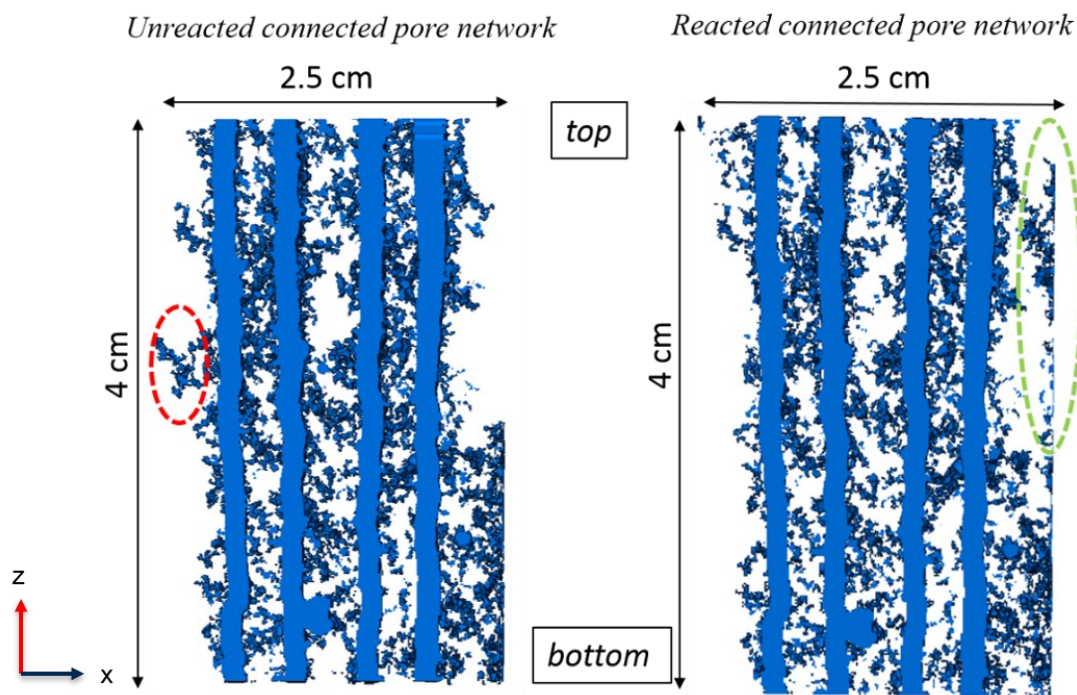


Figure 4.16: Connected pore network structure in the pre- and post-experimental grooved half core. The red dashed circle in the unreacted CPN is the old pore connection; while the green dashed circle in the reacted CPN is the new pore connection.

Callow and colleagues (2018) suggest connected porosity is a significant parameter to calculate CO_2 reservoir storage capacity, as isolated pores do not allow permeation of CO_2 -saturated

fluid and hence should be ignored with regards to CO₂ storage. However, our study shows that connected porosity changes during the reaction process. The impact of fluid-rock interaction on the CPN is very dynamic. New fluid pathways are opened due to the grain dissolution, and the neighbouring isolated pores or pore clusters are connected to the primary pore network. Simultaneously, initial pores were blocked from mineral precipitation, thus isolating them from the primary CPN. The volume of isolated pores or clusters in the grooved half core reduced by 8 % during the experiment.

One expects pores throats to become more modified than pores during dissolution and precipitation as they have a smaller diameter than pores. The images in pre- and post-experimental connected pore network were superimposed to identify the spatial location of the newly opened and blocked path. The total volume of the new pore and the old blocked pore connections were calculated. To estimate the volume of newly opened pathways, the reacted connected pore network was subtracted from unreacted connected pore network and vice versa for blocked pathways. Fig. 4.17. shows the total opened and blocked pathways.

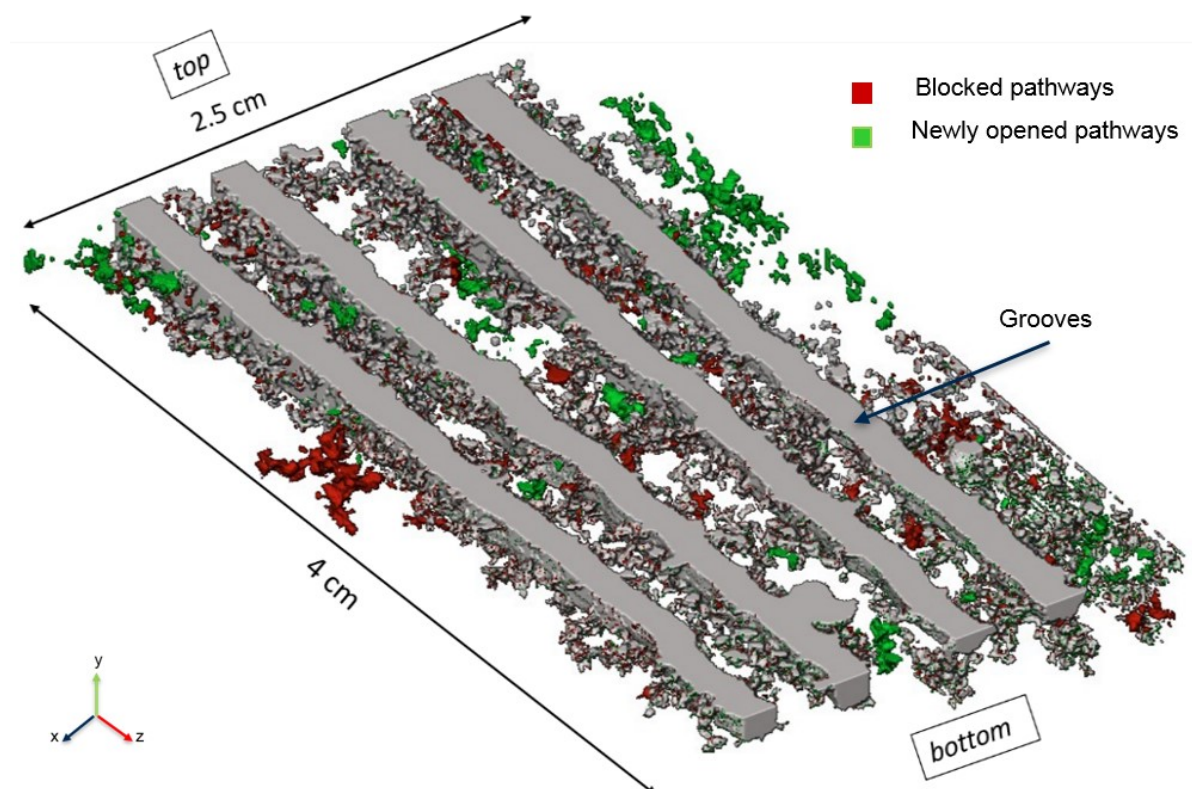


Figure 4.17: Change in total connected pore network. The red patches are the pores or pore clusters blocked due to mineral precipitation; while the green patches are the new pore connections opened after grain dissolution

The volume of connected pore network, which opened is 13.4 mm^3 and the volume of blocked or disconnected pore volume is 17.8 mm^3 after the experimental duration.

4.3.3.4 Pore-network model (PNM) of the un-grooved half core

The pore network model was generated for the pre- and post-experimental un-grooved half core to calculate the net change in the total number of pores and pore throats. Fig.4.18a and 4.18b shows the greyscale image of the unreacted un-grooved half core and the segmented total pores, respectively. Fig. 4.18c show the separated and voxelised pores where different colours represent individual pores.

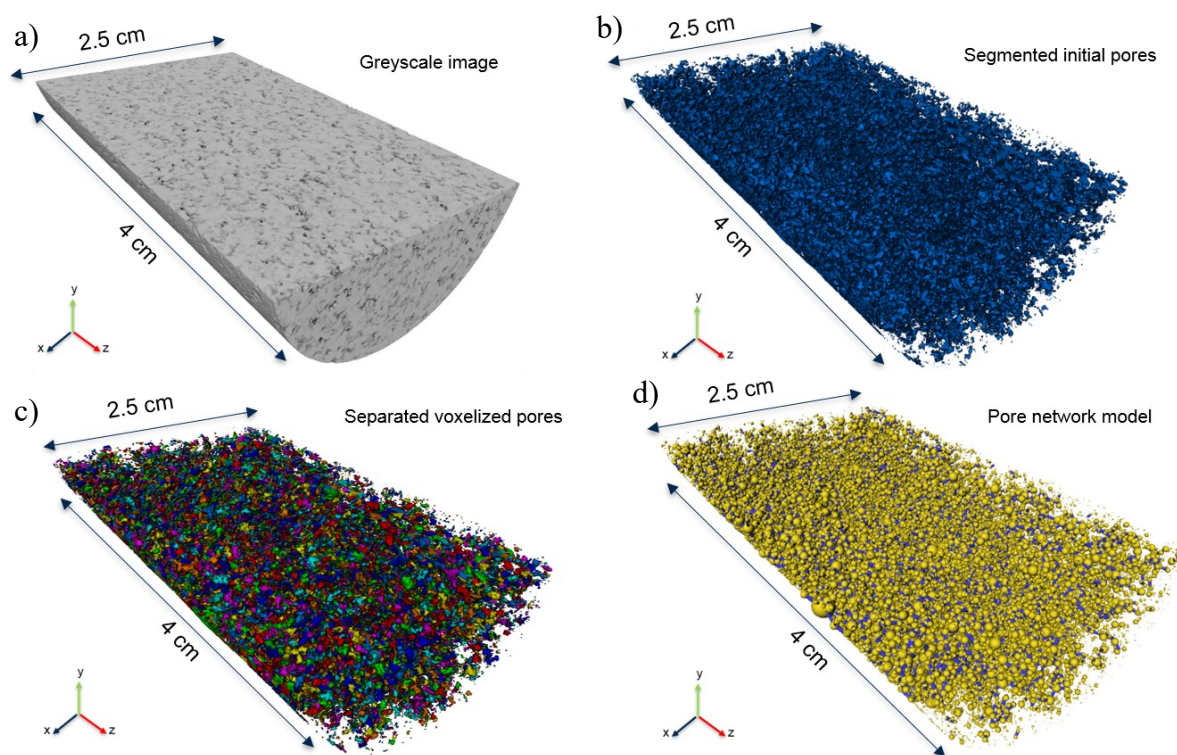


Figure 4.18: Framework to define pore network model of pores and throats of the un-grooved core (a) initial grey scale image of the un-grooved half core (b) initial total pores (c) pore separation of connected pore space (d) the pore network model distinguishing of the pores (yellow) and throats (blue).

These are the steps (Fig. 4.18a, b, and c) to generate the pore network model, which is represented in Fig. 4.18d, showing the pores and the pore throats. Similarly, the PNM was generated for the post-experiment un-grooved half core. In total, there was a reduction of 12090 pores and 506 throats, which is 15 % of the initial pores and 4.4 % of the initial throats, respectively.

Moreover, the PNM also calculated the number of isolated pores that are not connected by any throats. A significant reduction of 15 % was observed in the isolated pores in the post-reacted un-grooved half core. It is interesting to observe the reduction in isolated pores particularly at a greater distance from the grooves, as one expects no fluid-rock interaction at such a secluded and distant pore location. Xiong and colleagues (2018) also observed carbonate minerals in the pore space detached from the main fracture. The PNM was not generated for the grooved half core as it is the same sample, and the pore and the throat size are expected to be similar.

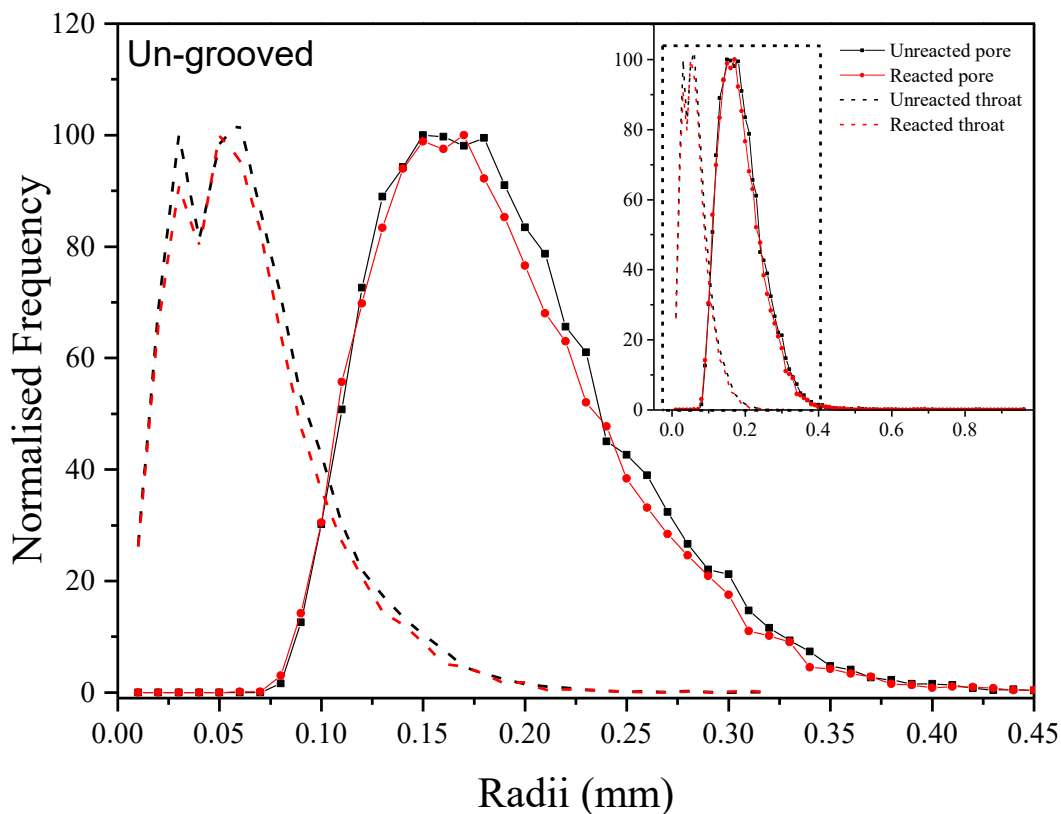


Figure 4.19: Normalised frequency distribution of equivalent radii of pores and throats of the unreacted and reacted un-grooved half core sample

Fig. 4.19 shows a frequency distribution plot of pore radii and throat radii in the pre- and post-experimental un-grooved cores. The data from the pore network model was placed in equally spaced bins representing the pore and the throat sizes, and the normalised frequency distribution was calculated. The frequency shows an initial increasing trend, and after attaining a peak, it gradually declines with an increase in the pore and throat size. The throat radii were observed to be < 0.33 mm and pores radii < 1 mm. Negligible variation were observed between the pre- and post-experimental pores with radii > 0.42 mm. Therefore, interpretation of the result is focused on the pore and throat radii < 0.42 mm. It is observed that the pores and the

throat have the highest frequency in size range of 0.15-0.17 mm and 0.03-0.05 mm respectively. A distinct change in the frequency of the pore and throat size is not observed. However, the frequency of pore sizes in the range of 0.02 mm-0.35 mm decreased (5 % - 8 %) after the experiment. A double peak with the maxima of the two at 0.03 mm and 0.06 mm is observed in the frequency of pore throats. The frequency decreased by an average of 9 % and 7 % in the post-experimental sample, suggesting a reduction in throat size due to mineral precipitation. Overall, the abundance of throats and pores is smaller in the reacted un-grooved half core.

