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Marine cements reveal the structure of an anoxic, ferruginous Neoproterozoic ocean

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2 Supplementary data files (including three tables; two diagrams and text)

Abstract

Neoproterozoic oceans provided the setting for the rise of animals, yet little is known of their chemical composition. Marine carbonates from the Cryogenian Oodnaminta Reef Complex, South Australia, reveal the chemical structure of a Neoproterozoic ocean. Pseudo-depth profiles from shallow- to deep-water reef facies have been constructed from geochemical and sedimentological analysis of marine cements. Evidence suggests that under peritidal oxic/anoxic chemocline, the water column was largely anoxic, strongly ferruginous and had a chemistry profoundly different from modern seawater. These geochemical data suggest early Archean-like conditions for this Late Cryogenian ocean, posing problems for metazoan evolution in extremely anoxic conditions.

Supplementary material: detailed methods and data tables are available at www.geolsoc.org.uk/SUP00000.

The slow buildup of oxygen in the ocean-atmosphere system is arguably the most important evolutionary process in Earth history. Oxygenation of the Earth's surface environments probably occurred in two major episodes, the first; the Great Oxidation Event (Bekker et al., 2004) (~2400-2200 Ma), and the second; the Neoproterozoic Oxygenation Event (Och and Shields-Zhou, 2012) (~800-540 Ma). This latter event is implicated in the evolution of animals and other complex organisms during the Neoproterozoic (Canfield et al., 2007). However, oxygenation was not a simple one-way process (e.g. Lyons et al., 2014) and the details of Precambrian ocean chemistry remain poorly understood.

Geochemical studies of Cryogenian and Ediacaran marine sediments indicate that there was a large increase in oxygenation of the oceans during the late Neoproterozoic (Canfield et al., 2007; Och and Shields-Zhou, 2012). Shale geochemistry (iron speciation, trace metals, rare earth element (REE) and several isotope systems) has been the main tool used to constrain Neoproterozoic ocean redox to date. But there are a number of complications in using shales as paleoceanographic proxies. While sediments may record ocean redox conditions, it is often difficult to distinguish between water-mass chemistry and pore-water chemistry, and even more difficult to constrain chemical depth gradients (Piper and Calvert, 2009). Furthermore, deciphering seawater signatures from detrital contamination is problematic. Marine carbonates, which record the chemistry of the parent seawater via trace element incorporation during precipitation, offer a potentially more direct way of determining ancient ocean chemistry (Webb and Kamber 2000; Kamber and Webb, 2001; 2007; Nothdurft et al., 2004). Carbonate microbialites have been successfully used in paleoredox studies (Kamber and Webb, 2007). However, marine cements should record the most reliable marine chemical signatures because they are chemical precipitates that do not incorporate significant detrital material (Nothdurft et al., 2004).

A major problem in using carbonates to monitor Neoproterozoic seawater chemistry has been the apparent lack of primary marine precipitates. Marine carbonates of this age are thought to be dominated by an originally aragonitic mineralogy (Hardie, 2003) (which is dolomitised, or converts to calcite during diagenesis and loses its marine chemical signature). However, the recognition of marine dolomite cements from Cryogenian reef complexes (Hood et al., 2011; Hood and Wallace, 2012), provides for the first time,

