Uranium Isotope Fractionation During Coprecipitation with

Aragonite and Calcite

Xinming Chen^{1*}, Stephen J. Romaniello¹, Achim D. Herrmann², Laura E. Wasylenki³,
Ariel D. Anbar^{1,4}

¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ, 85287,
USA (*correspondence: Xinming.Chen@asu.edu)

²Coastal Studies Institute and Department of Geology and Geophysics, Louisiana State
University, Baton Rouge, LA, 70803, USA

³Department of Geological Sciences, Indiana University, Bloomington, IN, 47405, USA

⁴School of Molecular Science, Arizona State University, Tempe, AZ, 85287, USA

Correspondence author: Xinming Chen

Email: Xinming.Chen@asu.edu

Tel: +1480-295-57901

Abstract

Natural variations in $^{238}\text{U}/^{235}\text{U}$ 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. $^{238}\text{U}/^{235}\text{U}$ 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 $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$, 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 $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$. 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 ($<0.13\text{ ‰}$), but are nevertheless potentially significant because of the small natural range of variation of $^{238}U/^{235}U$.

1. Introduction

Tracking ocean redox conditions through time is a major goal in paleoceanography 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](#); [Lyons et al., 2014](#); [Lenton et al., 2014](#)). Thus, tracking redox change is critical to understand the co-evolution of life and Earth.

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., $\delta^{56}Fe$, $\delta^{53}Cr$, $\delta^{98/95}Mo$, $\delta^{238}U$, $\delta^{34}S$, $\Delta^{33}S$; [Pufahl and Hiatt, 2012](#); [Lyons et al., 2009](#); [Asael et al., 2013](#); [Brennecke et al., 2011a](#)). 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 (Shields and Veizer, 2002; Morse and Mackenzie, 1990). 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 a very useful paleoredox proxy because oxidized U(VI) is readily incorporated into calcium carbonate mineral structures during carbonate precipitation (i.e., “coprecipitation”) in relatively high concentrations of 0.1 to 10 ppm (Chung and Swart, 1990; Kelly et al., 2006; Reeder et al., 2000). 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; Morford and Emerson, 1999; Wignall and Twitchett, 1996). 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., 2012; 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; Brennecke et al., 2011a; Andersen et al., 2014; Dahl et al., 2014; Kendall et

al., 2013, 2015; Asael et al., 2013; Goto et al., 2014; Noordmann et al., 2015; Tissot and
 Dauphas, 2015; Lau et al., 2016). Although natural variations in $^{238}\text{U}/^{235}\text{U}$ 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 $^{238}\text{U}/^{235}\text{U}$ 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 $^{238}\text{U}/^{235}\text{U}$ 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 $^{238}\text{U}/^{235}\text{U}$ in carbonate rocks is being explored as a paleoredox proxy.
 $^{238}\text{U}/^{235}\text{U}$ 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 $^{238}\text{U}/^{235}\text{U}$ of
 coexisting seawater. Based on this finding, variations of $^{238}\text{U}/^{235}\text{U}$ 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; Ridgwell, 2005), the relative abundance of cations (Ca^{2+} , Mg^{2+} , and Sr^{2+} , Horita et al., 2002; Lowenstein et al., 2003), and the primary polymorph of CaCO_3 (i.e., aragonite vs. calcite, Ries, 2004, 2010). This might have caused U isotope fractionation during U incorporation into carbonate rocks in the geological past. In particular, variations in aqueous U speciation might lead to isotopic fractionation of $^{238}\text{U}/^{235}\text{U}$ ratios during coprecipitation with carbonates if different aqueous U species are isotopically fractionated from one another and certain U species are preferentially incorporated into the solid phase. It is also possible that $^{238}\text{U}/^{235}\text{U}$ could be fractionated during incorporation into different polymorphs of CaCO_3 due to coordination changes required to accommodate U in the mineral structures. Previous experimental studies found that the predominant U(VI) species in seawater, $\text{UO}_2(\text{CO}_3)_3^{4-}$, was directly incorporated into aragonite without coordination change (Reeder et al., 2000). In contrast, the coordination of $\text{UO}_2(\text{CO}_3)_3^{4-}$ was altered during incorporation into calcite adopting an equatorial coordination number of 5 (Reeder et al., 2000, 2001). Similarly, studies of natural calcite samples have suggested that uranyl substitutes for Ca with an equatorial coordination number of 4 (Kelly et al., 2003, 2005). This difference in the local bonding environment could lead to isotopic fractionation. For example, coordination changes are known to cause resolvable isotope fractionation during adsorption of metal complexes (i.e., U, Mo, Tl, Zn and Cu)

onto synthetic K-birnessite (Brennecke et al., 2011b; Wasylenki et al., 2011; Little et al., 2014; Bryan et al., 2015).

In this study, we conducted U(VI) coprecipitation experiments with aragonite and calcite to investigate the effect of varied U speciation (induced by pH) on U isotope fractionation during U incorporation into these two CaCO_3 polymorphs. The goal of these experiments was to test whether calcite and aragonite record seawater $^{238}\text{U}/^{235}\text{U}$ under a variety of conditions. Experiments were conducted at two different pHs (~ 7.5 and ~ 8.5) that capture most of the range of pH expected in different marine environments over the Phanerozoic. Although the dissolved U concentrations in our experiments were much higher than that in seawater, we do not expect U speciation and U isotope fractionation to depend on U concentration, as discussed below. Additionally, we find that the growth rates of CaCO_3 in our experiments fell within those of natural CaCO_3 (Owen et al., 2002; Stoll et al., 2002; Winograd et al., 2006), suggesting that our experimental work is relevant to natural environments.