4.3.4 Carbonate mineral formation

The surfaces of the grooves were analysed under an optical microscope to observe textural and mineralogical changes in the surface. The post-experimental grooves appear to be weathered with brownish crystal edges suggesting mineral precipitation (Fig. 4.20).

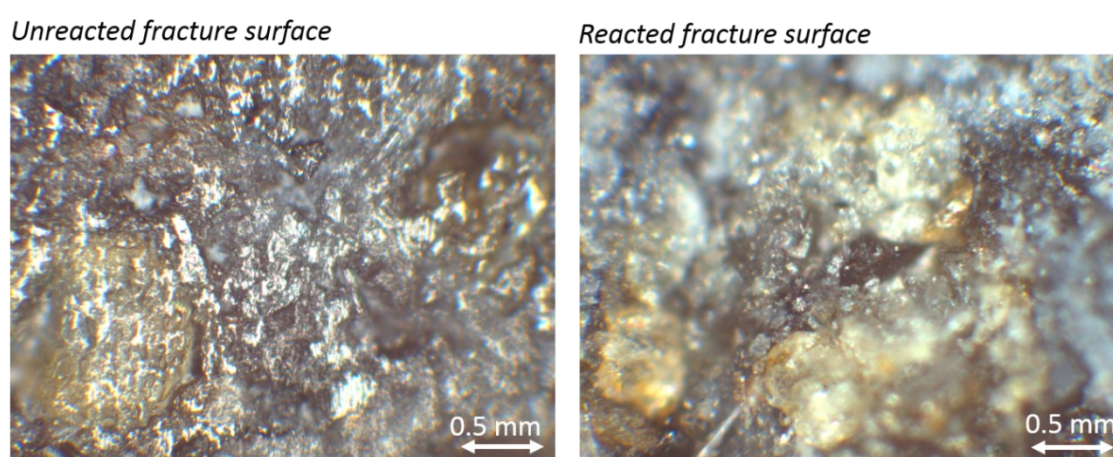


Figure 4.20: Optical microscopic image of the unreacted and reacted surface of the third groove

However, the nature of the secondary mineral precipitation could not be determined purely based on the optical microscopy. The groove with the most weathered appearance was selected for SEM-EDX analysis to understand the nature of the precipitated mineral.

SEM-EDX analysis was performed on the surface of the third groove, where a high carbon peak indicated the formation of carbonate mineral (Fig. 4.21). The Ca, Mg and Fe peaks showed similar intensity which indicates the formation of a Ca-Mg-Fe carbonate solid solution.

Moreover, Si, Al, and K peaks were also detected and suggested the formation of kaolinite or some other clay minerals (Fig. 4.21a).

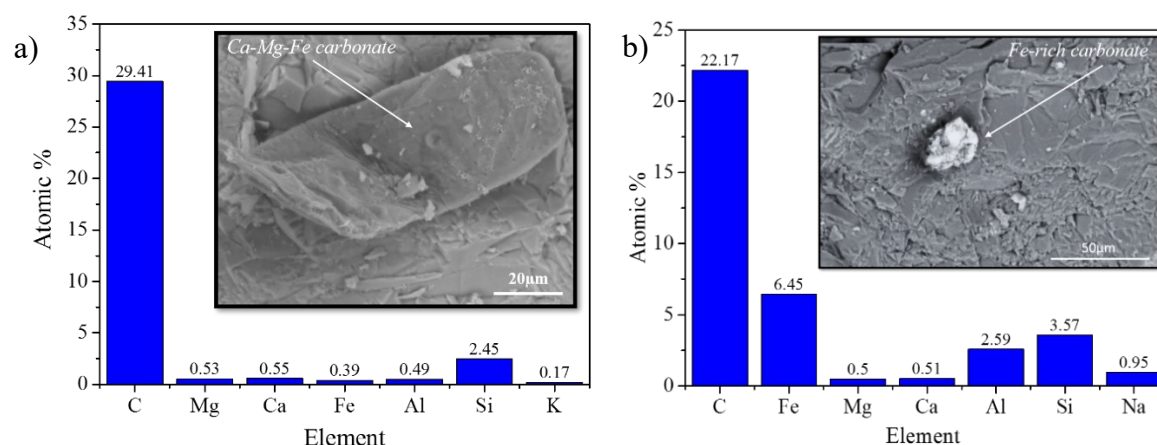


Figure 4.21: Semi-quantitative chemical composition and SEM image of secondary mineral phases depicting the formation of localized mixed carbonate minerals in the grooves.

The concentration of Fe in Fig. 4.21b is higher than the Mg and Ca concentrations and has a brighter intensity suggesting the presence of a higher amount of a heavy metal like Fe and, hence it could be interpreted as Fe-rich carbonate mineral with minor incorporation of Ca and Mg. It also has comparatively high amount of Na, Si, and Al, which could suggest the formation of Na-rich zeolite.

4.4 Discussion

4.4.1 Changes in water composition

Baseline experiment B-2 with a higher rock surface compared to B-1 showed relative low concentrations of Mg^{2+} and Fe^{2+} in the fluid at the end of 7 days. This could be explained by the precipitation of Mg- and Fe-rich phases. The three possible reasons for the low concentrations of these cations are: (1) Mg and Fe reacts with HCO_3^- and forms carbonate minerals or precursors of carbonate minerals; (2) Mg and Fe reacts with Si to form secondary silicates minerals like smectites and zeolites; and (3) Fe reacts with residual O_2 to form Fe-oxides. The Na concentrations in the B-2 experiment and M-core experiment are generally high and even exceed the Si concentration at times. The release of Na^+ is presumably from the dissolution of Na-rich matrix. Xiong and colleagues (2018) observed a higher release rate of Na compared to Si and suggested incongruent dissolution as a cause where proportionally more

Na than Si was released from the Na-matrix. In their experiment, the Na concentration was ≈ 0.05 mmol/L while Si only reached a concentration of 0.003 mmol/L after 6 weeks. Alternatively, if incongruent dissolution prevails preferential precipitation of Si over Na^+ , could lower the Si concentration in the fluid. The low Si, Mg, and Fe concentrations in the B-2 experiment suggests precipitation of Mg-Fe silicates. Si is usually rapidly incorporated into Si-rich secondary phases, forming a layer on top of the primary mineral (Sissmann et al. 2014, Hellevang et al. 2017, Menefee et al. 2018, Wolff-Boenisch and Galeczka 2018). The mineral saturation states are calculated based on the ionic concentrations in the fluid. Experiment B-2 shows a slightly lower saturation state for most of the considered minerals compared to B-1. It is likely that the cations in B-2 are instantaneously incorporated into secondary phases such as kaolinite and smectites, decreasing their dissolved concentrations in the fluid.

Siderite is the only carbonate mineral showing moderate supersaturation in the M-core experiment, followed by ankerite. However, a Ca-Mg-Fe carbonate mineral was observed in the groove after 85 days of reaction time. This suggests preferable precipitation of solid-solution carbonate minerals instead of pure carbonate minerals. This observation is consistent with previous studies where the presence of sufficient amounts of olivine (Mg-FeSiO_2) as a primary mineral lead to precipitation of siderite or Mg-Fe-Ca mixed carbonate minerals (Gudbrandsson et al. 2011, Sissmann et al. 2014, Kanakiya et al. 2017, Xiong et al. 2017). In the absence of olivine, the formation of Ca-carbonates or mixed Ca-Mg carbonate minerals is preferred (Kumar et al. 2017, Menefee et al. 2018). It has been shown that the precipitation of Fe-carbonate mineral is dominant at low pH (< 5) due to the faster dissolution of olivine, and the incorporation of Mg and Ca into secondary carbonate minerals at a later stage, when near neutral pH conditions were reached (Snæbjörnsdóttir et al. 2018).

4.4.2 Net precipitation and physical changes

The micro-CT analysis provided detailed information on the physical changes in the pre- and post- experimental fractured core. Porosity decreased by 0.5 % and 1 % in the grooved and un-grooved half cores, respectively. A net reduction in porosity and the total grain surface area with a net increase in total grain volume suggested mineral precipitation in both the grooved and un-grooved half cores. The total volume of secondary mineral precipitation is $\approx$ about 1.5 times higher than the primary mineral dissolution in the reacted core. Dissolved and

precipitated mineral volumes were higher in the grooved half core compared to the un-grooved half core. The presence of grooves increases the connected porosity and the surface area for fluid-rock interaction, which enhanced the concurrent dissolution and precipitation of minerals in the fracture and the adjacent pores. It seems that the grain surface surrounding the pore was initially exposed to the cation-rich fluid, and over time due to local mineral saturation, precipitation occurs primarily within the pores. This process may have blocked the pores and initial surface area is no longer available causing a net decrease in surface area and a net increase in grain volume.

A net reduction of 66.18 mm^3 (5.1 %) in total pore volume due to mineral precipitation, was derived based on the difference between pre-and post-pore volume, which is similar to the net mineral precipitation of 62.42 mm^3 (4.8 %) calculated using the AND arithmetic operation in the grooved half core. However, the net reduction in the connected pore network (CPN) is only 0.7 %. The quantity of dissolved and precipitated minerals could not be applied in the CPN due to changes in its CPN structure in the post- reacted core and only connected and disconnected pore volume were estimated.

Previous studies observed a reduction of the fracture volume due to secondary mineral precipitation upon fluid-rock interaction (Singurindy and Berkowitz 2005, Huerta et al. 2012, Brunet et al. 2016, Jones and Detwiler 2016). Precipitation commences and is particularly prominent in transport-limited zones where fluid residence time is long enough to reach supersaturation of the fluid with respect to minerals (Oelkers et al. 2008). In a study by Menefee and colleagues (2018), fractures with small aperture ($<100 \text{ }\mu\text{m}$) involving mineral precipitation mostly occurred in the transport limited zones, and a reduction of 35 % and 48 % in fracture volume at 100°C and 150°C , respectively were observed. Xiong and colleagues (2017) observed 5.4 % and 15 % precipitates, filled in the fracture volume reacted at 100°C and 150°C after 40 weeks. A small annuli in cement with an aperture size $< 90 \text{ }\mu\text{m}$ is expected to seal in 30 minutes upon CO_2 -fluid interaction in constant pressure differential experiments (3 bar) and 22°C with flowrate of 0.006 mL/min (Brunet et al. 2016).

The pore network model of the un-grooved half core shows a significant reduction in the initial connected pore volume compared to the pore throats. This is evidence for preferential precipitation in pores and does not much affect the pore connectivity, i.e., pore throats.

However, an equal volume of isolated pore was reduced. The micro-CT analysis has its own limitations as it does not generate data below the scanned resolution of the voxel, which is $14.99\text{ }\mu\text{m}$. Grains and pores $< 14.99\text{ }\mu\text{m}$ might be impacted by the dissolution and precipitation process. The reduction of isolated pore volume could be due to the blockage of smaller pores or throats size by mineral precipitation. These undetectable small pores and throats could be physically connected to the isolated pores. This could mean isolated pores may be actually connected to the main CPN by pore or throat sizes $< 14.99\text{ }\mu\text{m}$ and were impacted by CO_2 -fluid reaction. Scan resolution also plays an important factor in this case.

The reduction in net pore volume by mineral precipitation in the un-grooved basalt half core further ensures its capacity to act as cap rock and contain CO_2 , ideally in a low fractured zone. Flow-through studies conducted on unfractured basalt core at 150°C , and 150 bars under advection-controlled conditions observed a net reduction of 0.7 % to 0.8 % micro-CT porosity, analysed at a resolution of $25\text{ }\mu\text{m}$ (Luhmann et al. 2017).

The extent of mineral precipitation was dominant in the associated pores of the grooves. As the core was initially not saturated with water, the adjacent pores to the grooves were filled with air. The wetting fluid in the form of CO_2 -saturated water invaded the connected pores adjacent to the fracture by capillary force.

The presence of air in the pores could lead to other scenarios: (a) The air inside the pores might have been pushed away by the acidic fluid which might have escaped through new paths after grain dissolution (b) the air is trapped in the pore pressed by fluid and as there were no escape route for the air, then it could have created microfracture in the rock to break away. Microfractures were observed on the outer edges of the post-experimental sample which led to analysis of only the mid-section of the core.

4.4.3 Impact of isolated pores on connected pore network

Fluid-rock interaction impacted the effective porosity of the massive basalt under diffusion transport reactions. A fraction of CPN was blocked due to mineral precipitation, and new pathways were opened after mineral dissolution and isolated pore volume were connected. This could also lead to a change in direction of fluid migration in the subsurface. A net reduction of

the isolated pores of 62.16 mm^3 in the grooved half core due to coupled mineral dissolution and precipitation was estimated. The reduction of isolated pores could also mean that they are now connected to main pore network and are no longer isolated. In that case, an increase in volume in the CPN should be observed. However, a minor net reduction of 0.7 % CPN volume was calculated suggesting a similar volume of the initial CPN became disconnected through precipitation.

