

Integrated geochemical-petrographic insights from component-selective $\delta^{238}\text{U}$ of Cryogenian marine carbonates

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ABSTRACT

Emerging geochemical proxies have improved our understanding of the broad-scale history of Earth's oxygenation. However, paleoredox work does not always include extensive consideration of sample preservation and paleoenvironmental setting. This is particularly an issue with marine carbonates, which although being potentially ideal ocean redox archives, are commonly altered during diagenesis. Here we provide new insight into the robustness of uranium isotopes ($^{238}\text{U}/^{235}\text{U}$ ratios; $\delta^{238}\text{U}$ values) as paleoredox tracers by determining texture-specific $\delta^{238}\text{U}$ values from a well-described Cryogenian (Balcanoona) reef complex in South Australia. We found high variability in $\delta^{238}\text{U}$ values between different carbonate components, even within a single sample. Petrographically, the best-preserved components from the Balcanoona reef are marine cements, which have a mean $\delta^{238}\text{U}$ value of -0.23‰ , essentially unfractionated from riverine inputs. These values are interpreted as reflecting a marine system with widespread anoxic and iron-rich settings. Less-well-preserved phases have $\delta^{238}\text{U}$ values spanning almost the entire extent of the documented isotopic range. This integrated petrographic-geochemical work demonstrates the need for petrographic analysis and careful sample selection on a case-by-case basis in future carbonate metal isotope geochemistry.

INTRODUCTION

The application of novel isotope systems to Precambrian sediments has provided valuable insights into the redox evolution of Earth's atmosphere and oceans (e.g., Frei et al., 2009; Rouxel et al., 2005; Kendall et al., 2013). Extensive recent paleoredox work has led to the development of a much more complex and likely realistic view of Earth's oxygenation than the simple two-stage oxygenation model (Holland, 2006; Lyons et al., 2014). In contrast to the traditional view, geochemical work has suggested significant fluctuations in the redox state of Proterozoic oceans and the persistence of ferruginous conditions even during the early stages of metazoan evolution (e.g., Lyons et al., 2014; Sperling et al., 2015).

Metal isotopes have the potential to continue to transform and improve our understanding of Earth's protracted oxygenation. However, many studies include little consideration of the preservation and original depositional characteristics of the sedimentary rocks being analyzed, with limited petrographic analysis. This missing link in redox-proxy work can result in geochemical data sets that may not represent marine or depositional signals. This is particularly true for carbonates where trace metal concentrations are commonly altered by post-marine diagenesis (e.g., Brand and Veizer, 1980; Swart, 2015).

Uranium isotope ($^{238}\text{U}/^{235}\text{U}$; $\delta^{238}\text{U}$) work in marine carbonates is developing as a new proxy that can track the redox state of ancient oceans (e.g., Weyer et al., 2008; Andersen et al., 2014, 2016). The $^{238}\text{U}/^{235}\text{U}$ isotope system is fractionated primarily by the biotic low-temperature (T) reduction of U^{VI} to U^{IV} as a result of the nuclear volume effect, concentrating heavy