55 an opportunity to directly analyse unaltered marine precipitates from the Neoproterozoic. Evidence for the
56 primary dolomite mineralogy of these reefal marine cements has been documented in detail and includes
57 both the consistently length-slow nature of the cements and the well-preserved primary growth zonation
58 observed in cathodoluminescent microscopy (Hood and Wallace, 2012; Hood et al., 2011). Additional
59 sedimentological evidence includes the presence of these dolomite marine cements in allochthonous reef
60 blocks in debris flows associated with reef progradation.
61 As these dolomite cements are a product of marine diagenesis in an open reef system and have
62 accordingly precipitated in largely unmodified seawater, they should record the redox state of the water
63 column (e.g. Nothdurft et al., 2004). Geochemical analysis of these dolomite cements reveals the chemical
64 and redox structure of a Cryogenian ocean from the surface to approximately one kilometre depth.
65
66 **Background Geology and Sedimentology**
67 The marine cements analysed in this study are derived from the Late Cryogenian Oodnaminta Reef
68 Complex, consisting of a series of reefal platforms with kilometre-scale relief, in the northern Flinders
69 Ranges, South Australia (Giddings et al., 2009). Although few age constrains exist in this Adelaidean
70 Cryogenian sequence, the upper part of the underlying Sturtian diamictites has been dated at 658Ma using
71 zircon U-Pb dating (Fanning and Link, 2008). The overlying Marinoan glaciation in Australia has been
72 recently dated to terminate at ~636 Ma (Calver et al., 2013). Therefore reef formation is thought to have
73 occurred at approximately 650Ma.
74 The reefs are developed in the dolomitic Balcanoona Formation and generally comprise a
75 relatively flat back-reef platform and a reef margin with two distinct frameworks (Giddings et al., 2009).
76 Shoreward, and laterally equivalent to the reefs, the peritidal facies of the Angepena Formation consist of
77 hematitic dolomites and dolomitic shales (Fromhold and Wallace, 2011). Depositional components of the
78 reefs were originally composed of $CaCO_3$, but were dolomitised by seawater immediately after their
79 formation (Hood and Wallace, 2012; Hood et al., 2011).
80 We categorize the dolomite marine cements by their depositional facies within the reef complex,
81 which from shallowest to deepest are: 1. Nearshore peritidal (~0-2m water depth); 2. Shallow marine

platformal (~0-25m water depth); and 3. deep marine margin (~25m to 1km water depth) (abbreviated as nearshore, shallow and deep respectively). Shallow and deep facies are representative of open marine conditions.

'Nearshore' marine cements are hosted by large sheet cavities within hematitic oolitic, intraclastic or micritic dolomites of the Angepena Formation (Fromhold and Wallace, 2011). The presence of abundant teepees and mudcracks within the Angepena Formation provide evidence of a peritidal environment of deposition for this facies. Frequently, ooids from this facies contain hematitic laminae.

The 'shallow' marine cements occur in sheet cavities in the platformal facies of the Balcanoona Formation (Giddings et al., 2009; Giddings and Wallace, 2009). These comprise oolitic, intraclastic and micritic dolomites with a complete absence of hematitic lithologies. The shallow marine origin of the facies is indicated by their stratigraphic position within the reef complexes (Giddings et al., 2009; Giddings and Wallace, 2009), the abundance of fenestral and oolitic lithologies, and the presence of stalactitic marine cements (indicating intermittent intertidal conditions).

The deep marine margin facies consists of a non-stromatolitic reef framework that underlies a 200-300 m thick stromatolitic framework facies. The stratigraphic position of this facies within the reef complex indicates a deep marine environment (200 to 1000m water depth) (Giddings et al., 2009; Giddings and Wallace, 2009). 'Deep' marine cements occur within growth cavities, and within neptunean dykes in this facies.

Marine cements from each of the facies have distinctive optical and cathodoluminescence characteristics. Nearshore cements may have radial-slow, fascicular-slow or radiaxial slow optical fabrics (Hood and Wallace, 2012), and are generally characterized by well-preserved non- and bright cathodoluminescent zoning. In thin section, nearshore cements may have micro-inclusions of hematite, giving a reddish colour in transmitted light. In contrast, most shallow and deep cements are characterized by radial and fascicular slow fabrics and have weakly dull luminescent zonation.