Fractures increase the connected porosity of the rock, and it is considered to increase the CO_2 storage capacity of the reservoir (McGrail et al. 2006, Goldberg et al. 2008, Hellevang et al. 2017, Xiong et al. 2017). The understanding of the change in the structure of the connected porosity (CPN) is of utmost importance for safe storage of CO_2 . Isolated pores should not be ignored in the studies with fluid-rock interaction in an acidic to mildly acidic environment as grain dissolution changes the CPN. Underestimating the impact of isolated pore on the effective porosity, permeability, and direction of fluid migration could lead to incorrect assessment of CO_2 storage potential in a fractured basalt reservoir. The net but minor reduction of CPN in the reacted sample where diffusion-controlled transport prevailed depicts self-sealing behaviour of fractures and the associated pores by secondary mineral precipitation.

4.4.4 Capacity of CO_2 fixation into secondary carbonate minerals in the initial pore volumes

Based on the CT segmentation, the net reduction of pore volume due to precipitation is 158 mm^3 . Assuming the injected CO_2 is fixed as siderite (FeCO_3) in the initial pore volume (CPN volume + isolated volume), and given siderite has a density of 3.74 g/cm^3 and the mass of CO_2 in siderite is 38 wt. % ($1.67 \text{ g of CO}_2/\text{cm}^3$), a total of 0.233 g of CO_2 is fixed to form siderite and blocked 0.158 cm^3 of the pore volume. However, only $6.10^{-3} \text{ g of CO}_2$ combined with Fe to form siderite to reduce 0.004 cm^3 of net CPN volume. To block the whole fracture with initial CPN volume of 0.518 cm^3 , 0.8 g of CO_2 needs to be fixed, corresponding to a total of $3.40 \text{ g of carbonate mineral}$ needs to form in the initial total pore volume of 2.024 cm^3 . However, in Chapter 2, formation of clay and zeolites minerals were observed to be dominant. In this case, the fixing of CO_2 will be significantly reduced.

Previous studies reported enhanced carbonate mineral precipitation in diffusion-limited experiments (Xiong and Giammer 2014, Adeoye et al. 2017, Xiong et al. 2017, Xiong et al. 2017, Menefee et al. 2018, Xiong et al. 2018). Thereby, intermittent CO₂ injection, given adequate time gap between injections, into the permeable (vesicular) zone overlain by massive fractured basalt will allow high residence time for fluid-rock interaction. Longer residence time will lead to mineral supersaturation and lead to secondary mineral precipitation. The dead-end of the fractures in the basalt will be blocked by mineral formation as the buoyant CO₂ would migrate into the connected pores by capillary force.

4.5 Conclusion

A diffusion-controlled static experiment was performed on an artificially fractured basalt core with CO₂ saturated water at 60°C and 80 bars over 12 weeks. The impact of mineral dissolution and precipitation on the pore network geometry was assessed in order to constrain the processes and conditions potentially leading to self-sealing of fractures.

The fluid was enriched in cations, by packing basalt powder in diffuser bags leading to a high basalt dissolution rate outside of the core. The mineral speciation calculation of the cation concentration in the baseline experiments aided in estimating the rock:water ratio for the main experiment to reach supersaturation of the secondary minerals. Ca-Mg-Fe carbonate solid solution minerals were observed on the groove surface together with Si-Al rich phases. X-ray micro-CT analysis showed an increase in grain volume and a decrease in porosity. The total of 237.8 mm³ secondary minerals precipitated and 95.2 mm³ of primary minerals dissolved. A net precipitation of 142.6 mm³ was observed within a total rock volume of 17824 mm³ over 86 days. The structure of the connected pore network changed over time and reduced by 0.7 %. A volume of 13.4 mm³ newly fluid pathways opened after mineral dissolution and volume of 17.8 mm³ blocked by mineral precipitation. The impact of mineral precipitation was higher in the pores compared to the pore throats. Isolated pores have the potential to change the permeability of the host rock over time and should not be neglected while assessing the CO₂ storage potential of a reservoir. The net precipitation under diffusion limited transport conditions may contribute to containment of buoyant CO₂ by sealing the pore volume. The commencement of minor net reduction in the connected pore network under realistic CO₂ storage depth condition underpins

the potential of sealing fractures through precipitation. However, the enhanced sealing of the fractures will only be observed once the connected adjacent pores are clogged.

Chapter 5: Conclusions

5.1 Conclusions

The presented study provides a better understanding of the nature and extent of initial reactions between CO₂-rich water and fractured continental flood basalts. The information is based on experiments, high-resolution sample characterisation, and modeling. The findings help evaluating continental flood basalt deposits as potential CO₂ storage reservoirs by determining the type of minerals forming at an early stage of a CO₂ injection and storage operation by quantifying the dissolved and precipitated mineral volumes and respective changes in the pore network geometry.

The basalt rock sample used during the study was not previously characterized and assessed with regards to CO₂ storage. The chemical, mineralogical and petrophysical properties were determined for this research as this is crucial for understanding the geochemical reactions on interaction with CO₂-saturated water.

The release rate of elements from basalt due to the interaction with CO₂-saturated water provides information on the balance between dissolution and precipitation reactions. Experimental studies coupled with reaction path modeling (Chapter 3) reveals that at high P/T conditions, the dissolution rate of primary minerals such as olivine is high but the concurrent precipitation of secondary minerals is also high resulting in a more moderate net release rate of the elements. Secondary Si-Al-rich minerals predominantly form at low pH conditions (Chapter 2) and were found to precipitate on the surface of basalt fractures. Consequently, this mechanism could eventually lead to the self-sealing of fractures and contain buoyant CO₂ at depth > 800 m in the long-term. Concurrent mineral dissolution and precipitation in the pore network adjacent to a fracture was evident in an experiment where ionic transport was diffusion-controlled (Chapter 4). Overall, mineral precipitation exceeded dissolution.

The major findings of this thesis are as follows

- Olivine controls the overall dissolution rate of basalt at far-from-equilibrium conditions and which is in agreement with previous studies.

- Dissolution and precipitation occur concurrently. The release rate of mineral-forming elements such as Mg, Fe, and Si is lower at higher P/T conditions due to a high rate of mineral precipitation even in an acidic environment.
- Smectites, zeolites and siderite form at low pH conditions over shorter reaction time. These secondary minerals form coatings on the surface of primary minerals reducing the dissolution rate as referred to as surface passivation.
- A novel technique for quantifying the dissolved mineral and precipitated volume was achieved and concurrent dissolution and precipitation reactions are demonstrated.
- Precipitation exceeded dissolution under the given experimental conditions.
- Presence of fractures increase the connected pore network leading to more extensive mineral dissolution and precipitation.
- Coupled dissolution and precipitation processes change the structure of the connected pore network. However, net precipitation in the connected pore network is low leading to only a minor solid phase volume change.
- Both connected and isolated pores were more impacted by mineral precipitation compared to pore throats.

5.2 Limitations and future studies

Based on the results and analysis of this current thesis, experimental conditions can be varied in future to achieve complete sealing of the fractures. One limitation of this study was the short experimental time. Longer lasting experiments would lead to more extensive precipitation potentially demonstrating the self-sealing of fractures. The following objectives are recommended for further studies:

1. Higher precipitation could be achieved if seawater was used instead of deionised water. Seawater is rich in cations and has a pH buffer capacity. This will be an ideal case study for CO₂ injection near a coastal continental flood basalt reservoir, for example a potential CO₂ storage site in Deccan Trap Province in the vicinity to the Arabian Sea.
2. Secondary silicates (smectites and zeolites) and carbonate minerals compete for the same major cations (Ca²⁺, Mg²⁺, and Fe²⁺). Therefore, if carbonate mineral precipitation is desired then precipitation of SiO₂ minerals like amorphous silica, chalcedony should

also be favoured. In this way, the released Si will combine to form SiO_2 mineral making it deficient for secondary silicate formation and the cations will combine with CO_3^- and HCO_3^- to form carbonate minerals. Increasing the total alkalinity, pH, and HCO_3^- concentration of the reactive fluid may favour SiO_2 mineral and carbonate mineral precipitation.

3. The reaction path model can be improved by updating the current thermodynamic database to allow for carbonate mineral solid solutions containing Mg, Fe and Ca at variable ratios. Further tests on the effect of secondary (cross-affinity) mineral precipitation on dissolution rate of primary minerals can be performed in order to achieve a better agreement with volumes of minerals.
4. Pore-scale reactive transport modeling could be carried out to better understand concurrent mineral dissolution and precipitation and to estimate the time required to substantially reduce the connected pore network volume and the associated fracture by mineral precipitation.

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Appendix 1:

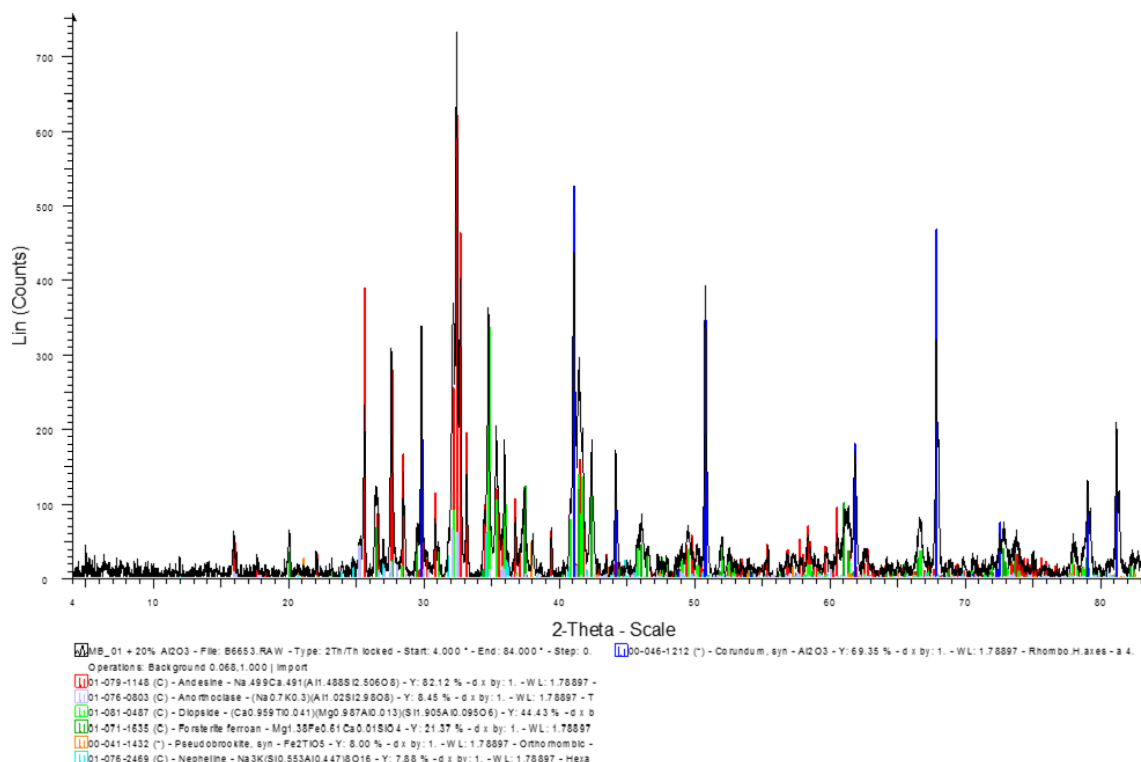


Figure A1.1: X-ray diffraction pattern of massive basalt of experimental powdered samples. The XRD pattern shows presence of andesine (plagioclase), anorthoclase (alkali feldspar), diopside (pyroxene), forsterite (olivine), and accessory minerals (nepheline and apatite)

Fig A1.1 shows X-ray diffraction patterns of massive basalt powdered samples. The X-ray intensity is recorded as counts which is represented by the vertical axis. The detector moves in circle around the sample and it records the number of X-rays observed at each angle 2θ , represented by horizontal axis. The intense peaks diffract X-ray efficiently such as andesine in the figure.

A semi-quantitative mineral composition was performed on unidentified mineral matrix inside a pore of a pre-reacted thin section of massive basalt. This was done to affirm the absence of basaltic glass. The chemical composition of the unidentified mineral matrix was compared with the composition of the edge of the glass slide of the thin section. The composition of the matrix inside the pore was similar to the composition of the glass slide. Additionally, the matrix was analysed under secondary images (SE), under this light, topography can be understood. The

matrix inside the pore was observed as an etched surface and its elevation was lower than the surrounding mineral grain surfaces suggesting the matrix is just the underlying glass slide of the thin section.