^{238}U in the reduced product (Schauble, 2007; Stylo et al., 2015). The concentration and isotopic composition of U in seawater vary over geological time depending on marine redox conditions (Weyer et al., 2008). The U isotope composition of the modern oceans ($-0.39\text{‰} \pm 0.02\text{‰}$; Andersen et al., 2016) reflects the balance between riverine inputs (approximating the crustal composition and thought to be constant, post-Archean; $0.29\text{‰} \pm 0.03\text{‰}$; Tissot and Dauphas, 2015) and U burial in oxic, suboxic, and euxinic sediments (Dunk et al., 2002; Weyer et al., 2008; Kendall et al., 2013; Andersen et al., 2016; Fig. 1A). Authigenic reduced U phases in sediments deposited under euxinic bottom waters have the heaviest $\delta^{238}\text{U}$ values (mean = $0.03\text{‰} \pm 0.04\text{‰}$). In contrast, Fe-Mn crusts have an average $\delta^{238}\text{U}$ composition of $-0.64\text{‰} \pm 0.02\text{‰}$ (Andersen et al., 2016). Uranium removal into carbonates represents the second largest sink, and recent work on $\delta^{238}\text{U}$ in Holocene–recent Bahaman carbonates indicates that primary calcite and aragonite precipitates (mean $-0.37\text{‰} \pm 0.12\text{‰}$) preserve the $\delta^{238}\text{U}$ composition of seawater with limited fractionation, bolstering the case that uranium isotopes in carbonates can be a reliable redox proxy (Dunk et al., 2002; Romaniello et al., 2013). However, even with an improved understanding of modern marine U isotope fractionation and cycling, the U isotope proxy needs to be tested in the geological record.

Here we assess the variation in $\delta^{238}\text{U}$ between carbonate components from a well-studied carbonate system, the Cryogenian Balcanoona reef (South Australia), including ooids, finely crystalline carbonate (commonly referred to as micrite, though neomorphism has increased crystal size), marine cements, late diagenetic cements, and recrystallized carbonates

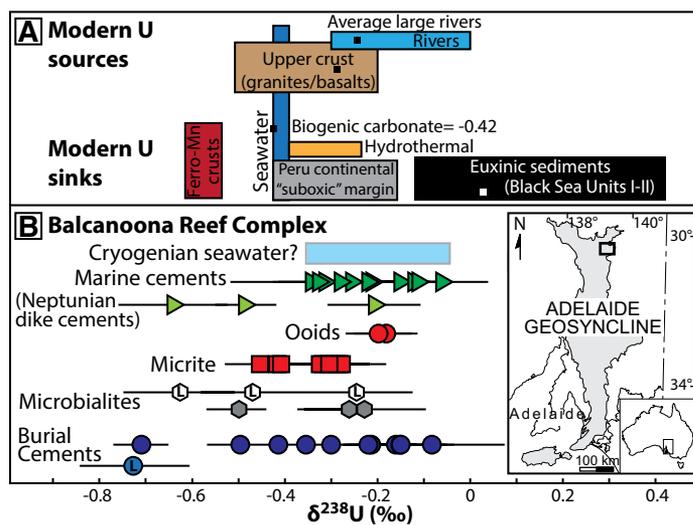


Figure 1. A: Modern seawater U isotope mass balance (Kendall et al., 2013, and references therein). B: U isotope composition of Balcanoona carbonate components. L—limestone. Inset shows the location of the Balcanoona reef complex.

in both dolomite and limestone mineralogies (Fig. 2). Our aim is to use this setting as an example to highlight the effects of variable diagenetic histories on U isotopes between microfacies. In addition, determining the most pristine seawater $\delta^{238}\text{U}$ value can contribute to our understanding of Cryogenian marine conditions.

BALCANOONA REEFS

Reef complexes from the interglacial Neoproterozoic stratigraphy of South Australia provide a setting amenable to texture-specific uranium isotope studies in ancient carbonates. Reef complexes are ideal for this test because they preserve a variety of recognizable framework and platform marine components over an identifiable paleodepth range. The ca. 650 Ma Balcanoona Formation reefs of the Adelaide Geosyncline formed extensive platforms between the Sturtian and Marinoan glaciations (Wallace et al., 2015) (Fig. 1B). These reefs developed steep margins and contain a range of well-described depositional and diagenetic carbonate components, including abundant marine cements (Fig. 2) (Hood and Wallace, 2012; Wallace et al., 2015).