Methods

The petrology and cathodoluminescence character of cements was used as a first step in sample selection. In order to avoid silicate or oxide contamination during analysis, dolomite marine cement analyses were only taken from clean, well preserved samples with sharp, well-preserved cathodoluminescent zonation. Samples with diffuse zonation, areas of recrystallisation, thin carbonate-filled fractures, or non-carbonate inclusions were rejected. Major element concentrations (including Fe and Ca) were analysed using a Cameca SX50 Electron Microprobe at the University of Melbourne with an 80s count time, an accelerating voltage of 15kV, and a beam current of 35nA. LA-ICP-MS analyses were carried out on the same samples using a Helex 193 nm ArF excimer laser ablation system connected to an Agilent 7700x quadrupole ICP-MS at the School of Earth Sciences, the University of Melbourne (after Woodhead et al., 2007). An ablation spot size of 93 μm was used, with a laser repetition rate of 10Hz for 60 seconds of ablation time. Samples were analysed in blocks of ~50 analyses, with a NIST SRM612 standard analysed every ~7 samples. Data was standardized to Ca (measured by electron microprobe) and reduced by Iolite Software (Paton et al., 2011). The ICP-MS was tuned to give low oxide levels (ThO/Th <0.25%). Analyses from petrologically unaltered samples were further screened using very stringent geochemical contamination factors (e.g. Th<0.01, Al<10 ppm, total REE<4 ppm, and coherent REE profiles), tens to hundreds of times lower than previously used for silicate and oxide contamination (Nothdurft et al., 2004; Ling et al., 2013). Detailed methods are available in Supplementary data (**)

Geochemical Results and Discussion

Iron and Manganese

Uncontaminated marine cements record significant chemical variation between near-shore, shallow and deep facies. Electron microprobe analysis reveals high levels of Fe in cements from the shallow and deep cements (mean: 2300 and 3400 ppm respectively) (Fig. 1). In contrast, nearshore cements have low Fe contents, (mean 360 ppm, just above limit of detection). Individual Mn analyses of the nearshore cements reveals that most of this cement has very low levels of Mn (e.g. 10 ppm), with some spots giving very high values (e.g. 1800 ppm). In the shallow and deep cements, spot analyses for Mn have more uniform concentrations that correlate well with Fe.

This Fe-Mn behaviour indicates that the nearshore cements were precipitated in oxic/suboxic conditions (where Fe is absent, but Mn may or may not be present) and the shallow and deep cements were precipitated in anoxic conditions (where both Fe and Mn are present)(Barnaby and Rimstidt, 1989). The cathodoluminescent character of the cements, from non- to bright-luminescent in the nearshore cements, and generally dull-luminescent in the shallow and deep cements reinforces this observed geochemical gradient. This interpretation is also consistent with the abundance of hematitic ooidal laminae and other synsedimentary iron oxides in the nearshore facies and their complete absence in the shallow and deep facies. Together, this petrology, sedimentology and geochemistry indicates that with the exception of the uppermost few metres in the nearshore zone, the entire water column was anoxic and strongly ferruginous.

Trace metals

The nearshore facies cements show significant enrichment in the elements Cd, Cu, Co, Ni, and U, and depletion in Ba, Cr, Th and total REE, relative to the deeper water facies (Fig. 1). The most extreme enrichments are in Cd and Cu, with average Cu abundance being two orders of magnitude greater than in deeper water facies.

Copper and Cd have this behaviour in modern anoxic basins; being enriched in shallow oxic water and strongly depleted in the deeper anoxic water (Calvert and Pedersen, 1993). The disappearance of these metals from the anoxic water in the modern basins is explained by the formation of Cu and Cd sulfides (Jacobs et al., 1985). Thermodynamic modelling shows that sulfide can be present to some degree even in a highly ferruginous ocean because of the formation of aqueous metal-sulfide complexes which buffer total sulfide in the system (Saito et al., 2003). Cu and Cd have such a strong affinity for reduced sulfur that these metals form metals-sulfides in preference to metals like Fe, Mn, Ni, and Co. In particular, Cd has only one valence state and a very strong affinity for sulfide (Saito et al., 2003), indicating that large changes in its concentration between facies represents a change in the presence of dissolved sulphide rather than simply a change in redox.

The relative depletion of Ba in the oxic peritidal cements is a corollary for the depletion of Cd in the anoxic facies. Barium has a strong affinity for sulfate, forming the mineral barite. The depletion in Ba in the oxic/suboxic peritidal cements is likely a result of the presence of sulfate in this nearshore environment. The different behaviours of Ba and Cd are therefore reflecting the presence of the sulfate/sulfide interface between the nearshore facies and the more open marine (shallow and deep) facies. The dissolution of barite (and resulting release of Ba) across this interface should account for the high concentrations of Ba in shallow water settings.