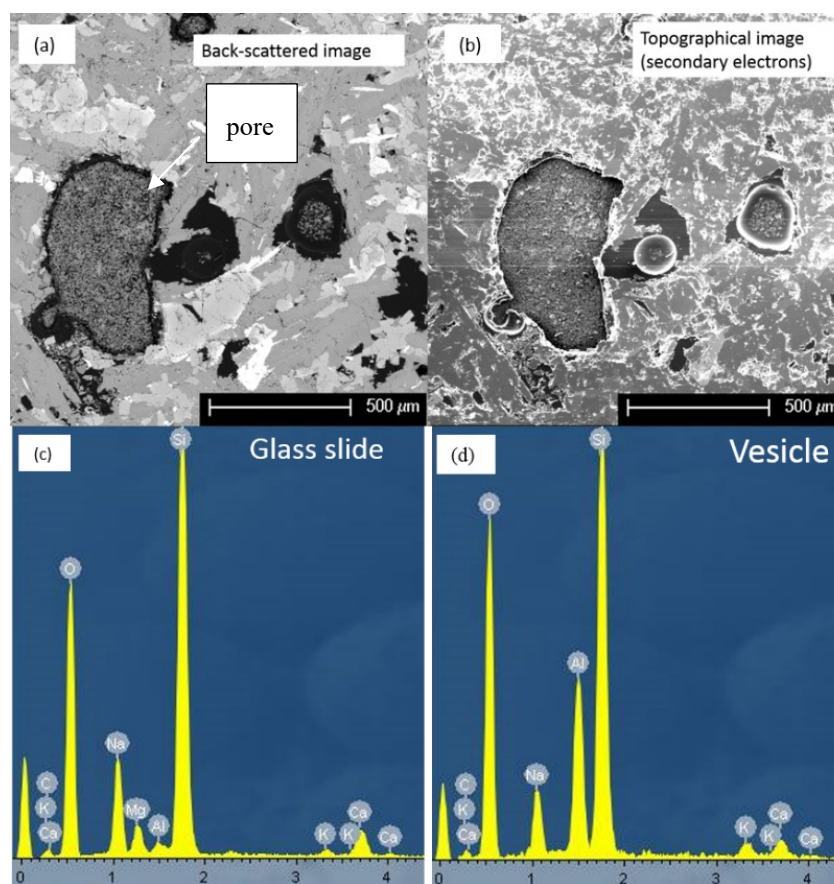


Figure A1.2: SEM analysis of basalt (a) backscattered and topographical image of a vesicle (b) chemical composition of the (c) glass slide edge and (d) the vesicle (hole)

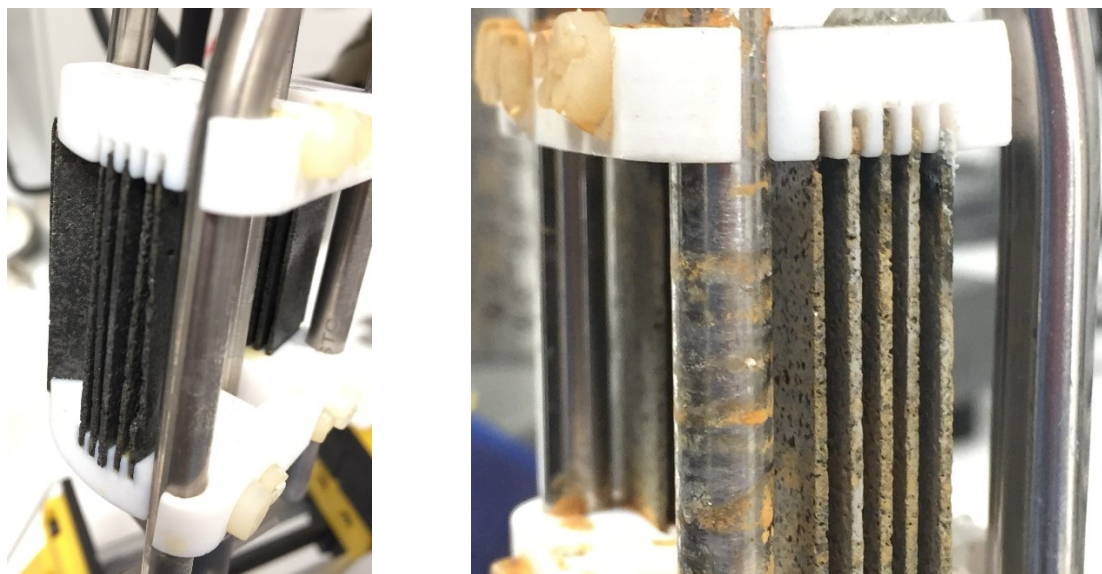


Figure A1.3: Basalt wafers with sample holder before and after the reaction time period. Prior to the reaction, the wafers were clean and dark grey. The reacted wafers have a yellowish coat on the surface and the edges shows white mineral phases.

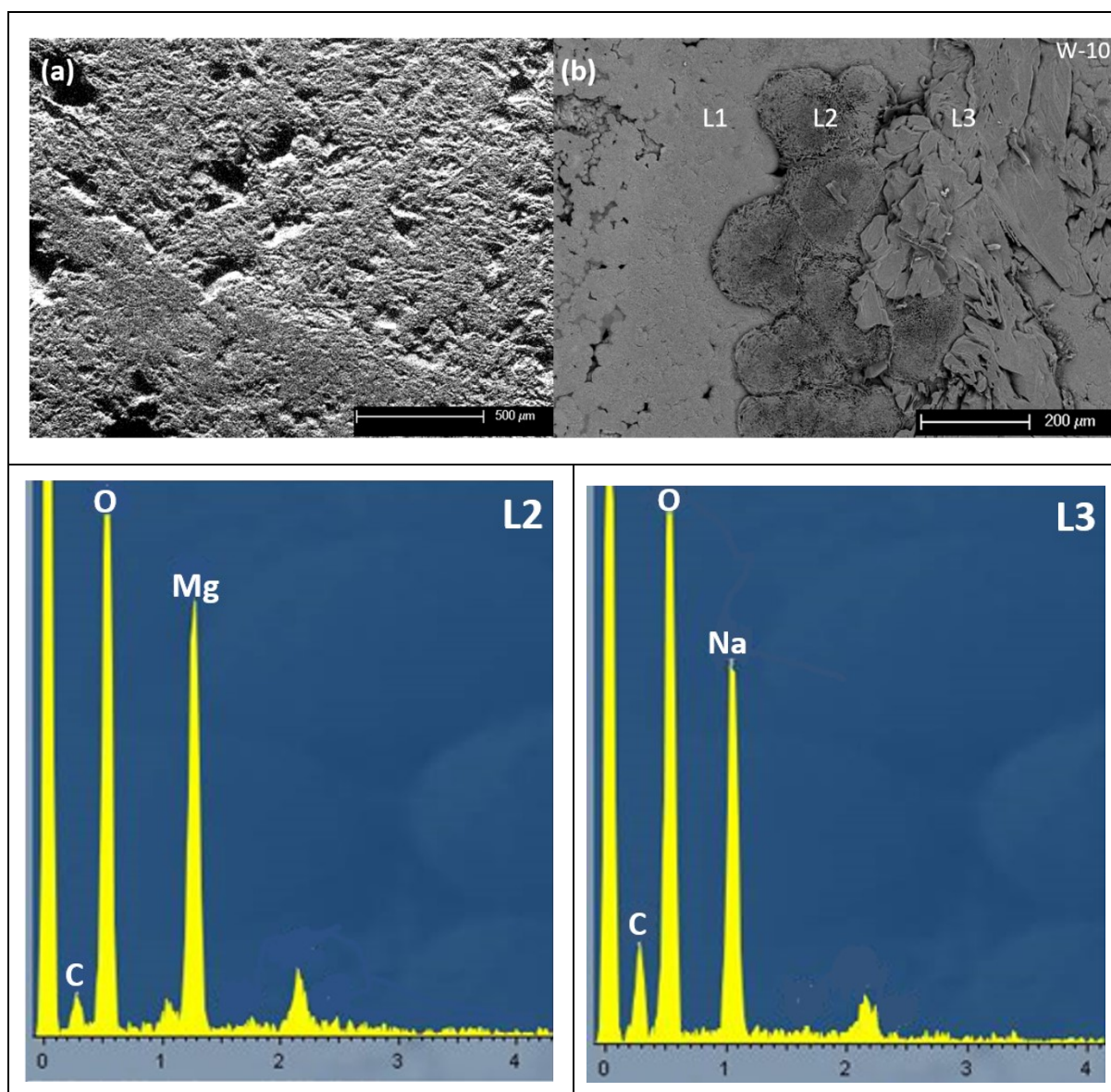


Figure A1.4: Back scattered image of layer 2 and 3 (L2 and L3) coatings on the surface wafer 10 (W-10) showing qualitative composition. L2 predominantly consist of Mg and O peaks and minor carbon peak. It suggests precipitation of poorly crystalline Mg – rich carbonates. The L3 has a high Na peak along with minor carbon and suggests precipitation of Na-rich carbonate.

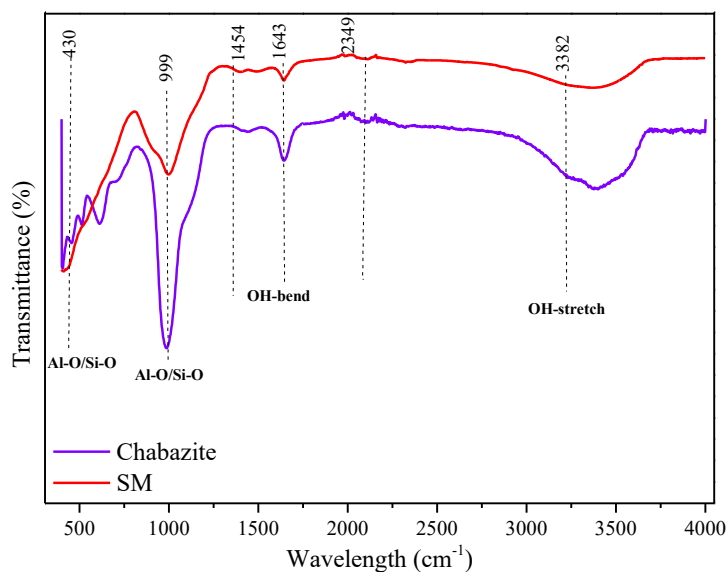


Figure A1.5: FTIR spectra of suspended matter (SM) showing peaks with chabazite (a zeolite)

Data 1

Fourier Transform Infrared spectroscopy information

The following standards are from RRUF database

Mineral Name: **Stilbite**

RRUFF ID: R050012

Ideal Chemistry: $\text{NaCa}_4(\text{Si}_{27}\text{Al}_9)\text{O}_{72} \cdot 28\text{H}_2\text{O}$

Locality: Harborville, Nova Scotia, Canada

Source: University of Arizona Mineral Museum 11419

Owner: RRUFF

Description: Globular aggregate of thin tabular white single crystals

Status: The identification of this mineral has been confirmed by X-ray diffraction and chemical analysis

Mineral name: **Chabazite-Ca**

RRUFF ID=R050014

Ideal Chemistry= $\text{Ca}_2[\text{Al}_4\text{Si}_8\text{O}_{24}] \cdot 13\text{H}_2\text{O}$

Locality: Tablo Mountain, Baja California, Mexico

Source: University of Arizona Mineral Museum

Owner: RRUFF

Description: Light tan colored rhombohedral single crystals

Status: The identification of this mineral has been confirmed by X-ray diffraction and chemical analysis

Mineral name: **Heulandite-Ca**

RRUFF ID: R040021

Ideal Chemistry: $(\text{Ca}, \text{Na}, \text{K})_5(\text{Si}_{27}\text{Al}_9)\text{O}_{27} \cdot 26\text{H}_2\text{O}$

Locality: Prospect Park, Patterson, Passaic County, New Jersey, USA

Owner: RRUFF

Source: University of Arizona Mineral Museum

Description: Group of colorless lamellar crystals

Status: The identification of this mineral has been confirmed by X-ray diffraction and chemical analysis

Mineral Name: **Nontronite**

RRUFF ID: R070286

Ideal Chemistry: $\text{Na}_{0.3}\text{Fe}^{3+}_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$

Locality: Andreasberg, Sachsen, Germany

Source: Michael Scott S103144

Owner: RRUFF

Description: Green granular massive mixed with quartz

Status: The identification of this mineral has been confirmed by X-ray diffraction and chemical analysis

Mineral Name: **Montmorillonite**

RRUFF ID: H-31

Ideal Chemistry: $\text{Na}_{0.3}\text{Fe}^{3+}_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$

Locality: Cameron, Arizona

Source: Caltech ATR database

Owner: Mineral Spectroscopy server, Caltech

Description: N/A

Status: N/A

Mineral names: **Calcite**

RRUFF ID: R040070

Ideal Chemistry: CaCO_3

Locality: Pryor Mountain, Big Horn County, Montana, USA

Owner: RRUFF

Source: University of Arizona Mineral Museum

Description: Orange scalenohedral crystals

Status: The identification of this mineral has been confirmed by X-ray diffraction and chemical analysis

Mineral Name: **Siderite**

RRUFF ID: R040034

Ideal Chemistry: FeCO_3

Locality: Příbram, Czech Republic

Source: University of Arizona Mineral Museum

Owner: RRUF

Description: Group of tan colored flattened rhombohedra

Status: The identification of this mineral has been confirmed by X-ray diffraction and chemical analysis

Mineral Name: **Magnesite**

RRUFF ID: R040114

Ideal Chemistry: MgCO_3

Locality: Příbram, Czech Republic

Source: University of Arizona Mineral Museum

Owner: RRUF

Description: Tan colored cleavage fragment

Status: The identification of this mineral has been confirmed by X-ray diffraction and chemical analysis

Table A1: Example of output file of GWB aqueous speciation modelling;
The input cation and anion concentrations can be seen in the end of the
output data in the file.

```

Temperature = 60.0 C      Pressure = 1.013 bars
pH = 4.151               log fO2 = -35.000
Eh = 0.3710 volts        pe = 5.6123
Ionic strength = 0.011308
Activity of water = 1.000000
Solvent mass = 0.31500 kg
Solution mass = 0.32848 kg
Mineral mass = 0.00000 kg
Solution density = 0.987 g/cm3
Solution viscosity = 0.005 poise
Chlorinity = 0.000000 molal
Dissolved solids = 41043 mg/kg sol'n
Elect. conductivity = 714.92 uS/cm (or umho/cm)
Hardness = 283.61 mg/kg sol'n as CaCO3
    carbonate = 283.61 mg/kg sol'n as CaCO3
    non-carbonate = 0.00 mg/kg sol'n as CaCO3
Carbonate alkalinity= 392.53 mg/kg sol'n as CaCO3
Water type = Mg-HCO3
Bulk volume = 333. cm3
Fluid volume = 333. cm3
Mineral volume = 0.000 cm3
Inert volume = 0.000 cm3
Porosity = 100. %
Permeability = 9.87e-09 cm2

```

No minerals in system.