2. Materials and methods

As detailed below, U(VI) coprecipitation experiments with aragonite and calcite were conducted at pH ~ 7.5 and ~ 8.5 . Aqueous and solid samples were collected during each experiment to measure U concentration and $^{238}\text{U}/^{235}\text{U}$. After completion of each experiment, approximately 1 g of the bulk precipitate was collected for X-ray diffraction (XRD) analysis to verify the CaCO_3 polymorph. The U(VI) speciation in the aqueous solution was calculated using the software PHREEQC (Parkhurst and Appelo, 2004) to explore the relationship between pH, U speciation, and isotope fractionation.

2.1.1 Materials

All labware was washed using reagent-grade nitric acid (20%), hydrochloric acid (20%), and 18.2 MΩ-cm deionized water, following standard trace metal cleanlab protocols ([Howard and Statham, 1993](#)). Nitric acid and hydrochloric acid used to dissolve samples and purify U for isotope analyses were Omega trace metal grade (Fisher Scientific, Lot #4114020 (HCl) and #1114010 (HNO₃)). Chemical reagents (NaCl, anhydrous MgCl₂, Na₂CO₃, NaHCO₃, CaCl₂·2H₂O, 30% H₂O₂) were ACS grade (Fisher Scientific). ICP-MS standard (PU1KN, Ricca Chemical Company LLC, Lot #: 4101230) was used as the uranyl nitrate solution in the U coprecipitation experiments.

2.1.2 Experimental setup

U coprecipitation experiments were performed using the constant addition method ([Zhong et al., 1989](#); [Reeder et al., 2000](#)) with a 1 L Erlenmeyer flask as the reactor (Figure 1). Prior to each experiment, a background NaCl electrolyte solution with U(VI) (50 μM) was added into the reactor. CaCl₂ and Na₂CO₃ or NaHCO₃ (concentrations were given below) were delivered at the same flow rate into the reactor via a dual-channel syringe pump (Model: NE-1600, New Era Pump Systems, Inc.) to precipitate CaCO₃. The solution in the reactor was well mixed with a Teflon stir bar and bubbled with air to maintain constant P_{CO2} in the aqueous solution. Experiments were run at ambient lab temperature which is tightly controlled at 24 ± 0.5 °C. However, we found that it was necessary to isolate the reactor from the magnet stir-plate using a thermally insulating pad in order to keep the heat of the stirrer motor from warming the reactor by several

degrees centigrade ($\sim 3\text{ }^{\circ}\text{C}$). The pH meter was connected to a computer to record the pH in the aqueous solution every 5 minutes.

2.2 U coprecipitation with aragonite and calcite procedures

Four aragonite experiments (A_1 , A_2 , A_3 , and A_1^*) and three calcite experiments (C_1 , C_2 , and C_3) were conducted. Aragonite experiment A_1^* was a replicate of experiment A_1 . Experiments A_1 , A_3 , A_1^* , C_1 , and C_3 were conducted at $\text{pH } 8.5 \pm 0.1$, while experiments A_2 and C_2 were performed at $\text{pH } 7.5 \pm 0.1$. The pH was set by adjusting the delivery rates of chemical reagents into the reactor. The experimental conditions are summarized in Table 1.

All aragonite experiments were conducted using 0.5 M CaCl_2 and 1.0 M NaHCO_3 . In order to maintain a stable pH over several days while precipitating several grams of CaCO_3 , it is critical that Ca and carbonate alkalinity are delivered in exact stoichiometric proportions. In order to achieve this, large batches of reagents were prepared gravimetrically and then iteratively refined in a series of preliminary experiments to ensure that a stable pH could be maintained at the desired flow rate. Between preliminary experiments, small adjustments to the reagent concentrations were made by slightly diluting the excess reagent in order to achieve stoichiometric precisions much better than 0.1%. These solutions were delivered into the reactor simultaneously via two Teflon tubes (0.51 mm diameter) using a dual-channel syringe pump equipped with 60 mL syringes. NaCl (0.5 M) was used as the background electrolyte. In aragonite experiments, a $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio > 2 was maintained, which inhibits calcite growth by

destabilizing the crystal lattice and increasing its solubility (Choudens-Sánchez and González, 2009; Morse et al., 1997). To maintain a high and constant $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio, MgCl_2 was added to the NaCl and CaCl_2 solutions. The Mg^{2+} concentration was 50 mM in experiments A_1 , A_2 , and A_1^* and 100 mM in experiment A_3 . Prior to coprecipitation, uranyl nitrate was added into the NaCl solution to achieve an initial U concentration of $\sim 50 \mu\text{M}$. The high U concentration (about 3600 times that of seawater, $\sim 14 \text{ nM}$) ensures that there is enough dissolved U for isotope analysis of the aqueous solution even when $>95\%$ of U has been incorporated into the precipitate. Aqueous samples ($\sim 2 \text{ mL}$) were collected every 12 hours and immediately filtered through a $0.45 \mu\text{m}$ filter. Subsequently, the filtered samples were diluted with concentrated nitric acid to a final concentration of 3 M HNO_3 . At the termination of each experiment, a portion of the bulk CaCO_3 precipitate was dissolved with concentrated HNO_3 for U concentration and isotope ratio measurements.

