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Uranium isotope fractionation during coprecipitation with aragonite and calcite

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Abstract

Natural variations in $^{238}U/^{235}U$ of marine calcium carbonates might provide a useful way of constraining redox conditions of ancient environments. In order to evaluate the reliability of this proxy, we conducted aragonite and calcite coprecipitation experiments at pH ~7.5 and ~8.5 to study possible U isotope fractionation during incorporation into these minerals.

Small but significant U isotope fractionation was observed in aragonite experiments at pH ~8.5, with heavier U isotopes preferentially enriched in the solid phase. $^{238}U/^{235}U$ of dissolved U in these experiments can be fit by Rayleigh fractionation curves with fractionation factors of $1.00007 + 0.00002/-0.00003$, 1.00005 ± 0.00001, and 1.00003 ± 0.00001. In contrast, no resolvable U isotope fractionation was observed in an aragonite experiment at pH ~7.5 or in calcite experiments at either pH. Equilibrium isotope fractionation among different aqueous U species is the most likely explanation for these findings. Certain charged U species are preferentially incorporated into calcium carbonate relative to the uncharged U species $Ca_2UO_2(CO_3)_3(aq)$, which we hypothesize has a lighter equilibrium U isotope composition than most of the charged species. According to this hypothesis, the magnitude of U isotope fractionation should scale with the fraction of dissolved U that is present as $Ca_2UO_2(CO_3)_3(aq)$. This expectation is confirmed by equilibrium speciation modeling of our experiments. Theoretical calculation of the U isotope fractionation factors between different U species could further test this hypothesis and our proposed fractionation mechanism.

These findings suggest that U isotope variations in ancient carbonates could be controlled by changes in the aqueous speciation of seawater U, particularly changes in seawater pH, P_{CO_2}, Ca^{2+}, or Mg^{2+} concentrations. In general, these effects are likely to be small (<0.13‰), but are nevertheless potentially significant because of the small natural range of variation of $^{238}U/^{235}U$.

Keywords: U isotopes; Paleoredox; Calcium carbonate; Speciation

1. INTRODUCTION

Tracking ocean redox conditions through time is a major goal in paleooceanography because redox conditions strongly affect the oxidation states and speciation of elements, and hence element cycling and bioavailability (e.g., Anbar and Knoll, 2002; Scott et al., 2008, 2011). Biological extinctions and radiations also correlate with changes in the amount of O_2 in the atmosphere and ocean (e.g., Berner et al., 2007; Canfield et al., 2007; Lenton et al., 2014; Lyons et al., 2014). Thus, tracking redox change is critical to understand the co-evolution of life and Earth.

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However, it is difficult to reconstruct a continuous and global record of Earth's environmental redox history because the distributions of key lithologies used for this purpose in the geologic record are spatially and temporally sporadic. These lithologies include iron formations, phosphorites, and black shales. Frequently used paleoredox proxies in these lithologies include the abundances of redox sensitive elements (e.g., Cu, Cr, V, Cd, Mo, Y, U, Zn; Algeo and Maynard, 2004; Tribovillard et al., 2006; Algeo and Rowe, 2011) and variations in their isotopic compositions (e.g., δ^{56}Fe, δ^{53}Cr, $\delta^{98/95}$Mo, δ^{238}U, δ^{34}S, Δ^{33}S; Lyons et al., 2009; Brennecka et al., 2011a; Pufahl and Hiatt, 2012; Asael et al., 2013). Unfortunately, iron formations are only common in the Archean and Paleoproterozoic, while phosphorites formed almost exclusively in the Phanerozoic (Pufahl and Hiatt, 2012). Black shales are distributed irregularly across the geological record (Tourtelot, 1979; Condie et al., 2001; Le Heron et al., 2009), and were often formed in restricted marginal basins that may not represent the global marine environment (Herrmann et al., 2012).

In contrast to these lithologies, the distribution of carbonate sedimentary rocks is more continuous both temporally and spatially (Morse and Mackenzie, 1990; Shields and Veizer, 2002). The oldest preserved carbonate rocks on Earth were deposited at ~3.8 Ga (Shields and Veizer, 2002). The abundance of carbonate rocks increases to ~20 volume % of all sedimentary rocks during the early Proterozoic (Ronov, 1964) and persists at this percentage or higher throughout the Phanerozoic (Wilkinson and Walker, 1989). Therefore, a reliable paleoredox proxy that can be applied to carbonate sedimentary rocks would be extremely useful.