Aqueous species act.	molality	mg/kg sol'n	act. coef.	log

CO2(aq)	0.9541	4.027e+04	1.0000	-
0.0204				
HCO3-	0.008177	478.5	0.8905	-
2.1378				
SiO2(aq)	0.002565	147.8	1.0000	-
2.5909				
Mg++	0.002411	56.20	0.6600	-
2.7982				
Na+	0.001577	34.76	0.8905	-
2.8526				
Ca++	0.0003287	12.63	0.6441	-
3.6742				
Fe++	0.0002262	12.12	0.6441	-
3.8365				
MgHCO3+	0.0001898	15.53	0.8905	-
3.7721				
K+	0.0001664	6.240	0.8871	-
3.8308				
H+	7.807e-05	0.07546	0.9046	-
4.1510				
Al+++	4.216e-05	1.091	0.4021	-
4.7707				

AlOH++	3.775e-05	1.592	0.6311	-
4.6230				
CaHCO3+	2.498e-05	2.422	0.8905	-
4.6528				
NaHCO3 (aq)	7.940e-06	0.6397	1.0000	-
5.1002				
Al (OH) 2+	6.858e-06	0.4012	0.8905	-
5.2142				
HAlO2 (aq)	9.063e-07	0.05214	1.0000	-
6.0427				
AlO2-	2.056e-08	0.001163	0.8905	-
7.7373				
MgCO3 (aq)	1.945e-08	0.001572	1.0000	-
7.7111				
HSiO3-	1.387e-08	0.001025	0.8905	-
7.9083				
CO3--	1.210e-08	0.0006963	0.6311	-
8.1171				
CaCO3 (aq)	7.717e-09	0.0007407	1.0000	-
8.1126				
OH-	1.496e-09	2.440e-05	0.8888	-
8.8762				
NaHSiO3 (aq)	4.514e-10	4.332e-05	1.0000	-
9.3455				
Ti (OH) 4 (aq)	2.206e-10	2.452e-05	1.0000	-
9.6564				
FeCO3+	6.367e-11	7.074e-06	0.8905	-
10.2464				
Fe+++	3.590e-11	1.923e-06	0.4021	-
10.8406				
Cl-	2.974e-11	1.011e-06	0.8871	-
10.5787				
NaCO3-	1.369e-11	1.090e-06	0.8905	-
10.9138				
NaAlO2 (aq)	7.704e-12	6.056e-07	1.0000	-
11.1133				
NaOH (aq)	3.148e-13	1.207e-08	1.0000	-
12.5020				
MgCl+	4.156e-14	2.382e-09	0.8905	-
13.4317				
NaCl (aq)	8.276e-15	4.638e-10	1.0000	-
14.0822				
FeCl+	3.970e-15	3.476e-10	0.8905	-
14.4516				
CaCl+	1.618e-15	1.172e-10	0.8905	-
14.8415				
HCl (aq)	3.818e-16	1.335e-11	1.0000	-
15.4182				
KCl (aq)	2.367e-16	1.692e-11	1.0000	-
15.6258				
Formate	8.260e-22	3.566e-17	0.8888	-
21.1342				
FeCl++	5.326e-22	4.663e-17	0.6311	-
21.4735				
Formic_acid (aq)	3.303e-22	1.458e-17	1.0000	-
21.4810				

H2 (aq)	1.148e-22	2.219e-19	1.0000	-
21.9401				
Mg (For) +	2.579e-23	1.714e-18	0.8905	-
22.6390				
Fe (For) +	6.030e-24	5.833e-19	0.8905	-
23.2700				
Ca (For) +	4.980e-24	4.064e-19	0.8905	-
23.3531				
CO (aq)	1.869e-24	5.020e-20	1.0000	-
23.7284				
Na (For) (aq)	1.214e-24	7.915e-20	1.0000	-
23.9159				
K (For) (aq)	1.418e-25	1.144e-20	1.0000	-
24.8483				
CaCl2 (aq)	3.464e-26	3.687e-21	1.0000	-
25.4604				
FeCl2 (aq)	6.159e-28	7.486e-23	1.0000	-
27.2105				
H-Oxalate	2.965e-28	2.531e-23	0.8905	-
27.5784				
Oxalate	2.082e-28	1.758e-23	0.6266	-
27.8845				
Oxalic_acid (aq)	4.364e-31	3.768e-26	1.0000	-
30.3601				
O2 (aq)	8.644e-39	2.652e-34	1.0000	-
38.0633				
HO2-	1.579e-41	4.998e-37	0.8905	-
40.8520				
Mg (For) 2 (aq)	7.325e-44	8.032e-39	1.0000	-
43.1352				
Fe (For) 2 (aq)	3.840e-44	5.372e-39	1.0000	-
43.4156				
ClO-	3.089e-44	1.524e-39	0.8905	-
43.5606				
Ca (For) 2 (aq)	2.156e-44	2.690e-39	1.0000	-
43.6664				
Formaldehyde (aq)	1.281e-45	3.690e-41	1.0000	-
44.8923				
Na (For) 2-	3.379e-46	3.662e-41	0.8905	-
45.5216				
K (For) 2-	4.589e-47	5.682e-42	0.8905	-
46.3887				
FeCl4--	2.830e-48	5.364e-43	0.6266	-
47.7512				
Methanol (aq)	1.370e-54	4.210e-50	1.0000	-
53.8632				
Methane (aq)	6.212e-59	9.556e-55	1.0000	-
58.2068				
Glycolate	6.492e-60	4.672e-55	0.8905	-
59.2380				
Glycolic_acid (aq)	3.011e-60	2.196e-55	1.0000	-
59.5212				
Mg (Glyc) +	2.587e-61	2.465e-56	0.8905	-
60.6376				
Fe (Glyc) +	1.052e-61	1.320e-56	0.8905	-
61.0284				

Ca (Glyc) + 61.2276	6.649e-62	7.340e-57	0.8905	-
Na (Glyc) (aq) 61.9872	1.030e-62	9.682e-58	1.0000	-
Acetic_acid(aq) 62.2249	5.958e-63	3.431e-58	1.0000	-
Acetate 62.8818	1.471e-63	8.332e-59	0.8921	-
K (Glyc) (aq) 62.9196	1.203e-63	1.317e-58	1.0000	-
MgCH ₃ COO+ 64.4533	3.954e-65	3.160e-60	0.8905	-
FeCH ₃ COO+ 65.3961	4.511e-66	4.970e-61	0.8905	-
CaCH ₃ COO+ 65.5017	3.537e-66	3.363e-61	0.8905	-
AlCH ₃ COO++ 65.8271	2.359e-66	1.946e-61	0.6311	-
NaCH ₃ COO (aq) 65.7692	1.701e-66	1.338e-61	1.0000	-
KCH ₃ COO (aq) 66.8261	1.492e-67	1.405e-62	1.0000	-
H-Malonate 69.0224	1.066e-69	1.054e-64	0.8905	-
ClO ₂ - 69.7426	2.031e-70	1.314e-65	0.8905	-
Malonic_acid(aq) 70.2676	5.400e-71	5.389e-66	1.0000	-
Malonate 70.7329	2.952e-71	2.889e-66	0.6266	-
ClO ₃ - 83.5174	3.418e-84	2.735e-79	0.8888	-
Acetaldehyde (aq) 84.5933	2.551e-85	1.078e-80	1.0000	-
Ethanol (aq) 97.5510	2.812e-98	1.242e-93	1.0000	-
Ethylene (aq) 101.3113	4.883e-102	1.314e-97	1.0000	-
ClO ₄ - 101.3731	4.765e-102	4.545e-97	0.8888	-
Lactate 102.8320	1.653e-103	1.412e-98	0.8905	-
Ethyne (aq) 103.0464	8.986e-104	2.244e-99	1.0000	-
Lactic_acid(aq) 103.0660	8.591e-104	7.421e-99	1.0000	-
Mg (Lac) + 104.0790	9.362e-105	1.018e-99	0.8905	-
Fe (Lac) + 104.6579	2.469e-105	3.431e-100	0.8905	-
Ca (Lac) + 105.0146	1.086e-105	1.345e-100	0.8905	-
Ethane (aq) 105.5428	2.865e-106	8.262e-102	1.0000	-
Na (Lac) (aq) 105.5635	2.732e-106	2.936e-101	1.0000	-

K(Lac) (aq)	3.192e-107	3.923e-102	1.0000	-
106.4959				
Propanoic_acid(a	2.846e-108	2.022e-103	1.0000	-
107.5457				
Propanoate	5.219e-109	3.657e-104	0.8905	-
108.3328				
Mg(Prop) +	4.189e-111	3.912e-106	0.8905	-
110.4283				
Fe(Prop) +	2.691e-111	3.327e-106	0.8905	-
110.6204				
Na(Prop) (aq)	8.522e-112	7.850e-107	1.0000	-
111.0695				
Ca(Prop) +	7.459e-112	8.093e-107	0.8905	-
111.1777				
K(Prop) (aq)	9.957e-113	1.071e-107	1.0000	-
112.0019				
Succinic_acid(aq	6.616e-114	7.492e-109	1.0000	-
113.1794				
H-Succinate	6.445e-114	7.236e-109	0.8905	-
113.2412				
Succinate	2.552e-115	2.840e-110	0.6266	-
114.7961				
Fe(Glyc) 2 (aq)	1.741e-119	3.438e-114	1.0000	-
118.7592				
Mg(Glyc) 2 (aq)	9.791e-120	1.637e-114	1.0000	-
119.0092				
Ca(Glyc) 2 (aq)	5.954e-120	1.086e-114	1.0000	-
119.2252				
Na(Glyc) 2-	4.258e-122	7.067e-117	0.8905	-
121.4212				
K(Glyc) 2-	5.485e-123	9.951e-118	0.8905	-
122.3112				
Acetone (aq)	2.258e-126	1.258e-121	1.0000	-
125.6463				
Mg(CH3COO) 2 (aq)	1.842e-127	2.515e-122	1.0000	-
126.7348				
Ca(CH3COO) 2 (aq)	6.113e-128	9.272e-123	1.0000	-
127.2137				
Al(CH3COO) 2+	5.948e-128	8.274e-123	0.8905	-
127.2760				
Fe(CH3COO) 2 (aq)	5.337e-128	8.902e-123	1.0000	-
127.2727				
Na(CH3COO) 2-	8.139e-130	1.101e-124	0.8905	-
129.1398				
Propanal (aq)	2.872e-130	1.600e-125	1.0000	-
129.5418				
K(CH3COO) 2-	6.219e-131	9.374e-126	0.8905	-
130.2567				
1-Propanol (aq)	1.068e-143	6.153e-139	1.0000	-
142.9716				
1-Propene (aq)	1.838e-145	7.418e-141	1.0000	-
144.7356				
1-Propyne (aq)	1.317e-145	5.061e-141	1.0000	-
144.8804				
2-Hydroxybutanoa	2.869e-149	2.836e-144	0.8905	-
148.5927				

2-Hydroxybutanoi 148.8738	1.337e-149	1.335e-144	1.0000	-
Propane (aq) 151.2707	5.362e-152	2.267e-147	1.0000	-
Butanoic_acid(aq) 153.4829	3.290e-154	2.779e-149	1.0000	-
Butanoate 154.2361	6.520e-155	5.446e-150	0.8905	-
Mg(But) + 156.4800	3.718e-157	3.972e-152	0.8905	-
Fe(But) + 156.5023	3.533e-157	4.843e-152	0.8905	-
Na(But) (aq) 156.9782	1.051e-157	1.110e-152	1.0000	-
Ca(But) + 157.2118	6.896e-158	8.411e-153	0.8905	-
K(But) (aq) 157.9106	1.229e-158	1.487e-153	1.0000	-
Glutaric_acid(aq) 158.2280	5.915e-159	7.494e-154	1.0000	-
H-Glutarate 158.4808	3.712e-159	4.667e-154	0.8905	-
Glutarate 159.8685	2.160e-160	2.695e-155	0.6266	-
Ethylacetate(aq) 161.3402	4.569e-162	3.861e-157	1.0000	-
Butanal (aq) 176.6354	2.315e-177	1.601e-172	1.0000	-
1-Butanol (aq) 189.4771	3.334e-190	2.370e-185	1.0000	-
1-Butyne (aq) 190.7552	1.757e-191	9.114e-187	1.0000	-
1-Butene (aq) 190.7745	1.681e-191	9.044e-187	1.0000	-
2-Hydroxypentano 194.2026	7.043e-195	7.911e-190	0.8905	-
2-Hydroxypentano 194.6816	2.081e-195	2.358e-190	1.0000	-
n-Butane(aq) 197.0451	9.014e-198	5.024e-193	1.0000	-
Pentanoic_acid(a 199.2363	5.804e-200	5.684e-195	1.0000	-
Pentanoate 200.0219	1.068e-200	1.036e-195	0.8905	-
Fe(Pent) + 202.2855	5.819e-203	8.760e-198	0.8905	-
Mg(Pent) + 202.4416	4.062e-203	4.886e-198	0.8905	-
Na(Pent) (aq) 202.7163	1.922e-203	2.288e-198	1.0000	-
Ca(Pent) + 203.1649	7.682e-204	1.040e-198	0.8905	-
K(Pent) (aq) 203.6487	2.246e-204	3.020e-199	1.0000	-
Adipic_acid(aq) 205.2829	5.213e-206	7.306e-201	1.0000	-

H-Adipate 205.6278	2.646e-206	3.683e-201	0.8905	-
Mg (Lac) 2 (aq) 205.8945	1.275e-206	2.475e-201	1.0000	-
Fe (Lac) 2 (aq) 205.9443	1.137e-206	2.551e-201	1.0000	-
Ca (Lac) 2 (aq) 206.6939	2.023e-207	4.234e-202	1.0000	-
Adipate 207.0134	1.547e-207	2.139e-202	0.6266	-
Na (Lac) 2- 208.5143	3.436e-209	6.628e-204	0.8905	-
K (Lac) 2- 209.4043	4.427e-210	9.223e-205	0.8905	-
Phenol (aq) 217.9413	1.145e-218	1.033e-213	1.0000	-
Fe (Prop) 2 (aq) 217.9841	1.037e-218	2.009e-213	1.0000	-
Mg (Prop) 2 (aq) 218.5092	3.096e-219	5.061e-214	1.0000	-
Ca (Prop) 2 (aq) 219.1126	7.716e-220	1.378e-214	1.0000	-
Na (Prop) 2- 219.7149	2.165e-220	3.512e-215	0.8905	-
K (Prop) 2- 220.6056	2.785e-221	4.947e-216	0.8905	-
Pentanal (aq) 222.2137	6.113e-223	5.049e-218	1.0000	-
Benzene (aq) 229.3444	4.525e-230	3.390e-225	1.0000	-
Benzoic_acid (aq) 232.3302	4.676e-233	5.476e-228	1.0000	-
Benzoate 232.4166	4.273e-233	4.963e-228	0.8966	-
1-Pentanol (aq) 234.1874	6.495e-235	5.490e-230	1.0000	-
1-Pentyne (aq) 236.6169	2.416e-237	1.578e-232	1.0000	-
1-Pentene (aq) 236.6558	2.209e-237	1.486e-232	1.0000	-
o-Phthalate 238.9902	1.632e-239	2.569e-234	0.6266	-
2-Hydroxyhexanoa 240.1405	8.127e-241	1.022e-235	0.8905	-
2-Hydroxyhexanoi 240.4896	3.239e-241	4.105e-236	1.0000	-
n-Pentane (aq) 242.8677	1.356e-243	9.382e-239	1.0000	-
Hexanoic_acid (aq) 245.0895	8.137e-246	9.064e-241	1.0000	-
Hexanoate 245.8826	1.472e-246	1.625e-241	0.8905	-
Pimelic_acid (aq) 249.9936	1.015e-250	1.559e-245	1.0000	-
H-Pimelate 250.4055	4.415e-251	6.738e-246	0.8905	-