The experimental conditions and procedures for calcite experiments C_1 and C_2 were the same as for aragonite experiments A_1 and A_2 , except that no MgCl_2 was used. The experimental procedure for calcite experiment C_3 was slightly different from the other calcite experiments. It was modified to precipitate a greater proportion of dissolved U in order to achieve a more precise measurement of the isotope fractionation. To achieve this goal, higher concentrations of CaCl_2 (2.0 M) and Na_2CO_3 (2.0 M) were used. To keep ionic strength constant, 2.0 M NaCl was used as the background electrolyte. One gram of calcite seed crystal synthesized with reagent grade CaCl_2 and NaHCO_3 was added into the NaCl solution and mixed with a stir bar for 18 hours. Subsequently, uranyl nitrate was introduced into the NaCl solution to attain a U concentration of $50 \mu\text{M}$.

During the calcite coprecipitation process, aliquots of aqueous solution (~ 2 ml) were collected every 12 hours. To compare the U isotope ratios of aqueous solution and instantaneous solid, each day a clean glass microscope slide was submerged into the solution to collect daily precipitate and retrieved after 24 hours. When experiment C₃ ended, bulk solid was also taken for XRD and isotopic analysis. The preparation procedures for U concentration and its isotopic ratio analysis in aqueous and solid samples were the same as in all other experiments.

2.3 X-Ray Diffraction (XRD) analysis

Approximately 1 g of the bulk precipitate from each experiment was collected, ground using an agate mortar and pestle, and loaded into a sample holder. The crystal structures of synthetic carbonates were characterized by powder XRD (Bruker-AXS D8 Advance, ASU) using Cu K α radiation (40 kV and 30 mA) and a Ni filter with a scanning speed of 0.005° 2 θ s⁻¹. The time constant was 2 seconds. The crystal structures of the synthetic calcium carbonates were confirmed by comparing the spectra with those of calcite standard (R040070) and aragonite standard (R040078) from the International Center for Diffraction Data.

2.4 Specific surface area measurement

In order to estimate the crystal growth rate, the specific surface area of calcite in experiments C₁ and C₂ was measured using the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938; Gregg and Sing, 1982). About 1 gram of the calcite precipitate

was dried at 150 °C for 24 h to remove moisture, and the specific surface area was measured at 77 K using N₂ as adsorption gas.

2.5 U concentration analysis

Aqueous samples collected during coprecipitation experiments were diluted to 0.32 M nitric acid for U concentration analysis using quadrupole inductively-coupled plasma mass spectrometry (ICP-MS, Thermo X-series) at Arizona State University (ASU). Solid samples (typically ~ 0.1 g) from each experiment were dissolved with 1 ml of 3 M HNO₃ and diluted similarly. The estimated precision for the U concentration measurements by ICP-MS was ± 2% based on repeated analysis of check standard solutions during each run.

2.6 U isotope analysis

The ²³³U-²³⁶U double-spike method was used to measure U isotope ratios, using multiple collector ICP-MS (MC-ICP-MS) (Weyer et al., 2008). The double-spike method is the most effective way to correct for instrumental mass bias and potential isotope fractionation during U purification (Rudge et al., 2009; Dodson, 1963). About 500 ng of U from each sample was well mixed with sufficient double-spike U solution (IRMM-3636) to achieve a spike:sample molar ratio of ~ 0.0363 (Verbruggen et al., 2008; Weyer et al., 2008). The samples were spiked prior to chromatographic separation to correct for any U isotope fractionation that might occur during U purification.

U purification was carried out following the protocol of Weyer et al. (2008). Polypropylene columns (BioRad #7311550) were first rinsed with 10 ml 18.2 MΩ-cm

deionized water. A volume of 0.8 ml UTEVA resin (Eichrom Technologies, LLC) was loaded on a column. The resin was then washed with 4×2.5 ml 0.05 M HCl to remove impurities. The resin was then converted to the nitric form by loading 3×0.8 ml 3 M HNO₃. The double-spiked U sample (dissolved in 3 M HNO₃) was loaded on the column and rinsed with 5×2 ml 3 M HNO₃ to remove all matrix ions except U and Th. Then 10 M HCl (3×0.8 ml) was added to the column to convert the UTEVA resin to chloride form. Th was removed from the resin using a mixture of 5 M HCl and 0.05 M oxalic acid (3×0.8 ml). The oxalic acid left on the resin was rinsed with 3×0.8 ml 5 M HCl. The U adsorbed on the resin was eluted with 7 ml (1 + 1 + 1 + 2 + 2) 0.05 M HCl. The U cuts were dried down and heated with concentrated HNO₃ + 30% H₂O₂ (1 ml + 0.3 ml) to remove any organic residue eluted from the UTEVA resin. The last step was repeated until all organic residue was removed.

The U isotope ratios were measured at ASU using MC-ICP-MS (Thermo Scientific Neptune). Purified samples were dissolved in 0.32 M HNO₃ with a U concentration of ~ 50 ppb and introduced into the instrument via an Apex-Q desolvation introduction system. Ion beams of ²³³U, ²³⁵U, ²³⁶U, and ²³⁸U were collected with Faraday cups connected to $10^{12} \Omega$, $10^{12} \Omega$, $10^{12} \Omega$, and $10^{11} \Omega$ resistors respectively. The typical voltage for ²³⁸U from a 50 ppb U solution was ~ 30 V. U isotopic compositions are reported in δ notation relative to the standard CRM-145 using the following equation:

$$\delta^{238}\text{U} = \left[\frac{\left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{sample}}}{\left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{standard}}} - 1 \right] \times 1000$$

where $(^{238}\text{U}/^{235}\text{U})_{\text{sample}}$ and $(^{238}\text{U}/^{235}\text{U})_{\text{CRM-145}}$ are the U isotope ratio of a sample and the standard, respectively.