Primary reefal components were precipitated originally as aragonite, but were either mimetically dolomitized by seawater within the reef, or converted to calcite in isolated reef blocks (Hood and Wallace, 2012). Abundant fibrous dolomite marine cements make crusts up to several centimeters thick in reefal cavities and neptunian dikes (intrareef syndimentary fractures, which may also be sediment filled). These cements have well-preserved cathodoluminescent (CL) chemical zonation, crystallographic features, and a length-slow optical character, indicating that they originally precipitated with a stable dolomite mineralogy and have retained the chemical signature of the parent seawater (Figs. 2E and 2F) (Hood et al., 2011; Hood and Wallace, 2014). Porosity-occluding burial

cements generally consist of coarse euhedral ferroan dolomite spar, which is often zoned and brightly luminescent under CL.

Limestone allochthonous blocks shed from the reef during margin collapse have undergone variable amounts of dolomitization. These limestones have poor fabric preservation, and depositional textures are commonly absent due to extensive recrystallization during conversion of aragonite to calcite (Hood and Wallace, 2012).

METHODS

Samples were selected for U isotope geochemistry based on their petrographic, cathodoluminescent, and geochemical characteristics (e.g., Hood and Wallace, 2014). Carbonate components were chosen from near-shore (0–2 m), shallow subtidal (2–20 m), and deep platform (>200 m paleodepth) reef facies from a range of sections through the reef platforms. The samples include depositional components, which retain original textures (e.g., tangential ooid cortices) via fabric-preserving dolomitization, and poorly preserved samples affected by mixed phases of burial cementation and/or recrystallization.

Samples were microdrilled and trace elements were measured on a Thermo Scientific Finnigan Element XR inductively coupled plasma–mass spectrometer (ICP-MS) at Yale University (Connecticut, USA) on splits from each digest. Uranium isotopes (^{233}U to ^{236}U , and ^{238}U) were measured at Yale University on a Thermo Finnigan Neptune Plus multicollector ICP-MS (following previous methods; e.g., Weyer et al., 2008; Wang et al., 2016; see the GSA Data Repository¹). External reproducibility was

¹GSA Data Repository item 2016313, age constraints, sample localities, data table, extended methods, and supplementary figures, is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org.