Pimelate	2.375e-252	3.602e-247	0.6266	-
251.8274				
Hexanal (aq)	7.938e-269	7.625e-264	1.0000	-
268.1003				
Toluene (aq)	2.331e-273	2.060e-268	1.0000	-
272.6324				
p-Toluic_acid(aq	4.303e-276	5.618e-271	1.0000	-
275.3662				
p-Toluate	2.639e-276	3.420e-271	0.8905	-
275.6289				
m-Toluic_acid(aq	2.314e-276	3.021e-271	1.0000	-
275.6356				
m-Toluate	1.825e-276	2.365e-271	0.8905	-
275.7892				
o-Toluate	2.410e-278	3.124e-273	0.8905	-
277.6683				
o-Toluic_acid(aq	1.718e-278	2.243e-273	1.0000	-
277.7649				
1-Hexanol (aq)	3.166e-281	3.102e-276	1.0000	-
280.4995				
1-Hexene (aq)	4.299e-283	3.470e-278	1.0000	-
282.3666				
1-Hexyne (aq)	2.729e-283	2.150e-278	1.0000	-
282.5640				
2-Hydroxyheptano	1.268e-286	1.766e-281	0.8905	-
285.9472				
2-Hydroxyheptano	5.042e-287	7.068e-282	1.0000	-
286.2974				
n-Hexane (aq)	1.370e-289	1.132e-284	1.0000	-
288.8632				
Heptanoic_acid(a	1.541e-291	1.924e-286	1.0000	-
290.8122				
Heptanoate	2.611e-292	3.235e-287	0.8905	-
291.6335				
Suberic_acid(aq)	9.540e-298	1.594e-292	1.0000	-
297.0205				
H-Suberate	3.917e-298	6.505e-293	0.8905	-
297.4574				
Suberate	2.325e-299	3.839e-294	0.6266	-
298.8366				
Fe (But) 2 (aq)	1.921e-310	4.237e-305	1.0000	-
300.0000				
Mg (But) 2 (aq)	2.785e-311	5.301e-306	1.0000	-
300.0000				
Ca (But) 2 (aq)	7.702e-312	1.583e-306	1.0000	-
300.0000				
Na (But) 2-	3.557e-312	6.727e-307	0.8905	-
300.0000				
K (But) 2-	4.576e-313	9.359e-308	0.8905	-
300.0000				
Heptanal (aq)	1.708e-315	1.870e-310	1.0000	-
300.0000				
H-Azelate	0.0000	0.0000	0.8905	-
300.0000				
n-Propylbenzene (	0.0000	0.0000	1.0000	-
300.0000				

n-Pentylbenzene (300.0000	0.0000	0.0000	1.0000	-
2-Hydroxyoctanoa 300.0000	0.0000	0.0000	0.8905	-
n-Octylbenzene (a 300.0000	0.0000	0.0000	1.0000	-
n-Octane (aq) 300.0000	0.0000	0.0000	1.0000	-
n-Hexylbenzene (a 300.0000	0.0000	0.0000	1.0000	-
n-Heptylbenzene (300.0000	0.0000	0.0000	1.0000	-
n-Heptane (aq) 300.0000	0.0000	0.0000	1.0000	-
n-Butylbenzene (a 300.0000	0.0000	0.0000	1.0000	-
2-Hydroxynonanoi 300.0000	0.0000	0.0000	1.0000	-
Undecanoic_acid(300.0000	0.0000	0.0000	1.0000	-
Undecanoate 300.0000	0.0000	0.0000	0.8905	-
2-Hydroxynonanoa 300.0000	0.0000	0.0000	0.8905	-
Sebacic_acid(aq) 300.0000	0.0000	0.0000	1.0000	-
Sebacate 300.0000	0.0000	0.0000	0.6266	-
Octanoic_acid(aq 300.0000	0.0000	0.0000	1.0000	-
Octanoate 300.0000	0.0000	0.0000	0.8905	-
Octanal (aq) 300.0000	0.0000	0.0000	1.0000	-
Fe (Pent) 2 (aq) 300.0000	0.0000	0.0000	1.0000	-
Nonanoic_acid(aq 300.0000	0.0000	0.0000	1.0000	-
Nonanoate 300.0000	0.0000	0.0000	0.8905	-
Nonanal (aq) 300.0000	0.0000	0.0000	1.0000	-
Azelate 300.0000	0.0000	0.0000	0.6266	-
Azelaic_acid(aq) 300.0000	0.0000	0.0000	1.0000	-
Na (Pent) 2- 300.0000	0.0000	0.0000	0.8905	-
2-Hydroxydecanoi 300.0000	0.0000	0.0000	1.0000	-
1-Heptanol (aq) 300.0000	0.0000	0.0000	1.0000	-
Ethylbenzene (aq) 300.0000	0.0000	0.0000	1.0000	-
2-Hydroxydecano 300.0000	0.0000	0.0000	0.8905	-

Mg (Pent) 2 (aq)	0.0000	0.0000	1.0000	-
300.0000				
Dodecanoic_acid(	0.0000	0.0000	1.0000	-
300.0000				
1-Octyne (aq)	0.0000	0.0000	1.0000	-
300.0000				
Dodecanoate	0.0000	0.0000	0.8905	-
300.0000				
Decanoic_acid(aq	0.0000	0.0000	1.0000	-
300.0000				
Decanoate	0.0000	0.0000	0.8905	-
300.0000				
Decanal (aq)	0.0000	0.0000	1.0000	-
300.0000				
2-Hexanone (aq)	0.0000	0.0000	1.0000	-
300.0000				
1-Octene (aq)	0.0000	0.0000	1.0000	-
300.0000				
1-Heptyne (aq)	0.0000	0.0000	1.0000	-
300.0000				
K (Pent) 2-	0.0000	0.0000	0.8905	-
300.0000				
2-Heptanone (aq)	0.0000	0.0000	1.0000	-
300.0000				
2-Pentanone (aq)	0.0000	0.0000	1.0000	-
300.0000				
2-Butanone (aq)	0.0000	0.0000	1.0000	-
300.0000				
1-Octanol (aq)	0.0000	0.0000	1.0000	-
300.0000				
Ca (Pent) 2 (aq)	0.0000	0.0000	1.0000	-
300.0000				
2-Octanone (aq)	0.0000	0.0000	1.0000	-
300.0000				
H-Sebacate	0.0000	0.0000	0.8905	-
300.0000				
2-Hydroxyoctanoi	0.0000	0.0000	1.0000	-
300.0000				
1-Heptene (aq)	0.0000	0.0000	1.0000	-
300.0000				

Mineral saturation states

	log Q/K		log Q/K
Nontronite-Mg	9.8757s/sat	Zoisite	-10.0616
Nontronite-H	9.6899s/sat	Prehnite	-10.0835
Nontronite-Ca	9.6386s/sat	Wollastonite	-10.2361
Nontronite-Na	9.1221s/sat	Pseudowollastonite	-10.4202
Nontronite-K	9.0499s/sat	Okenite	-10.4880
Beidellite-Mg	7.1171s/sat	Annite	-10.8191
Beidellite-H	6.9298s/sat	Huntite	-11.0165
Beidellite-Ca	6.8797s/sat	Greenalite	-11.2714
Pyrophyllite	6.7865s/sat	Cordierite_anhyd	-11.5431
Muscovite	6.7560s/sat	Saponite-Mg	-11.6552
Clinoptilolite-C	6.4826s/sat	Ca-Al Pyroxene	-11.8094
Beidellite-Na	6.3634s/sat	Saponite-H	-11.8386
Kaolinite	6.3361s/sat	Saponite-Ca	-11.8889

Clinoptilolite-h	6.3114s/sat	Talc	-11.9638
Beidellite-K	6.2908s/sat	Mordenite-dehy	-12.0019
Hematite	5.5428s/sat	Saponite-Na	-12.4054
Montmor-Mg	5.0306s/sat	Saponite-K	-12.4778
Stilbite	4.9824s/sat	Artinite	-12.5452
Montmor-Ca	4.7345s/sat	Daphnite-14A	-12.5938
Illite	4.6144s/sat	Amesite-14A	-13.0607
Paragonite	4.3781s/sat	Periclase	-13.0760
Montmor-Na	4.2780s/sat	Hedenbergite	-13.2466
Montmor-K	4.2125s/sat	Diopside	-13.4040
Diaspore	2.5665s/sat	NaFeO2	-13.9920
Boehmite	2.2174s/sat	Forsterite-Megha	-14.0503
Goethite	2.2125s/sat	Na2CO3	-14.1228
Corundum	1.9796s/sat	Thermonatrite	-14.1419
Gibbsite	1.8538s/sat	Natron	-14.3048
Anorthoclase	1.7778s/sat	Na2CO3:7H2O	-14.3256
Clinoptilolite-h	1.6337s/sat	Phlogopite	-14.7687
Clinoptilolite-N	1.6231s/sat	Halite	-15.0489
Clinoptilolite-h	1.6003s/sat	Sylvite	-15.5319
Kyanite	1.4622s/sat	Portlandite	-15.5682
Mesolite	1.3347s/sat	Forsterite	-15.5968
Andalusite	1.2710s/sat	Chrysotile	-15.6685
Magnetite	1.2485s/sat	Daphnite-7A	-15.7013
Mordenite	1.2127s/sat	Ripidolite-14A	-17.1736
Maximum_Microcli	1.1953s/sat	Andradite	-18.1802
K-Feldspar	1.1909s/sat	Monticellite	-18.3720
Sillimanite	0.9667s/sat	CaAl2O4	-18.8794
Clinoptilolite-K	0.8863s/sat	Natrosilite	-19.6322
Quartz	0.8825s/sat	Gyrolite	-19.6918
Tridymite	0.7267s/sat	CaAl4O7	-20.0322
Chalcedony	0.6398s/sat	Ripidolite-7A	-20.2979
Cristobalite(alp)	0.4012s/sat	Clinochlore-14A	-20.6611
Scolecite	0.3632s/sat	Na2SiO3	-20.6613
Sanidine_high	0.2001s/sat	Sepiolite	-20.7009
Coesite	0.1520s/sat	Grossular	-22.2316
Cristobalite(bet)	0.0359s/sat	Hydromagnesite	-22.8600
SiO2(am)	-0.1842	MgOHCl	-22.9118
Dawsonite	-0.2607	Clinochlore-7A	-23.7939
Ice	-0.2855	Lime	-24.3828
Laumontite	-0.3205	Clinoptilolite-d	-24.4262
Albite	-0.3597	C	-25.0820
Albite_low	-0.3597	Gehlenite	-25.1452
Siderite	-0.9924	Hillebrandite	-26.3523
Margarite	-1.0701	Dicalcium_silica	-26.4235
Analcime	-1.2476	Larnite	-27.5435
Smectite-low-Fe-	-1.3207	Fe	-28.6616
Albite_high	-1.4758	Clinoptilolite-d	-29.2576
Cronstedtite-7A	-2.0859	Clinoptilolite-d	-29.9456
Magnesite	-2.2232	Akermanite	-30.2807
Fe(OH)3	-2.4913	MgCl2:4H2O	-30.4363
Hercynite	-2.6199	Lawrencite	-32.4255
Celadonite	-2.6417	MgCl2:2H2O	-34.9582
Lawsonite	-2.7261	Hydrophilite	-35.0217
Jadeite	-2.8741	Ferrite-Dicalciu	-35.5606
Calcite	-2.9940	Tremolite	-37.1234
Aragonite	-3.1372	Rankinite	-37.4869
Kalsilite	-3.3990	MgCl2:H2O	-37.7903

Andesine	-3.5158	Anthophyllite	-39.5207
Smectite-high-Fe	-3.7231	Chloromagnesite	-42.7963
Wairakite	-3.7347	Pargasite	-45.2566
Dolomite-ord	-3.7771	Afwillite	-45.3988
Dolomite	-3.7773	Merwinite	-46.2463
Monohydrocalcite	-3.9694	Foshagite	-48.3376
Chamosite-7A	-4.3394	Na	-49.5683
Ferrosilite	-4.4298	KMgCl3:2H2O	-50.8654
Natrolite	-4.6632	Tobermorite-14A	-51.6664
Nepheline	-4.8415	Tobermorite-11A	-52.3124
Dolomite-dis	-5.0961	Molysite	-53.1532
Nahcolite	-5.1682	K	-53.9236
Nesquehonite	-5.6037	Hatrurite	-54.0338
Anorthite	-5.9982	Tobermorite-9A	-54.9690
Wustite	-6.5968	KMgCl3	-57.0772
Enstatite	-6.8192	Na2O	-58.3880
Analcm-dehy	-6.8513	Na4SiO4	-61.9855
Epidote	-7.0730	Ca3Al2O6	-68.4953
Epidote-ord	-7.0751	Xonotlite	-70.1919
FeO	-7.1141	K2O	-75.5513
Ferrite-Mg	-7.1227	Ca4Al2Fe2O10	-82.4622
Augite	-7.5370	Mg	-84.2535
Fe(OH)2	-7.6905	Na6Si2O7	-90.2458
Minnesotaite	-8.6943	Al	-96.0041
Ferrite-Ca	-8.7505	Si	-97.3617
Brucite	-8.7635	Ca	-101.0147
Cordierite_hydr	-9.3923	Antigorite	-237.1790
Spinel	-9.4094	o-Phthalic_acid	-237.9793
Fayalite	-9.8908	Mayenite	-256.5856
Clinozoisite	-10.0239		

Gases	fugacity	log fug.				