After chemistry, each sample was measured at least three times. The U isotope precision is presented as twice the standard error (2 SE), calculated using the standard deviation of either the sample or standards, whichever was larger. The CRM-145 standard was run every third analysis to correct for small amounts of instrument drift. The reproducibility of replicate measurements of the U isotope composition of CRM-145 is within ± 0.08 ‰ (2 SD, n = 24). The accuracy of the U isotope measurement was assessed by measuring the standard CRM-129a. The measured average $\delta^{238}\text{U}$ of CRM-129a is -1.70 ± 0.10 ‰ (2 SD, n = 20, Table S8 in Supplementary Information), which agrees with previously published values (Wang et al., 2015; Weyer et al., 2008; Shiel et al., 2013). The blank from the U purification procedure was 0.0 ± 0.04 ng (2 SD, n=6, Table S8 in Supplementary Information), which was negligible relative to the 500 ng sample U.

2.7 U speciation calculations

The speciation of U(VI) over the pH range 7 - 9 was modeled with the software package PHREEQC (Parkhurst and Appelo, 2004), using database **sit.dat** with updated U thermodynamic data from Grenthe et al. (1992) and Guillaumont et al. (2003). Three new aqueous uranyl complexes $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, and $\text{MgUO}_2(\text{CO}_3)_3^{2-}$ were also added to the database (Dong and Brooks, 2006). Specific ion interaction theory (SIT) was used for aqueous U speciation calculations because it is effective for estimating single-ion activity coefficients for solutions of up to 3 M ionic strength in which NaCl is the dominant electrolyte (Bethke, 1996).

3. Results

3.1 U coprecipitation with aragonite and calcite

U coprecipitation experiments with aragonite and calcite were conducted under different conditions as shown in Table 1. The pH of these experiments increased from 7.0 to a maximum point (8.5 or 9.2) until the first calcium carbonate nucleated on the wall of the glass reactor (Fig. 2). Subsequently, the pH dropped quickly and stabilized within ± 0.1 pH unit when the amount of calcium pumped into the reactor was balanced via precipitation as CaCO_3 . The measured U concentrations in aragonite and calcite precipitates were about 2300 ppm and 300 ppm, respectively, and were at most only weakly dependent on pumping speed or pH (Table 1). Precise determination of the isotopic fractionation factor requires that most of the U is incorporated into the solid, thereby amplifying the isotopic fractionation in the residual solution. More than 94 % of the total U was incorporated into aragonite in experiments A₁ and A₂, whereas less than 18 % of U was incorporated into calcite in experiment C₁ and C₂. In experiment C₃, which was modified to increase the amount of coprecipitation, approximately 90 % of the total U was incorporated.

3.2 XRD analysis

The XRD spectra of the synthetic carbonates (C₁, C₂, C₃, A₁ and A₂) were compared to those of calcite and aragonite standards. Spectra of synthetic carbonates matched perfectly with their corresponding standards (Fig. 3). Although no XRD analysis

was done for precipitates in experiments A₃ and A₁^{*}, the higher Mg²⁺/Ca²⁺ ratios in these experiments (> 10) relative to that in aragonite experiment A₁ (~ 9) indicate that the polymorph of CaCO₃ in A₃ and A₁^{*} should also be aragonite (Choudens- Sánchez and González, 2009; Morse et al., 1997).

3.3 U speciation

The speciation of U(VI) over the pH range of 7 - 9 at different experimental conditions are shown in Fig. 4. U speciation varies significantly between pH 7.5 and 8.5 in all calcite and aragonite experiments. U speciation also varies between aragonite and calcite experiments (Fig. 4a vs. Fig. 4c) due to the presence of Mg-U species (e.g. MgUO₂(CO₃)₃²⁻) in the aragonite experiments.

U speciation is dominated by CaUO₂(CO₃)₃²⁻ (~ 33 %) in experiments A₁ and A₁^{*} at pH 8.5 (Fig. 4a). However, in experiment A₂, conducted at lower pH (7.5 vs. 8.5), (UO₂)₂(CO₃)(OH)₃⁻ is the dominant U species (50 %). The Mg²⁺ concentration in experiment A₃ is about twice that in experiments A₁ and A₁^{*}, and MgUO₂(CO₃)₃²⁻ becomes the dominant U species, accounting for 42 % of the total U species at pH 8.5.

Fig. 4c shows that UO₂(CO₃)₃⁴⁻ (50 %) is the predominant U species in experiment C₁ at pH 8.5, and that (UO₂)₂(CO₃)(OH)₃⁻ (~ 55 %) becomes another important U species in experiment C₂ at lower pH (7.5). In experiment C₃ (Fig. 4d), which is characterized by higher ionic strength, UO₂(CO₃)₃⁴⁻ (75 %) is the dominant U species. Although the U concentrations in the solution decreased during the course of

these calcium carbonate coprecipitation experiments, thermodynamics calculations using PHREEQC shows that U speciation was constant throughout each experiment.