Similarly, Cr has lowest concentrations in nearshore cements and highest concentrations in shallow water cements. However, Cr will be scavenged by (Fe-) oxides rather than dissolved sulphide (Calvert and Pedersen, 1993), and so it's peak concentrations should occur just below the level of Fe-oxide dissolution, reinforcing the presence of a peritidal redoxcline. The distribution of uranium, with highest concentrations in peritidal cements, and negligible concentrations in deeper cements also reflects the presence of this redox interface. Uranium has a soluble form in oxic seawater (i.e. nearshore facies), but will be removed from anoxic waters at the level that Fe-reduction occurs (by shallow marine facies) (Calvert and Pedersen, 1993).

Rare Earth Elements and Yttrium

The nearshore, shallow and deep cements display distinctive rare earth element-Yttrium (REY) profiles (Fig. 2). These elements are more abundant in the anoxic deep-water cements than in the oxic nearshore cements.

Rare earth element distributions in modern anoxic basins show similar enrichment in anoxic waters relative to oxic waters because of particle scavenging by Mn/Fe oxides (de Baar et al., 1988; Elderfield et al., 1988). These oxides are precipitated in the upper oxic waters, scavenge REYs, and then sink to be re-dissolved in the deeper anoxic waters releasing the REYs. Consistent with this hypothesis, Fe is strongly correlated with REYs in the shallow and deep cements.

The REY profiles for the shallow and deep water cements are dramatically different from Phanerozoic marine signatures, showing little to no light REE depletion, displaying a convex shape

188 (middle REE enriched) and having slight positive Eu and Y/Ho anomalies with a weakly positive Ce
189 anomaly. Ce and Eu anomalies have been calculated as "true" (vs. "apparent") using the calculations of
190 Bau and Dulski, (1996) and Kamber and Webb, 2001)(See Supplementary data).
191 These characteristics are instead consistent with an anoxic marine chemistry. The lack of light
192 REE depletion is found in anoxic marine basins (Bau and Möller, 1993), while middle REE enriched
193 profiles are found in anoxic ferruginous lakes, hydrothermal oceanic plumes and anoxic diagenetic waters
194 (Johannesson and Zhou, 1999; Sherrell et al., 1999; Haley et al, 2004). Middle REE enrichment has been
195 suggested as being due to anoxic dissolution of iron-oxides, a process which is likely to have occurred in
196 these Cryogenian oceans (Haley et al., 2004). Europium anomalies, also a feature of anoxic marine waters
197 (the strongly positive hydrothermal Eu signature being preserved in anoxic waters) (Bau, 1991) are
198 strongest in deep water cements. The preservation of this high-temperature Eu signature in open marine
199 settings (reefal cements) is reliant on widespread deep-water anoxia from source (i.e. mid-ocean ridge) to
200 continental margin in this fully marine basin. Therefore these positive Eu anomalies are compelling
201 evidence for extensive marine anoxia in Cryogenian oceans. The absence of negative Ce anomalies is
202 similarly a function of anoxic marine chemistry (Ce unlike other trivalent REEs can be oxidized to Ce
203 (IV) in oxic sea water producing negative Ce anomalies) (Bau and Koschinsky, 2009). Significantly,
204 Archean carbonates commonly show similar REY profiles, interpreted as being due to deep water anoxia,
205 but Archean profiles seldom show the middle REE enrichment found in these Cryogenian marine cements
206 (Kamber et al., 2004). This pattern may be the result of an extensive, almost completely anoxic water
207 column in the Cryogenian.
208
209 **Summary and Implications**
210 For the first time, direct marine carbonate precipitates from Neoproterozoic seawater have been
211 geochemically analysed to determine the structure of a Cryogenian ocean. The sum of this geochemical
212 and sedimentological data suggests that these Cryogenian marine cements have precipitated from a
213 severely anoxic and strongly ferruginous water column (except for the very nearshore zone, Fig. 3). This