CO2 (g)	58.06	1.764				
H2O (g)	0.1637	-0.786				
H2 (g)	1.583e-19	-18.801				
HCl (g)	2.380e-20	-19.623				
CO (g)	2.608e-21	-20.584				
O2 (g)	1.000e-35	-35.000				
Cl2 (g)	3.714e-51	-50.430				
CH4 (g)	6.547e-56	-55.184				
Na (g)	8.279e-62	-61.082				
K (g)	1.288e-63	-62.890				
C2H4 (g)	1.763e-99	-98.754				
Mg (g)	5.410e-102	-101.267				
Ca (g)	1.043e-123	-122.982				
C (g)	3.214e-130	-129.493				
Al (g)	2.320e-141	-140.634				
Si (g)	7.405e-161	-160.130				
			In fluid		Sorbed	
Kd						
Original basis	total moles	moles	mg/kg	moles	mg/kg	

Al+++	2.76e-05	2.76e-05	2.27			

Ca++	0.000111	0.000111	13.6
Cl-	9.39e-12	9.39e-12	1.01e-06
Fe++	7.13e-05	7.13e-05	12.1
H+	0.301	0.301	922.
H2O	17.2	17.2	9.42e+05
HCO3-	0.303	0.303	5.63e+04
K+	5.24e-05	5.24e-05	6.24
Mg++	0.000819	0.000819	60.6
Na+	0.000499	0.000499	34.9
O2(aq)	7.84e-12	7.84e-12	7.64e-07
SiO2(aq)	0.000808	0.000808	148.
Ti(OH)4(aq)	6.95e-11	6.95e-11	2.45e-05

Elemental composition		In fluid		Sorbed
	total moles	moles	mg/kg	moles

Aluminum	2.762e-05	2.762e-05	2.269	
Calcium	0.0001114	0.0001114	13.59	
Carbon	0.3032	0.3032	1.109e+04	
Chlorine	9.386e-12	9.386e-12	1.013e-06	
Hydrogen	34.97	34.97	1.073e+05	
Iron	7.126e-05	7.126e-05	12.12	
Magnesium	0.0008194	0.0008194	60.63	
Oxygen	18.10	18.10	8.814e+05	
Potassium	5.242e-05	5.242e-05	6.240	
Silicon	0.0008080	0.0008080	69.09	
Sodium	0.0004992	0.0004992	34.94	
Titanium	6.950e-11	6.950e-11	1.013e-05	

Appendix 2

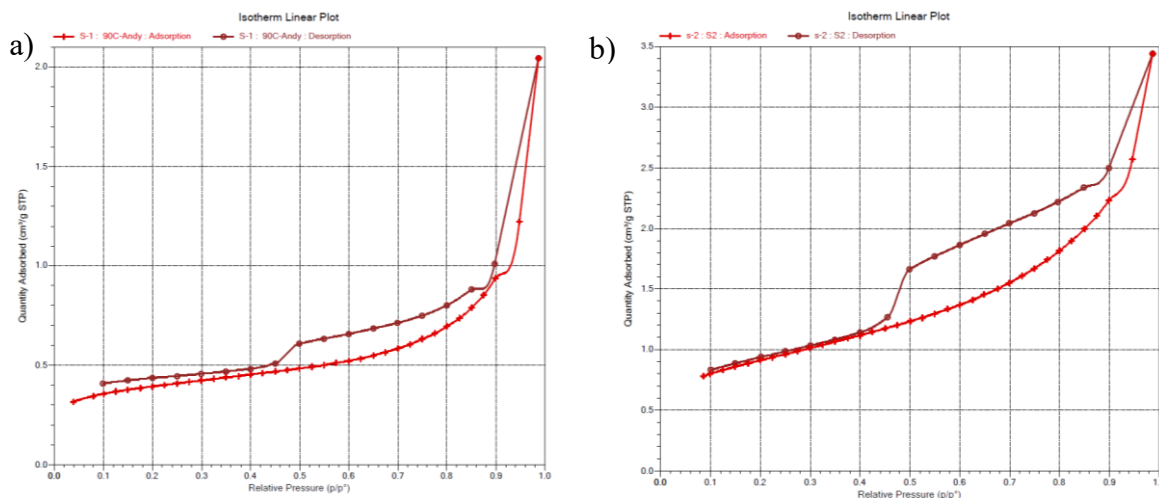


Figure A2: Isotherm linear plot a) massive basalt powdered sample (b) vesicular basalt powdered sample

The Fig. A2 shows the linear plot of isotherm of both MB and VB powdered basalt samples. In both the graph, at higher pressures the slope shows increased uptake of adsorbate as pores become filled. This trend is more intense in the case of VB compared to MB which suggest the presence of higher number micropores in VB.

Table A2.1: Detailed results from the Experiment with MB at 25°C and 5 bars

Sample no.	0	1	2	3	4	5	6	7
Reaction Time(hours)	0	3	27	51.2	75.2	99.2	123.2	143.05
Volume of brine in reactor (L)	0.380	0.373	0.365	0.357	0.348	0.340	0.332	0.321
Calculated in-situ pH		3.779	3.989	4.030	4.063	4.088	4.112	4.110
Measured alkalinity HCO_3^- (mg/L)	0	20.13	44.53	59.78	66.49	73.81	88.45	86.01
Ca(mg/L)	0	1.24	2.28	2.30	2.34	2.42	2.44	2.40
Mg(mg/L)	0	1.3	3.06	3.8	4.4	4.88	5.36	5.46
Si(mg/L)	0	1.96	5.42	6.52	7.48	8.26	8.92	9.1
Fe ^{total} (mg/L)	0	1.26	3.56	4.44	5.22	5.92	6.58	6.68
Na(mg/L)	0	1.8	3.36	3.5	3.66	3.86	4	3.78
K(mg/L)	0	0.98	1.3	1.16	1.18	1.1	1.36	1.14
Al (mg/L)	0	0.86	1.88	2.08	2.24	2.3	2.38	2.38

Table A2.2: Detailed results from the Experiment with MB at 60°C and 80 bars

Sample no.	0	1	2	3	4	5	6	7	8
Reaction Time(hours)	0	3	8	24	50	73.75	98.5	122.53 33	141.95
Volume of brine in reactor (L)	0.380	0.373	0.3656	0.3586	0.3516	0.3444	0.3369	0.3294	0.3214
Calculated in-situ pH		3.598	3.759	4.067	4.147	4.201	4.250	4.265	4.280
Measured alkalinity HCO_3^- (mg/L)	0	94.6	95.8	342.8	479.5	566.1	642.3	674.1	686.9
Ca(mg/L)	0	2.9	2.7	3.2	3.7	3.9	4.1	4.1	4.4
Mg(mg/L)	0	10.0	19.1	37.4	53.3	61.6	70.2	73.0	75.6
Si(mg/L)	0	11.0	21.2	41.5	58.2	67.0	75.6	77.8	80.7
Fe ^{total} (mg/L)	0	8.7	22.4	53.1	78.5	92.8	105.6	111.0	115.1
Na(mg/L)	0	7.4	4.6	24.5	7.0	6.1	5.9	6.0	6.1
K(mg/L)	0	3.8	2.5	3.6	3.5	3.6	3.9	2.1	3.4
Al (mg/L)	0	1.2	1.2	0.8	0.6	0.4	0.4	0.4	0.3

Table A2.3: Detailed results from the Experiment with MB at 100°C and 120 bars

Sample no.	0	1	2	3	4	5	6	7
Reaction Time(hours)	0	3	31.3	56.1	80.15	106.2	130.2	151.45
Volume of brine in reactor (L)	0.271	0.264	0.256	0.249	0.242	0.234	0.226	0.218
Calculated in-situ pH		3.798	3.935	4.045	4.112	4.113	4.144	4.186
Measured alkalinity HCO_3^- (mg/L)	0	89.67	163.48	237.29	291.58	294.02	326.35	363.56
Ca(mg/L)	0	3.9	4.7	5.4	5.9	6.3	6.6	7.2
Mg(mg/L)	0	9.6	17.9	24.3	28.7	28.9	31.6	34.5
Si(mg/L)	0	15.2	32.8	43.5	49.5	51.2	53.3	58.2
Fe ^{total} (mg/L)	0	11	24.3	34.9	40.2	39.7	43.2	49.4
Na(mg/L)	0	13.6	5.4	6.6	9.2	9.1	9.9	11
K(mg/L)	0	1.1	4.2	3.9	4.3	4.1	3.2	4.1
Al (mg/L)	0	0.2	0.1	0.1	0.1	0.1	0.1	0.2

Table A2.4: Detailed results from the Experiment with VB at 25°C and 5 bars

Sample no.	0	1	2	3	4	5	6	7
Reaction Time(hours)	0	3	30	54	78	100	124	144
Volume of brine in reactor (L)	0.380	0.372	0.3635	0.3555	0.347	0.3385	0.3304	0.3215
Calculated in-situ pH		3.789	4.026	4.068	4.094	4.103	4.117	4.130
Measured alkalinity HCO_3^- (mg/L)	0	26.84	64.05	75.03	77.47	77.47	86.01	82.96
Ca(mg/L)	0	2.2	4.36	4.96	5.24	5.38	5.5	5.66
Mg(mg/L)	0	1.44	3.14	3.56	3.8	3.88	4	4.12
Si(mg/L)	0	1.04	4.18	5.3	6	6.42	6.94	7.24
Fe ^{total} (mg/L)	0	0.72	5.24	6.14	6.54	6.66	6.98	7.1
Na(mg/L)	0	2.68	5.02	5.46	5.74	5.94	6.2	6.48
K(mg/L)	0	0.44	0.78	1.04	1.32	1.24	1.14	1.22
Al (mg/L)	0	0.38	0.84	0.9	1.04	1.1	1.2	1.28

Table A2.5: Detailed results from the Experiment with VB at 60°C and 80 bars

Sample no.	0	1	2	3	4	5	6	7	8
Reaction Time(hours)	0	3	7.15	27.2	54.2	78.3	100.25	122.16	142.46
Volume of brine in reactor (L)	0.380	0.373	0.365	0.358	0.350	0.342	0.334	0.326	0.317
Calculated in-situ pH		3.507	3.643	3.810	3.953	4.009	4.080	4.103	4.124
Measured alkalinity HCO_3^- (mg/L)	0	85.4	115.9	206.18	298.29	370.88	398.94	434.32	462.38
Ca(mg/L)	0	4.1	5.2	6.2	7.3	7.5	8.1	8.1	8.2
Mg(mg/L)	0	5.1	7.4	12.3	17.1	19.8	23.5	24.6	25.7
Si(mg/L)	0	6.3	11.4	22.5	34	40.2	47.8	50.9	53.4
Fe ^{total} (mg/L)	0	11.3	21.4	42.6	70.5	85.6	104.1	112	117.4
Na(mg/L)	0	4.3	6.3	6.5	7.6	8	9	9.3	10.3
K(mg/L)	0	3.5	3.3	2.7	3.7	1.8	2.6	1.8	4.1
Al (mg/L)	0	0.5	0.9	1	0.5	0.4	0.6	0.6	0.5

Table A2.6: Detailed results from the Experiment with MB at 100°C and 120 bars

Sample no.	0	1	2	3	4	5	6	7
Reaction Time(hours)	0	3	30	54.1	78.1	102.1	125.55	146
Volume of brine in reactor (L)	0.272	0.264	0.257	0.249	0.241	0.233	0.225	0.217
Calculated in-situ pH		3.958	4.166	4.251	4.271	4.294	4.274	4.303
Measured alkalinity HCO_3^- (mg/L)	0	204.96	359.9	410.53	437.98	466.04	450.18	475.19
Ca(mg/L)	0	6.4	8.7	11.2	10.3	10.8	10.5	11
Mg(mg/L)	0	12.2	19.5	22.6	23.3	25.2	22	23.8
Si(mg/L)	0	25.2	55	68	75.4	78.5	77.4	82.3
Fe ^{total} (mg/L)	0	39.1	74.7	92.9	100.6	102.5	101.3	107.5
Na(mg/L)	0	5.8	10.6	13.8	14.7	17.6	18.1	19.9
K(mg/L)	0	4.3	2.4	5.2	5.1	5.6	4.5	5.9
Al (mg/L)	0	0.1	0.1	0.1	0.1	0.1	0	0.1

Table A2.7: Detailed results from the Experiment with 20g of MB at 60°C and 80 bars

Sample no.	0	1	2	3	4	5	6	7
Reaction Time(hours)	0	1.60	2.42	20.00	27.41	31.07	98.07	142.82
Volume of brine in reactor (L)	0.380	0.374	0.366	0.357	0.349	0.342	0.336	0.330
Calculated in-situ pH	0	3.642	3.715	4.166	4.279	4.374	4.421	4.432
Measured alkalinity HCO_3^- (mg/L)	0	134.2	146.4	618.54	674.66	799.1	941.84	978.44
Ca(mg/L)	0	7.8	8.4	11.6	13	14.1	14.2	14.9
Mg(mg/L)	0	10.7	14	52.9	70.3	89.2	97.9	101.9
Si(mg/L)	0	13.6	17.5	61	80.4	100	106.2	112
Fe ^{total} (mg/L)	0	8.7	13.4	74.6	107.2	141.7	157.2	171.6
Na(mg/L)	0	11.2	11.5	14.8	16.5	18.3	20.5	22.3
K(mg/L)	0	bl	bl	bl	bl	1	16	2.1
Al (mg/L)	0	0.3	0.3	0.2	0.3	0.3	0.3	0.3

bl: below detection limit

Table A2.8: Release rate ($\text{mol m}^2 \text{s}^{-1}$) calculated from the Experiment with MB at 25°C and 5 bars