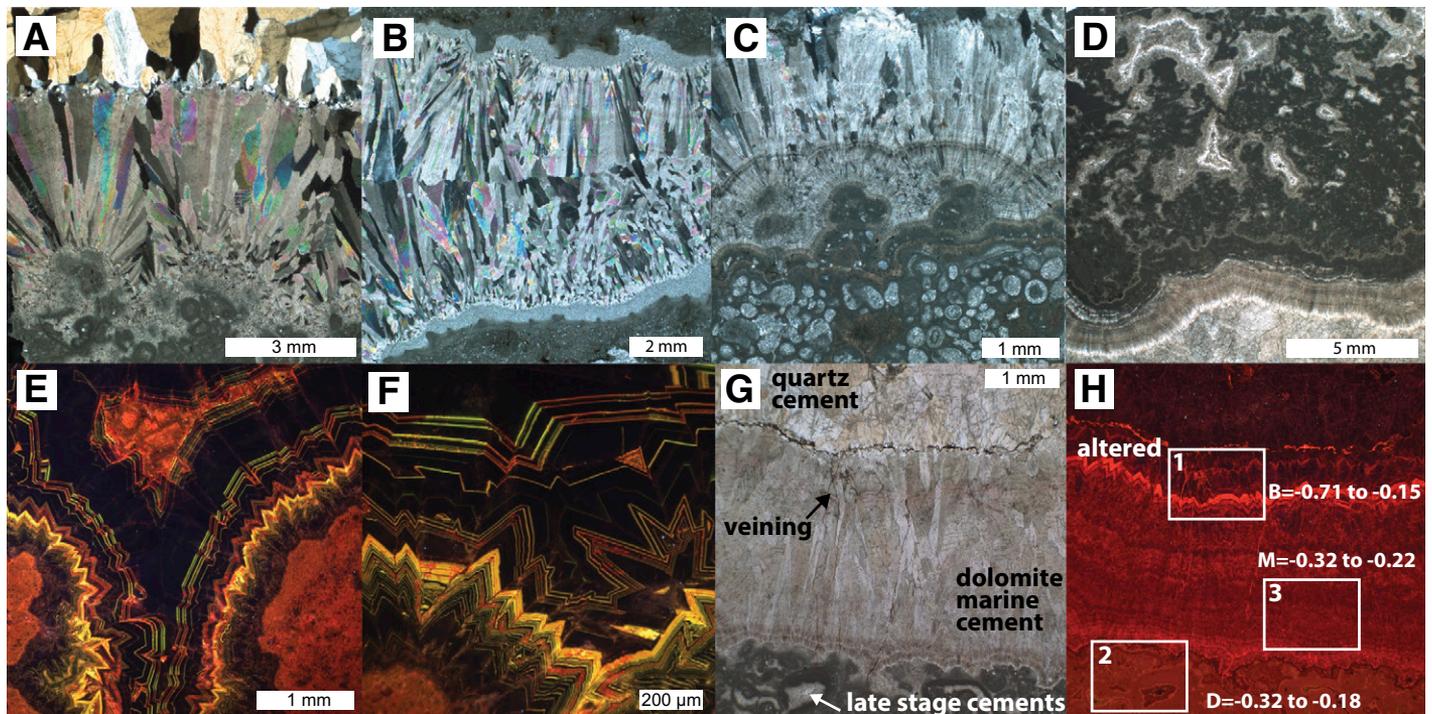


Figure 2. Carbonate components of the Balcanoona reef (South Australia). A, B: Petrographically pristine dolomite marine cements in shallow subtidal and peritidal facies. C: Oomolds (dolomite after aragonite), early and late marine cements, back-reef facies. D: Microbialites, marine cements, and burial cements from the reef margin facies. E, F: Well-preserved cathodoluminescence (CL) growth zonation in shallow-marine cements. Mottled, bright luminescence in ferroan dolomite burial cements. G, H: Paired plane-light (G) and CL (H) images of shallow reefal marine cements (sample Q) with $\delta^{238}\text{U}$ values. Sampling from areas such as area 1 would result in a mixed marine (M) burial (B) signal due to bright CL alteration and veining. Area 2 incorporates mixed peloids, micrite (D), and marine and late-stage cements, whereas area 3 shows well-preserved marine cements. 1, 2, and 3 represent examples of areas from which powders were drilled from sample Q, contributing to accompanying $\delta^{238}\text{U}$ values.

on average 0.07‰ based on duplicate measurements of the NOD-A-1 geostandard (http://crustal.usgs.gov/geochemical_reference_standards/mangana1.html), using a sample-matched mass of U.

COMPONENT-SPECIFIC GEOCHEMISTRY

Analysis of carbonate components within the Balcanoona reef reveals significant variation in U isotope composition between constituents, even within a single sample (Fig. 1B). The $\delta^{238}\text{U}$ values from unaltered marine cements in shallow subtidal facies (<50 m paleodepth) are relatively heavy compared to modern seawater values (mean cement $\delta^{238}\text{U} = -0.23\text{‰} \pm 0.16\text{‰}$, 2 standard deviations). There is no significant difference in $\delta^{238}\text{U}$ composition in cements between shallow subtidal and peritidal reef facies. Deeper water marine cement samples are represented by neptunian dike cements, which have a strong seawater influence, but a less straightforward paragenetic history (with $\delta^{238}\text{U}$ between -0.21‰ and -0.64‰). Within a single cement crust (sample ASD-M) two separate areas identified petrographically and under CL as pristine (preserving crystal-specific CL zonation) and altered (displaying bright luminescent veining and patchy recrystallization) show very different trace metal compositions. The altered cements have much higher Al, Th, and Zr concentrations, but their $\delta^{238}\text{U}$ values remain similar, within error (ASD-M altered: $-0.25\text{‰} \pm 0.08\text{‰}$; ASD-M: $-0.15\text{‰} \pm 0.09\text{‰}$).