3.4 CaCO₃ crystal growth rates

To compare the crystal growth rates of calcium carbonates in our experiments to those in nature, the CaCO₃ crystal growth rates were estimated using following two methods.

One is estimation of crystal growth rate from the surface area measured by BET. The specific surface areas for calcite C₁ and C₂ were 3500 cm²/g and 3184 cm²/g, respectively. Given the total mass of the calcite precipitated in these experiments, the respective total surface area of C₁ and C₂ were 6685 cm² and 5221 cm². The carbonate precipitation rate (in g CaCO₃/s) divided by the total surface area (cm²) and the density of calcite (g/cm³) yields estimated crystal growth rates of 0.002 nm/s and 0.020 nm/s for C₁ and C₂.

Alternatively, the calcite crystal growth rate can be estimated using the following empirical equation (Wolthers et al., 2012):

$$R = I^{-0.004} \text{pH}^{-10.71} r_{\text{aq}}^{-0.35} (S-1)^2 \quad \text{Eq. 1}$$

where R is the overall growth rate (m/s), r_{aq} is the ionic activity ratio of Ca²⁺ to CO₃²⁻, and S is the saturation ratio. Based on this empirical equation, the crystal growth rates for calcite experiments C₁ and C₂ were 0.008 nm/s and 0.024 nm/s, respectively. These values are very close to those estimated in the first method. Because the ionic strength in calcite experiment C₃ (2.0 M) was far beyond the range of the appropriate ionic strength in the empirical equation (0 - 0.7 M), a calcite growth rate of 0.02 - 0.08 nm/s was estimated for

C₃, which precipitated 10 times as much CaCO₃ as in C₁ during the same time period. Although we do not have direct estimates of the crystal growth rates for the aragonite experiments, the overall durations and masses of CaCO₃ precipitated in the calcite and aragonite experiments were very similar. Thus, while acknowledging that the specific surface area of calcite and aragonite may be dissimilar, we assume that the CaCO₃ crystal growth rate of experiments A₁ and A₂ were within an order of magnitude of those in C₁ and C₂, respectively. Thus, the CaCO₃ crystal growth rates in our experiments ranged from 0.0002 - 0.24 nm/s, which is well within the range of natural CaCO₃ crystal growth rates, 0.0000033 - 3.30 nm/s (Ter Kuile and Erez, 1984; Owen et al., 2002; Stoll et al., 2002; Genty et al., 2001; Winograd et al., 2006).

3.5 U isotope fractionation in aragonite and calcite experiments

3.5.1 Aragonite experiments

U isotopic compositions in the aqueous and bulk solid samples in aragonite coprecipitation experiments are displayed in Fig. 5. Based on repeated analysis, $\delta^{238}\text{U}$ of the starting stock (ICP standard PU1KN, Ricca Chemical) is -0.23 ± 0.10 ‰ (2 SD, n=12). Thus, U isotope compositions at the beginning of aragonite and calcite coprecipitation experiments were -0.23 ± 0.10 ‰. To verify mass balance, we compared $\delta^{238}\text{U}$ in the bulk aragonite at the end of the experiments, when > 94 % of the U in the solution was incorporated into the aragonite, to that of the initial solution. These values are identical to the starting stock within the uncertainties (A₁: -0.22 ± 0.06 ‰, A₁*: -0.23 ± 0.06 ‰, A₂: -0.30 ± 06 ‰, and A₃: -0.29 ± 06 ‰), consistent with expectations.

To estimate the magnitude of the U isotope fractionation factor in experiments, the data in each experiment were fitted using the Rayleigh fractionation model, which assumes that coprecipitated U was continuously incorporated into the solid phase and isolated from further isotope exchange with the aqueous solution. The instantaneous isotope fractionation factor, α , is defined as:

$$\alpha = \frac{\left({}^{238}\text{U}/{}^{235}\text{U} \right)_{\text{solid}}}{\left({}^{238}\text{U}/{}^{235}\text{U} \right)_{\text{solution}}},$$

where $({}^{238}\text{U}/{}^{235}\text{U})_{\text{solid}}$ and $({}^{238}\text{U}/{}^{235}\text{U})_{\text{solution}}$ are the isotopic ratios of U incorporated into the solid and that in the remaining solution, respectively, at an instant in time. If the isotope fractionation factor is statistically different from 1, there is isotope fractionation between U in the aqueous solution and in the instantaneous solid. The value of α was determined by linear fitting to the following equation:

$$\ln\left(\delta^{238}\text{U}_{\text{solution}} + 1000\right) = (\alpha - 1) \ln f + \ln\left(\delta^{238}\text{U}_0 + 1000\right), \quad \text{Eq. 2}$$

where $\delta^{238}\text{U}_{\text{solution}}$ and $\delta^{238}\text{U}_0$ ($-0.23 \pm 0.10 \text{ ‰}$) are the U isotopic compositions of the solution at the time of sampling and at the beginning of the experiments, respectively, and f is the fraction of U remaining in the aqueous solution (Mariotti et al., 1981). The uncertainty of the slope ($\alpha - 1$) in equation (1) is estimated using the ISOPLOT 3.75 software at 95 % confidence (Ludwig, 2012; York, 1966). With the average values and errors of isotope fractionation factors and fraction of U remaining in the aqueous solution, the confidence envelopes (gray areas in Fig. 5) were calculated using Monte Carlo simulation.