214 nearshore oxic/suboxic layer may be restricted to coastal waters, where wave action aerates and
215 oxygenates the ocean, or is influenced by oxidised continental waters.
216 Ferruginous deep-ocean conditions have been suggested previously for the Neoproterozoic, largely
217 based on Fe speciation of shales (Canfield et al., 2008; Och and Shields-Zhou, 2012). However, the results
218 from this study provide the first independent evidence of widespread ferruginous conditions during the
219 Cryogenian. Moreover, analysis of these dolomite cements (over a sedimentologically and
220 stratigraphically defined depth range) has enabled the development a detailed redox structure of these
221 Cryogenian oceans. Carbonate geochemistry can thus provide a more refined proxy for
222 palaeoceanographic structure that builds upon the broad foundations developed via shale geochemistry.
223 The enigmatic chemistry and extreme level of anoxia in this Cryogenian ocean requires an
224 explanation. One possibility is that the basin from which these reefal carbonates are derived is not fully
225 open marine (i.e. like the modern Black Sea). However, the geology of the Adelaide Fold Belt is
226 indicative of a fully marine basin, (including the complete absence of evaporites from this Cryogenian
227 succession)(Giddings and Wallace, 2009). The rare earth element profiles, and particularly the prominent
228 positive Eu anomalies in the deep-water cements of this study point to globally anoxic conditions.
229 Moreover, other Neoproterozoic marine sediments, including banded iron formations, globally show
230 chemical evidence for ferruginous and anoxic conditions (review in Och and Shields-Zhou, 2012).
231 Perhaps the reason for the return to Archean-like conditions at this time is linked to the cause of
232 extreme climatic variations in the Neoproterozoic. However, the occurrence of such pervasive ocean
233 anoxia up to ~10 million years after the Sturtian glaciation suggests that large-scale glaciation cannot be
234 the sole cause of these ferruginous conditions. Regardless of the exact cause of this marine anoxia, this
235 carbonate geochemistry has revealed a more complex set of ocean conditions than previously suggested.
236 Significantly, we no longer consider Precambrian ocean oxygenation as a simple two-step process.
237 If this anoxic marine scenario is correct, then the view of Cryogenian oceans being the cradle of
238 metazoan evolution (Erwin et al., 2011) must be viewed in a different light. Early metazoan evolution may
239 have been restricted to oxygenated marine conditions (that developed later in the Ediacaran, or in

Cryogenian nearshore conditions) or may have occurred in these anoxic Cryogenian marine settings (Mentel and Martin, 2010).