Depositional components (the focus of typical U isotope studies) have a more variable $\delta^{238}\text{U}$ composition than marine cements. Depositional micrites from dolomitic redbeds and peloid grainstones have an average $\delta^{238}\text{U}$ value of $-0.31\text{‰} \pm 0.19\text{‰}$. Dolomite and limestone microbial framework components have $\delta^{238}\text{U}$ values ranging between -0.18‰ and -0.63‰ (mean $-0.34\text{‰} \pm 0.27\text{‰}$). Late-stage diagenetic cements show even more variable $\delta^{238}\text{U}$ compositions (-0.71‰ to -0.08‰ $\delta^{238}\text{U}$; mean $-0.36\text{‰} \pm 0.51\text{‰}$). Allochthonous limestone material has lighter $\delta^{238}\text{U}$ values than facies-equivalent reefal dolomites. Overall, $\delta^{238}\text{U}$ values are not correlated strongly to U concentrations (all samples: $r^2 = -0.25$) or other trace metal concentrations (e.g., overall Al, Fe, Mn, and $\delta^{238}\text{U}$ have r^2 values < 0.25).

DISCUSSION

Uranium isotope data from the Balcanoona reef complex demonstrate the need for careful petrographic analysis for sample preservation prior to geochemical studies. Variations in both trace metal concentrations and $\delta^{238}\text{U}$ values are significant, even between components in a single hand sample. Comparison between strongly altered and pristine cement crusts shows changes in many detritally derived trace metal concentrations (e.g., Al, Th, Zr) without a significant change in U isotope composition. However, large variations in the $\delta^{238}\text{U}$ and trace metal compositions of late-stage components suggest that when sampling carbonates, the chemistry of diagenetic fluids must be considered. For example, in the case of high pore-water H_2S , $\delta^{238}\text{U}$ may become heavier than local seawater by 0.2‰–0.4‰ (Romaniello et al., 2013). If late-stage cements are metal rich, interpreting a bulk sample as representing a true marine signature would be problematic.

This variation in carbonate depositional fabrics between reef facies can correspond to variable diagenetic histories (e.g., in the Permian Capitan Reef, southwestern USA; Melim and Scholle, 1999). In the Balcanoona Formation, reef margin microbialites are cemented to a higher degree by late-stage dolomite spar. Back-reef carbonates have more detrital material and multiple cement generations developed between grains. Simple whole-rock sampling of these carbonates, particularly incorporating highly isotopically variable later-stage dolomites, would have resulted in a mixed marine-detrital-late diagenetic signal.

Our study illustrates that care must be taken when sampling in order to minimize facies-specific diagenetic alteration. CL and plane-light microscopy can be used to highlight samples showing detrital contamination, pervasive recrystallization, veining, and destruction of depositional fabrics

(Fig. 2). Well-preserved phases generally retain original CL characteristics (e.g., zonation confined to specific components, particularly identifiable as the preservation of crystal structure in marine cements and nonluminescence in carbonates from oxic environments), but any mottled, bright luminescence obscuring depositional fabrics should be avoided. Duplicate stratigraphic sections from different localities or through different facies is another important test for the veracity of stratigraphic trends and the presence of localized diagenetic resetting (e.g., Lau et al., 2016).

Of 16 cement samples of this study, 7 meet these criteria for being well preserved, whereas the most typically targeted carbonates (micrites and microbialites) generally did not. Marine cement samples from neptunian fractures and limestone blocks have not been used in this interpretation of $\delta^{238}\text{U}$ of seawater. Large variability in $\delta^{238}\text{U}$ suggests that neptunian cements may have been influenced by modified pore waters (e.g., under the influence of the dissolution of Fe or Mn oxides, explaining light isotope signatures; Weyer et al., 2008). Limestone depositional components are pervasively recrystallized, with a highly variable $\delta^{238}\text{U}$ composition, indicating that they are not representative of Cryogenian seawater.