The U isotope fractionation factors (α) derived in equation (1) for experiments A₁, A₁*, A₂, and A₃ were 1.00007 +0.00002/-0.00003, 1.00005 ± 0.00001, 1.00001 ± 0.00002, and 1.00003 ± 0.00001, respectively. In all cases, α is greater than 1, suggesting that the ²³⁸U isotope is preferentially incorporated into aragonite. Within uncertainty, the U isotope fractionation in experiment A₁ is indistinguishable from that in repeat experiment A₁*.

Alternatively, if the U coprecipitation process were predominantly an equilibrium isotope process characterized by continuous isotope exchange between the solution and precipitate, we would expect a simple linear relationship between f and $\delta^{238}\text{U}$. However, the respective regression coefficients (R^2) for A₁, A₁*, A₂ and A₃ (0.69, 0.76, 0.35 and 0.60) are lower than those derived from the Rayleigh fractionation model (0.89, 0.89, 0.56 and 0.90), thus supporting the Rayleigh model approximation.

3.5.2 Calcite experiments

U isotopic compositions of the aqueous, daily solid and bulk solid samples in calcite experiments are shown in Fig. 6. The U isotope data in calcite coprecipitation experiments were also fitted using the Rayleigh fractionation model (Table 2). The Rayleigh fractionation factors in calcite experiments C₁ (0.99979 +0.00021/-0.00027) and C₂ (1.00043 +0.00011/-0.00050) have large uncertainties due to the limited extent of U incorporation (< 18 %, Fig. 6a and Fig. 6b). Thus, the Rayleigh isotope fractionation factors in C₁ and C₂ are statistically indistinguishable from 1.

Experiment C₃ was designed to increase the extent of U incorporation in order to improve the precision of the estimated fractionation factor. The Rayleigh isotope fractionation factor of $1.00000 \pm 0.00005 / -0.00003$ determined for this experiment strongly suggests that there is no resolvable U isotope fractionation during calcite precipitation in experiment C₃. This is consistent with the unresolvable U isotope fractionation between aqueous samples and daily solid samples in Fig. 6c.

4. Discussion

The experimental results revealed a small U isotope fractionation in aragonite coprecipitation experiments at pH ~ 8.5. However, no resolvable U isotope fractionation was observed in the aragonite experiment at pH ~ 7.5 or calcite experiments. Below, we discuss possible explanations for these experimental results and implications for applying U isotopes in marine carbonates as a paleoredox proxy.

4.1 U isotope fractionation mechanism

The direction of the fractionation seen in most of the aragonite experiments favoring incorporation of heavy U isotopes into aragonite contradicts a simple kinetic isotope fractionation model, which would result in preferential incorporation of light U isotopes into the solid phase. Although we cannot strictly rule out a kinetic contribution to the isotope fractionation observed in these experiments, we did not observe systematic variations in isotopic fractionations between fast and slow co-precipitation experiments, and thus suggest that the kinetic contribution, if any, was probably minor. The most important driver of isotope fractionation for the heavy element U is the nuclear volume

effect, which leads to preferential enrichment of heavy U isotopes in U(IV) during U(VI) reduction (Bigeleisen 1996; Schauble, 2007; Abe et al., 2008; Brennecka et al., 2010; Bopp et al., 2009, 2010; Basu et al., 2014; Murphy et al., 2014; Noordmann et al., 2015; Stylo et al., 2015; Stirling et al., 2015). However, in our experiments, U is always in the (VI) oxidation state. As a result, the most likely driver of isotope fractionation in these experiments is equilibrium isotope fractionation driven by changes in chemical speciation in solution or during the co-precipitation process.

Below we consider two possible drivers of the observed effect: change in U speciation *during* incorporation of U into the solid phase; and speciation differences among various aqueous U(VI) species *prior* to incorporation. In both cases, isotopes may partition differentially among the species with different chemical bonding environments.

4.1.1 Change in U coordination during incorporation into CaCO₃

Change in U coordination during incorporation of U into the solid phase might be one mechanism driving U isotope fractionation in our experiments. It has been observed that coordination changes of Mo, U, Tl, Cu and Zn during adsorption onto Mn-oxyhydroxides lead to resolvable isotope fractionation (Wasylenki et al., 2011; Brennecka et al., 2011b; Little et al., 2014; Bryan et al., 2015). Generally, metal complexes with smaller coordination number and shorter bond length have stronger chemical bonds, favoring incorporation of heavier isotopes (Schauble et al., 2004).

However, this mechanism cannot explain our results. Previous studies found that the predominant U(VI) species $\text{UO}_2(\text{CO}_3)_3^{4-}$ in aqueous solution at pH > 8.2 was

incorporated wholesale into aragonite without a change in U coordination (Reeder et al., 2000). In contrast, coordination number and bond length both decrease during $\text{UO}_2(\text{CO}_3)_3^{4-}$ incorporation into calcite (Reeder et al., 2000, 2001; Kelley et al., 2003, 2006). Thus, if coordination change upon incorporation into the mineral causes resolvable isotope fractionation, it is reasonable to expect that heavier U isotopes will be preferentially incorporated into calcite, and that no U isotope fractionation will be observed in aragonite. If the U isotope fractionation driven by coordination change is too small to be resolved, no U isotope fractionation should be observed in either the aragonite or the calcite experiments. Since our data do not conform to either expectation, our results are not consistent with coordination change during U incorporation as the driver of the observed fractionation.