Time (hours)	Ca	Fe	Mg	Na	Al	K	Si
0	0	0	0	0	0	0	0
3	1.2E-10	8.6E-11	2.0E-10	3.0E-10	1.2E-10	9.5E-11	2.7E-10
27	1.2E-11	1.9E-11	3.3E-11	3.1E-11	1.7E-11	3.5E-12	5.7E-11
51.2	-3.5E-13	6.5E-12	1.2E-11	1.3E-12	2.6E-12	-1.9E-12	1.6E-11
75.2	-1.8E-13	5.3E-12	9.3E-12	1.4E-12	1.8E-12	-9.5E-14	1.3E-11
99.2	2.7E-13	4.5E-12	6.7E-12	2.1E-12	1.2E-13	-1.2E-12	9.3E-12
123.2	-4.2E-13	3.9E-12	6.3E-12	8.2E-13	3.6E-13	2.5E-12	6.9E-12
143.05	-1.5E-12	-1.1E-12	-1.7E-12	-7.7E-12	-1.5E-12	-3.4E-12	-2.2E-12

Table A2. 9: Release rate ($\text{mol m}^2 \text{s}^{-1}$) calculated from the Experiment with MB at 60°C and 80 bars

Time (hours)	Ca	Fe	Mg	Na	Al	K	Si
0	0	0	0	0	0	0	0
3	2.8E-10	5.9E-10	1.6E-09	1.2E-09	1.7E-10	3.7E-10	1.5E-09
8	-1.4E-11	5.4E-10	8.2E-10	-2.9E-10	-2.0E-12	-7.9E-11	8.0E-10
24	7.7E-12	3.7E-10	5.1E-10	5.9E-10	-1.1E-11	1.8E-11	4.9E-10
50	4.5E-12	1.8E-10	2.6E-10	-3.2E-10	-3.3E-12	-1.8E-12	2.3E-10
73.75	1.4E-12	1.0E-10	1.3E-10	-2.0E-11	-3.5E-12	3.1E-13	1.2E-10
98.5	1.2E-12	8.0E-11	1.2E-10	-6.1E-12	-1.4E-13	2.3E-12	1.1E-10
122.5	-9.8E-13	2.3E-11	2.1E-11	-6.3E-13	-1.4E-13	-2.0E-11	7.2E-12
141.95	2.5E-12	1.2E-11	1.6E-11	-1.1E-12	-2.1E-12	1.6E-11	1.7E-11

TableA2.10: Release rate ($\text{mol m}^2 \text{s}^{-1}$) calculated from the Experiment with MB at 100°C and 120 bars

Time (hours)	Ca	Fe	Mg	Na	Al	K	Si
0	0	0	0	0	0	0	0
3	3.7E-10	7.4E-10	1.5E-09	2.2E-09	2.8E-11	1.1E-10	2.0E-09
31.3	6.6E-12	9.0E-11	1.3E-10	-1.5E-10	-1.5E-12	3.0E-11	2.4E-10
56.1	6.1E-12	7.7E-11	1.0E-10	2.0E-11	-4.5E-14	-4.6E-12	1.5E-10
80.15	3.6E-12	3.3E-11	6.5E-11	4.5E-11	-4.8E-14	3.1E-12	7.2E-11
106.2	2.0E-12	-1.2E-11	-1.1E-11	-6.6E-12	-4.6E-14	-3.3E-12	1.6E-12
130.2	7.5E-13	1.5E-11	2.8E-11	8.3E-12	-5.4E-14	-1.1E-11	3.8E-12
151.45	3.9E-12	3.6E-11	3.2E-11	1.4E-11	1.6E-12	8.8E-12	4.6E-11

Table A2.11: Release rate of cations calculated from the Experiment with VB at 25°C and 5 bars

Time (hours)	Ca	Fe	Mg	Na	Al	K	Si
0	0	0	0	0	0	0	0
3	8.7E-11	2.0E-11	9.4E-11	1.9E-10	2.2E-11	1.8E-11	5.9E-11
30	9.1E-12	1.4E-11	1.2E-11	1.7E-11	2.9E-12	1.5E-12	1.9E-11
54	2.4E-12	2.7E-12	2.7E-12	2.7E-12	2.9E-13	1.2E-12	6.9E-12
78	7.3E-13	8.3E-13	1.2E-12	1.2E-12	8.1E-13	1.2E-12	3.8E-12
100	4.1E-14	-1.6E-13	-1.3E-13	4.8E-13	2.5E-13	-5.7E-13	1.9E-12
124	-5.2E-14	5.0E-13	1.8E-13	8.8E-13	4.8E-13	-5.9E-13	2.3E-12
144	4.0E-14	-2.7E-13	7.9E-14	9.7E-13	3.6E-13	2.6E-13	7.9E-13

Table A2.12: Release rate of cations calculated from the Experiment with VB at 60°C and 80 bars

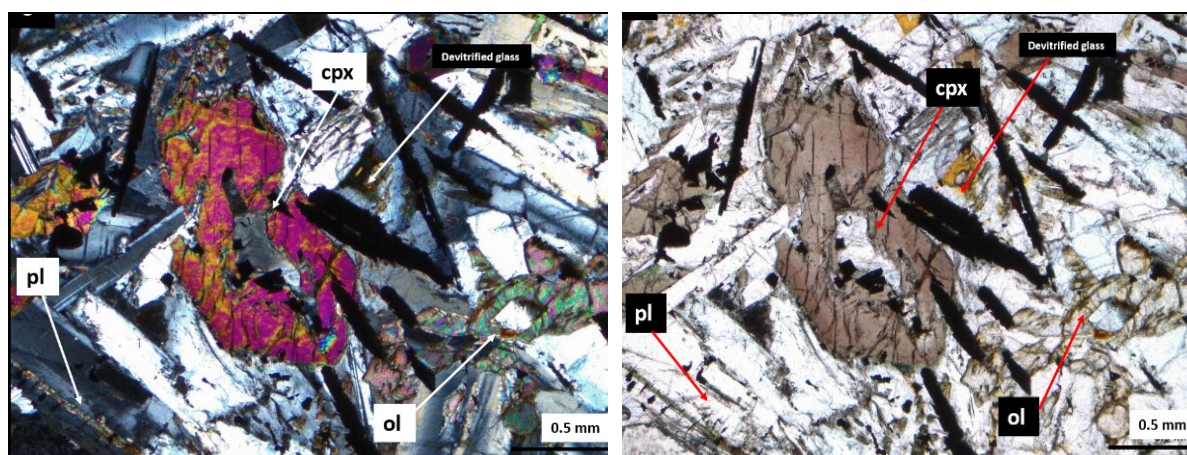
Time (hours)	Ca	Fe	Mg	Na	Al	K	Si
0	0	0	0	0	0	0	0
3	1.63E-10	3.22E-10	3.34E-10	2.98E-10	2.95E-11	1.42E-10	3.57E-10
7.15	2.86E-11	1.99E-10	1.02E-10	9.37E-11	1.63E-11	-7.84E-12	1.99E-10
27.2	5.14E-12	8.52E-11	4.48E-11	7.82E-13	7.01E-13	-3.88E-12	8.87E-11
54.2	3.93E-12	7.98E-11	3.07E-11	6.80E-12	-3.22E-12	3.96E-12	6.47E-11
78.3	1.42E-13	4.38E-11	1.72E-11	1.77E-12	-7.51E-13	-9.23E-12	3.50E-11
100.25	2.04E-12	5.74E-11	2.58E-11	6.85E-12	1.37E-12	3.77E-12	4.60E-11
122.16	-9.46E-13	1.82E-11	4.10E-12	6.54E-13	-1.04E-13	-4.21E-12	1.31E-11
142.46	-6.49E-13	7.94E-12	3.30E-12	6.40E-12	-8.67E-13	1.15E-11	7.50E-12

Table A2.13: Release rate of cations calculated from the Experiment with VB at 100°C and 120 bars

Time (hours)	Ca	Fe	Mg	Na	Al	K	Si
0	0	0	0	0	0	0	0
3	2.5E-10	1.1E-09	7.9E-10	4.0E-10	5.9E-12	1.7E-10	1.4E-09
30	9.1E-12	1.1E-10	4.9E-11	3.5E-11	-1.7E-14	-8.8E-12	1.8E-10
54.1	1.0E-11	5.2E-11	1.9E-11	2.3E-11	-2.3E-14	1.3E-11	7.4E-11
78.1	-5.6E-12	1.6E-11	-2.3E-14	3.7E-12	-2.1E-14	-1.2E-12	3.4E-11
102.1	6.3E-13	-4.9E-12	7.9E-12	1.8E-11	-2.2E-14	1.4E-12	3.1E-12
125.55	-2.9E-12	-1.5E-11	-2.9E-11	-7.6E-13	-6.6E-13	-5.7E-12	-2.3E-11
146	4.2E-13	7.6E-12	7.4E-12	9.0E-12	7.1E-13	6.0E-12	1.3E-11

Table A2.14: Release rate of cations calculated from the Experiment with 20g MB at 60°C and 80 bars

Time (hours)	Ca	Fe	Mg	Na	Al	K	Si
0	0	0	0	0	0	0	0
1.6	4.9E-10	3.9E-10	1.1E-09	1.2E-09	2.8E-11	0.0E+00	1.2E-09
2.42	5.1E-11	5.1E-11	6.1E-10	1.1E-11	-1.2E-12	0.0E+00	6.2E-10
20.00	1.6E-11	1.6E-11	3.5E-10	2.9E-11	-8.7E-13	0.0E+00	3.3E-10
27.41	1.4E-11	2.8E-10	3.3E-10	2.9E-11	1.8E-12	-1.4E-11	3.2E-10
31.07	2.1E-11	5.8E-10	7.2E-10	6.5E-11	-2.1E-13	5.4E-11	6.4E-10
98.07	-2.3E-13	1.2E-11	1.5E-11	4.3E-12	-1.2E-14	2.1E-11	8.2E-12
142.82	8.7E-13	1.6E-11	7.2E-12	-6.4E-12	1.4E-13	-2.9E-11	1.1E-11

**Figure.A2.1:** Photomicrographs of samples of vesicular basalts from Port Fairy showing the major mineralogy under XPL and PPL view. Pl- plagioclase; Cpx- clinopyroxene; Ol-olivine

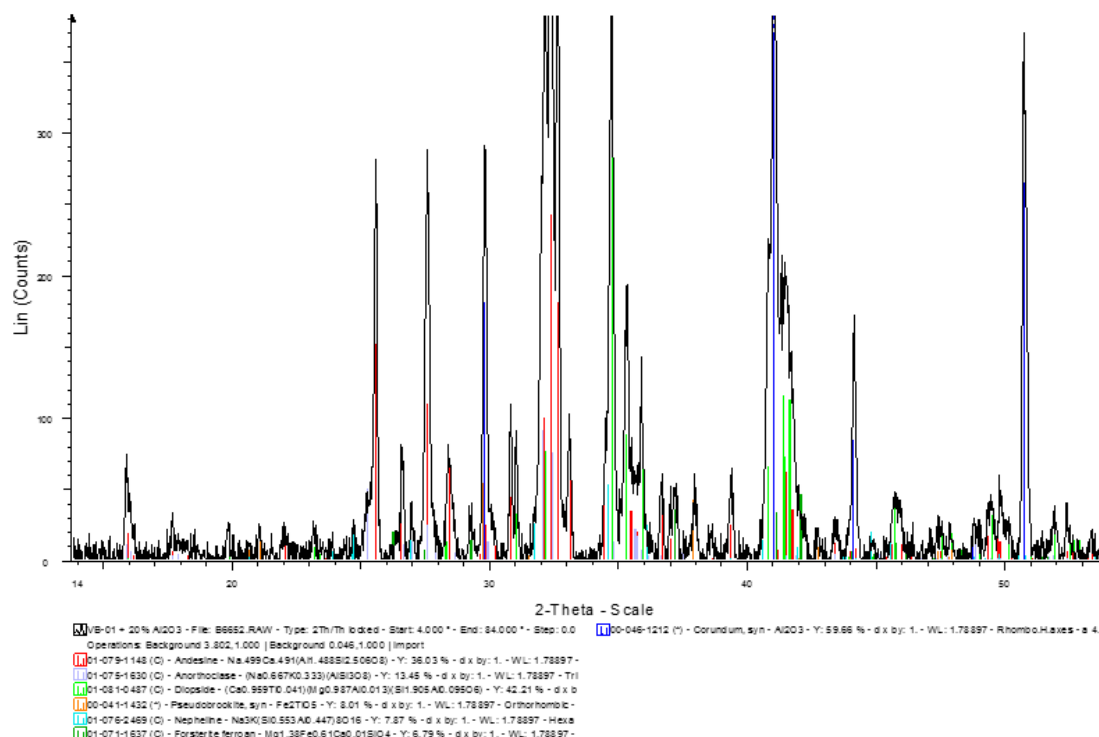


Figure A2.2. X-ray diffraction pattern of vesicular basalt of experimental powdered samples. The XRD pattern shows presence of andesine(plagioclase), anorthoclase (alkali feldspar), diopside(pyroxene), forsterite ferroan(olivine), and accessory minerals (nepheline, apatite and pseudobrookite)

Table A2.1: Chemical composition of vesicular basalt (VB) from Port Fairy obtained by microprobe analysis

Component (wt. %)	Py	Ol	Pl	Alk	Opq
SiO ₂	47.95	35.24	55.52	56.59	0.01
TiO ₂	2.51	0.06	0.19	0.18	53.39
Al ₂ O ₃	3.61	0.20	27.2	26.7	0.02
Cr ₂ O ₃	0.00	0.00	0.01	0.01	0.03
FeO	12.3	37.77	0.47	0.49	45.38
V ₂ O ₃	0.09	0.02	0.02	0.00	0.16
MnO	0.21	0.50	0.04	0.02	0.79
MgO	11.99	25.93	0.09	0.06	1.80
ZnO	0.03	0.12	0.00	0.01	0.00
NiO	0.04	0.11	0.02	0.02	0.00
K ₂ O	0.00	0.06	0.52	0.60	0.01
Na ₂ O	0.61	0.10	6.11	6.65	0.00
CaO	20.45	0.42	9.42	8.50	0.01
Nb ₂ O ₅	0.05	0.05	0.06	0.02	0.04
Sum	99.66	100.5	99.6	99.8	106.55

Py – pyroxene; Ol – olivine; Pl-plagioclase feldspar; Alk- alkali feldspar; Opq-opaque mineral