Well-preserved marine cements have $\delta^{238}\text{U}$ values (mean -0.23‰) essentially indistinguishable from average global riverine inputs, which have been documented as -0.3‰ to 0.0‰ $\delta^{238}\text{U}$ (Stirling et al., 2007; Weyer et al., 2008; Andersen et al., 2016). With these samples we have assumed minimal fractionation during the precipitation of dolomite from seawater (given that calcite shows limited offset even with a coordination change during incorporation; Reeder et al., 2001; Romaniello et al., 2013). This is because dolomite has a crystal structure similar to that of calcite, and under reducing conditions may also substitute U^{IV} in the Ca^{2+} site (Sturchio et al., 1998).

Several mechanisms could be responsible for the relatively heavy $\delta^{238}\text{U}$ of marine cement samples compared to modern seawater. For example, Romaniello et al. (2013) suggested that authigenic U accumulation in the presence of high pore-water H_2S results in bulk samples 0.2‰–0.4‰ heavier than primary carbonate precipitates. However, there is a distinct lack of sulfide minerals in the Balcanoona Formation, suggesting that this is an unlikely interpretation. Alternatively, a change in U reduction pathways in seawater under the widespread ferruginous conditions suggested for the Cryogenian (Hood and Wallace, 2014; Sperling et al., 2015) could result in a different global marine U isotope mass balance.

We propose that Precambrian Fe-rich ocean conditions would support a marine $\delta^{238}\text{U}$ value similar to the input source value (riverine flux). Near-quantitative low- T reduction of U(VI) to U(IV) by abundant soluble ferrous iron in seawater and pore waters (e.g., Sperling et al., 2015) may have been possible, resulting in burial of essentially unfractionated uranium. Although natural evidence is lacking, preliminary experimental studies suggest that soluble Fe(II) can rapidly reduce U at near-marine pH (Stylo et al., 2015). Even with Ca^{2+} and CO_3 present (resulting in formation of ternary $\text{Ca-UO}_2\text{-CO}_3$ complexes in seawater), Fe(II) concentrations are thought to be the main controlling factor on U reduction pathways, with higher Fe increasing rates of U(VI) to U(IV) reduction (Massey et al., 2014). With incomplete reduction of U in seawater, abiotic Fe(II) reduction may result in burial of isotopically light U (Stylo et al., 2015), resulting in a seawater $\delta^{238}\text{U}$ composition heavier than that of the modern ocean, despite extensive anoxia. This composition contrasts with the very light $\delta^{238}\text{U}$ seawater value predicted for widespread marine euxinia, where biotic reduction leads to heavy $\delta^{238}\text{U}$ accumulation in black shales (Weyer et al., 2008; Stylo et al., 2015). Additional U isotope data are needed in modern and ancient ferruginous settings to improve our understanding of $\delta^{238}\text{U}$ under these conditions.

CONCLUSIONS

This study highlights the need for integrated petrographic and sedimentologic research as a fundamental part of the future development of sedimentary-geochemical redox proxies. When marine carbonates may

have undergone significant diagenetic alteration (e.g., many Precambrian successions), they should be well-screened for fluid-rich alteration and, if possible, duplicated from different sections to test for a depositional origin. In addition, care must be taken when sampling to target specific carbonate components whose geochemical signatures are not obviously affected by the various states of diagenesis. Primary marine precipitates, especially marine cements, can provide an opportunity to obtain pristine marine geochemical signatures. However, we emphasize that in any sample set, a unique diagenetic pathway will affect samples, and so careful petrographic screening is important on a case-by-case basis. In the Balcanoona reef, ooids, micrite, and microbialites may also give marine values. “Riverine” $\delta^{238}\text{U}$ values in pristine marine cements from the Balcanoona reef may reflect globally extensive ferruginous conditions in Cryogenian oceans.

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