4.1.2 Differences in aqueous U speciation prior to incorporation

Differences in aqueous U speciation prior to incorporation might be another mechanism driving the U isotope fractionation. U speciation changes significantly with pH (Dong and Brooks, 2006). Our speciation calculations indicate that the distribution of U species was different in our experiments at pH ~ 7.5 and ~ 8.5 . In aragonite experiment A₁, A₁*, and A₃, at pH ~ 8.5 , four U(VI) species, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, $\text{MgUO}_2(\text{CO}_3)_3^{2-}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$, should be present in significant amounts (Fig. 4a). However, in calcite experiments C₁ and C₃, at pH ~ 8.5 , only three U species, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ should coexist. Finally, in experiments A₂ and C₂ at pH ~ 7.5 , we expect that $(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$ became the dominant U species.

Isotope fractionation of U between different aqueous species is controlled by the local chemical bonding environments, including the coordination number and bond length (Schauble et al., 2004). The coordination number of equatorial O atoms and bond lengths between U and axial O and between U and equatorial O for these U species are shown in Table 3. Differences in coordination and bond lengths suggest that there may be significant isotope fractionation between various species. Table 3 organizes U species with similar bonding environments into several groups. For example, Group 1, containing $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$, shares a similar 6-fold coordination, with axial bond length ($\text{U}-\text{O}_{\text{ax}}$) of 1.80 Å and equatorial bond lengths ($\text{U}-\text{O}_{\text{eq}}$) of 2.43 ± 0.01 Å. Because of the similarity in chemical bonding environments, these species are expected to have similar U isotopic composition. Group 2, containing $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{MgUO}_2(\text{CO}_3)_3^{2-}$, differs in the equatorial bond lengths are 2.39 ± 0.01 Å. Group 3 [$\text{UO}_2(\text{CO}_3)_2^{2-}$] and Group 4 [$(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$] contain the remaining species, which have variable bonding environments, but are major U species only below $\text{pH} < 8.0$. Because these groups have different chemical bonding environments, it is reasonable to expect U isotope fractionation between these groups.

Theoretical calculations and lab experiments have demonstrated the qualitative rule that chemical species with lower coordination number and shorter bond length, generally, preferentially incorporate heavier isotopes of an element (Schauble et al., 2004; Zeebe, 2005; Bogatko et al., 2013; Colla et al., 2013; Fujii et al., 2013; Huang et al., 2014). For example, B isotope fractionation as large as 19.1 ‰ was estimated between threefold coordinated $\text{B}(\text{OH})_3$ and fourfold coordinated $\text{B}(\text{OH})_4^-$, with heavier B isotopes enriched in $\text{B}(\text{OH})_3$ (Zeebe, 2005). Similarly, the aquo-complexes of cations like

Li⁺, Mg²⁺, Ca²⁺, and Cu²⁺ show enrichment of heavier isotopes when the coordination number of H₂O molecules is smaller and the metal-O bond lengths are shorter (Bogatko et al., 2013; Kowalski and Jahn, 2011; Colla et al., 2013; Fujii et al., 2013; Huang et al., 2014). For U, quantum chemical methods demonstrate that the carbonate ligand (CO₃²⁻) induces a weakening of the U-axial oxygen bond relative to hydroxide ligand (OH⁻) (Vallet et al., 2012). The OH⁻ ligand effect might be relatively small compared to effects exerted by coordination number and bond length. Based on these qualitative rules, it is reasonable to predict that U species of Group 1 (Ca₂UO₂(CO₃)₃(aq) and UO₂(CO₃)₃⁴⁻) might be the isotopically lightest, because these species have the longest U-O_{eq} bond lengths (identical in both species to within the ± 0.01 Å uncertainty of these data), the highest coordination number.

How might such a difference in bonding environment among the dissolved species explain the difference in isotope fractionation factors observed in these experiments? We hypothesize a scenario based on the different affinities of charged vs. uncharged U(VI) species for mineral surfaces. These differences are well known. For example, U(VI) adsorption to ferrihydrite and quartz decreased significantly when the fraction of the neutral U species Ca₂UO₂(CO₃)₃(aq) increased in the aqueous solution (Fox et al., 2006; Bernhard et al., 2001). Similarly, the presence of calcite in soils and subsurface sediments was found to significantly suppress U(VI) sorption onto CaCO₃ and soils because of the formation of a neutral uranyl complex Ca₂UO₂(CO₃)₃(aq) (Zheng et al., 2003; Dong et al., 2005). This neutral species should have a lower affinity for CaCO₃ surfaces than do anionic species because the CaCO₃ surface is positively charged at pH < 10.0 (Tunusoglu, 2007). Consistent with this expectation, spectroscopic investigation of

U(VI) sorption at the calcite-water interface shows that the U-O bond lengths of the U species adsorbed onto calcite are similar to those of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ at pH 8.3 (Elzinga et al., 2004; Kerisit et al., 2010). Thus, it is reasonable to assume that in our experiments the charged U species in the aqueous solution are preferentially incorporated into aragonite and calcite relative to the neutral U species, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$. The three negatively-charged U species in Group 1 and Group 2 (Table 3) might not partition to the same extent between the aqueous solution and CaCO_3 due to their differences in charges.