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Figure Captions

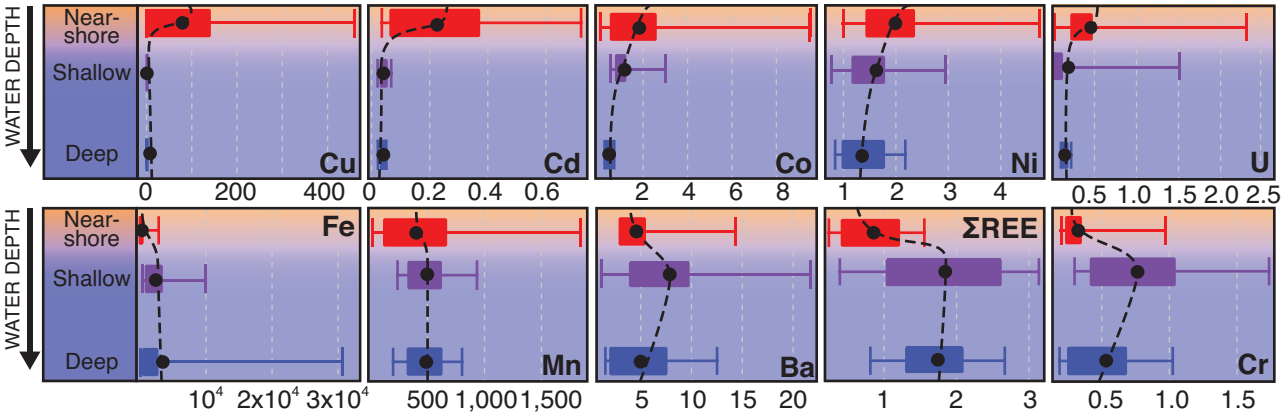

Figure 1. Pseudo-depth profiles of trace elements in this Cryogenian ocean. Average (black dot), total range of values (lines) and two sigma range (bar) are provided for nearshore, shallow and deep marine cements. Based on 55 'uncontaminated' cement analyses.

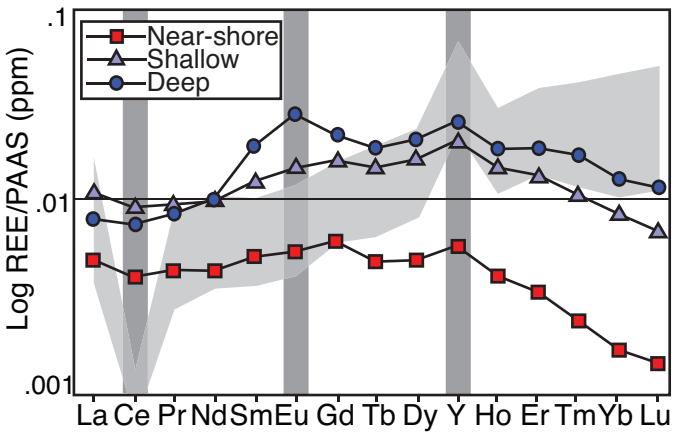

Figure 2. Average rare earth element and yttrium (REY) profiles for nearshore, shallow and deep marine cements, normalised to the post Archean Australian shale (PAAS; McLennan, 1989). The deep and shallow profiles display a middle REE enriched pattern with prominent Eu and Y anomalies, consistent

with anoxic marine conditions and very different from modern anoxic sea water (Kamber, 2010). Nearshore samples display different profiles with light REE enriched patterns.

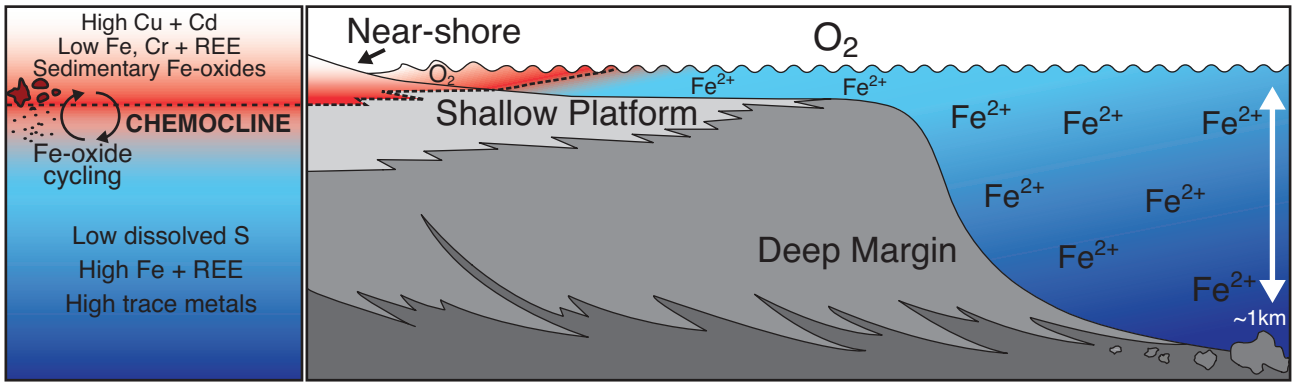

Figure 3. Conceptual model for the chemistry of Cryogenian seawater. The entire open ocean water column is anoxic and ferruginous, while nearshore marine waters are oxic/suboxic, perhaps due to an oxygenated continental influence, or to nearshore wave action in an oxidised atmosphere.