Rare earth elements (REEs) in carbonate rocks have been used as paleo-redox proxies for many years (German and Elderfield, 1990). In particular, the anomalous redox-sensitive behavior of cerium (Ce) compared to the other REE in the marine environment makes it useful as a paleoredox proxy (Kakuwa and Matsumoto, 2006). However, the residence time of Ce (50–130 yr) is short relative to the oceanic mixing time (~10^3 yr; Jenkins, 2003), so Ce can only provide information about local redox conditions (Alibo and Nozaki, 1999; Li et al., 2013). The redox sensitive element iodine in marine carbonates (I/Ca ratios) has been explored as another useful paleoredox proxy, however, it is also restricted to infer local redox conditions because I/Ca ratios in carbonates are mainly controlled by local redox conditions and primary productivity. (Lu et al., 2010; Hardisty et al., 2014; Zhou et al., 2014, 2015).

U concentrations and isotope compositions in carbonate rocks could be very useful paleoredox proxies because oxidized U(VI) is readily incorporated into calcium carbonate mineral structures during carbonate precipitation (i.e., "co precipitation") in relatively high concentrations of 0.1–10 ppm (Chung and Swart, 1990; Reeder et al., 2000; Kelly et al., 2006). Additionally, the long residence time of U (>10^5 yr; Dunk et al., 2002) suggests that, unlike Ce and I, U might provide globally integrated paleoredox information.

U concentrations and the U/Th ratios in sedimentary rocks have been widely used as paleoredox proxies (e.g., Anderson et al., 1989; Wignall and Twitchett, 1996; Morford and Emerson, 1999). Under oxic conditions, U exists as soluble U(VI) in the form of uranyl carbonate complexes (Langmuir, 1978). In anoxic marine settings, U (VI) is reduced to insoluble U(IV) and subsequently adsorbed or precipitated as UO_2, U_3O_7 or U_3O_8 in the anoxic sediments (Klinkhammer and Palmer, 1991; McManus et al., 2005). Thus, variations of U concentrations in anoxic facies like black shales can reflect changes in redox conditions (Algeo and Maynard, 2004; Tribovillard et al., 2006; Partin et al., 2013). Since Th is only present as relatively insoluble Th(IV) in seawater, there is no significant shift in authigenic uptake of Th under changing redox conditions. Hence, the variation of U/Th ratio in the sediments is also used as a redox proxy.

Uranium isotopes are being actively explored and applied as an additional source of ocean paleoredox information (Stirling et al., 2007; Weyer et al., 2008; Montoya-Pino et al., 2010; Brennecka et al., 2011a; Asael et al., 2013; Kendall et al., 2013, 2015; Andersen et al., 2014; Dahl et al., 2014; Goto et al., 2014; Noordmann et al., 2015; Tissot and Dauphas, 2015; Lau et al., 2016). Although natural variations in $^{238}U/^{235}U$ can be caused by processes such as leaching and adsorption (Stirling et al., 2007; Brennecka et al., 2011b; Heiss et al., 2012), redox variations are the primary drivers of U isotope fractionation on Earth, with heavier U isotopes ^{238}U preferentially enriched in reduced species (Stirling et al., 2007, 2015; Weyer et al., 2008; Basu et al., 2014; Bopp et al., 2010; Stylo et al., 2015). According to these studies, widespread anoxia in the oceans causes more U to be scavenged by anoxic sediments, preferentially sequestering ^{238}U from seawater and leading to a decrease in the $^{238}U/^{235}U$ ratio of seawater. Because of the long residence time of U, it has been proposed that U isotope variations can be used to infer changes in global redox conditions (Weyer et al., 2008; Tissot and Dauphas, 2015). For example, variations of $^{238}U/^{235}U$ and U concentration in black shales were used to quantify the spatial extent of marine anoxia during Oceanic Anoxic Event 2 (Montoya-Pino et al., 2010) and indicate oxidative U mobilization at 2.50 Ga (Kendall et al., 2013).

Because of the wide spatial and temporal distribution of carbonate sedimentary rocks, variation of $^{238}U/^{235}U$ in carbonate rocks is being explored as a paleoredox proxy. $^{238}U/^{235}U$ in modern primary carbonate precipitates (corals, green algae, ooids, etc) is close to that of seawater (Stirling et al., 2007; Weyer et al., 2008; Romaniello et al., 2013; Tissot and Dauphas, 2015), suggesting that marine carbonates capture the $^{238}U/^{235}U$ of coexisting seawater. Based on this finding, variations of $^{238}U/^{235}U$ and U/Th in a carbonate section at Dawen in southern China were interpreted as reflecting an enhancement of oceanic anoxia immediately before the end-Permian mass extinction (Brennecka et al., 2011a; Lau et al., 2016).

So far, no resolvable U isotope fractionation has been observed between modern aragonite and calcite samples and seawater (Weyer et al., 2008; Romaniello et al., 2013). However, many factors have varied in the past, including seawater pH and CO_3^{2-} ion concentration (Berner and Kothavala, 2001; Royer et al., 2004;