If we assume that only the charged species are incorporated into the mineral, and make the simplifying assumption that these charged species are all incorporated to the same extent as each other, then the isotopic composition of U incorporated into the solid at any instant (the “instantaneous solid”) will be the same as the average isotopic composition of all charged U species in the aqueous solution. In this scenario, isotope fractionation between dissolved and mineral-bound U occurs because $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$, which we hypothesize to have the lightest $\delta^{238}\text{U}$, is not incorporated into the mineral. As a consequence, the isotope fractionation between the U in the aqueous solution and U incorporated into the mineral should increase as the relative abundance of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ increases.

4.1.3 Quantitative modeling of U isotope variations due to changes in aqueous U speciation

Because the isotope fractionation between different aqueous U species is not known experimentally and is difficult to simulate accurately using quantum mechanical

approaches, the modeling approach described below takes advantage of groupings of similar bond strengths in Table 2 and mass balance calculations to determine the relative isotope fractionations between aqueous U species.

The basic hypothesis put forth in Section 4.1.2 is that the isotopic composition of U incorporated into the instantaneous calcium carbonate ($\delta^{238}\text{U}_{\text{instantaneous}}$) is equal to the abundance-weighted average isotopic composition of charged U species in solution ($\delta^{238}\text{U}_{\text{charged}}$). It follows that the experimentally determined U isotope fractionation factor (α) during coprecipitation experiments reflects the difference between $\delta^{238}\text{U}_{\text{charged}}$ and the average composition of total dissolved aqueous U species ($\delta^{238}\text{U}_{\text{total}}$):

$$(\alpha - 1) \times 1000 \approx \delta^{238}\text{U}_{\text{instantaneous}} - \delta^{238}\text{U}_{\text{total}} = \delta^{238}\text{U}_{\text{charged}} - \delta^{238}\text{U}_{\text{total}} \quad \text{Eq. 3}$$

The isotopic composition of the charged species is related to the isotopic composition of the total dissolved U species via an isotopic mass balance equation involving the charged ($\delta^{238}\text{U}_{\text{charged}}$) and uncharged U ($\delta^{238}\text{U}_{\text{neutral}}$) species:

$$f_{\text{neutral}} \times \delta^{238}\text{U}_{\text{neutral}} + (1 - f_{\text{neutral}}) \times \delta^{238}\text{U}_{\text{charged}} = \delta^{238}\text{U}_{\text{total}} \quad \text{Eq. 4}$$

where f_{neutral} is the molar fraction of neutrally-charged U species— $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ —in aqueous solution.

Because Eq. 4 contains two unknowns ($\delta^{238}\text{U}_{\text{neutral}}$, $\delta^{238}\text{U}_{\text{charged}}$) it cannot be solved without a second isotopic mass balance equation. For the pH ~ 8.5 experiments, the aqueous U speciation is dominated by four U species in Group 1 and Group 2 representing > 99.99 % of total dissolved U. These four species can be grouped into two groups (Group 1 and 2 in Table 2) based on similarities in their local bonding environments, and thus the isotopic composition of U species within each group should

be identical. Based on these groupings, a second isotopic mass balance equation can be written:

$$f_1 \times \delta^{238}\text{U}_1 + (1-f_1) \times (\delta^{238}\text{U}_1 + \Delta^{238}\text{U}_{2-1}) = \delta^{238}\text{U}_{\text{total}} \quad \text{Eq. 5}$$

where f_1 is the fraction of Group 1, $\delta^{238}\text{U}_1$ is the U isotope composition of Group 1, and $\Delta^{238}\text{U}_{2-1}$ is the $\delta^{238}\text{U}$ difference between the two groups of U species due to the equilibrium isotope fractionation. Because the neutral U species is a member of Group 1, $\delta^{238}\text{U}_{\text{neutral}}$ in Eq. 4 is equal to $\delta^{238}\text{U}_1$ in Eq. 5. Using this information, the difference in isotopic compositions between neutral U species and total dissolved U species ($\Delta^{238}\text{U}_{\text{neutral-total}}$) can be derived:

$$\Delta^{238}\text{U}_{\text{neutral-total}} = \delta^{238}\text{U}_{\text{neutral}} - \delta^{238}\text{U}_{\text{total}} = (f_1 - 1)\Delta^{238}\text{U}_{2-1} \quad \text{Eq. 6}$$

A step-by-step derivation of Eq. 6 is provided in the Supplementary Information.

Combining Eq. 3 and 4, the difference in isotopic compositions between neutral U species and total dissolved U species ($\Delta^{238}\text{U}_{\text{neutral-total}}$) can also be written as:

$$\begin{aligned} \Delta^{238}\text{U}_{\text{neutral-total}} &= \delta^{238}\text{U}_{\text{neutral}} - \delta^{238}\text{U}_{\text{total}} \\ &= \frac{f_{\text{neutral}} - 1}{f_{\text{neutral}}} (\alpha - 1) \times 1000 \end{aligned} \quad \text{Eq. 7}$$

From Eq. 6 and 7, the U isotope fractionation factor (α) can be derived as:

$$\alpha = \frac{\Delta^{238}\text{U}_{2-1}}{1000} \times \frac{f_{\text{neutral}}(f_1 - 1)}{f_{\text{neutral}} - 1} + 1 \quad \text{Eq. 8}$$

Eq. 8 predicts a linear relationship between $\{f_{\text{neutral}}(f_1 - 1)/(f_{\text{neutral}} - 1)\}$ and observed experimental fractionation. From the slope of this relationship, it is possible to infer $\Delta^{238}\text{U}_{2-1}$.

Figure 7 shows the linear fitting of Rayleigh isotope fractionation factors (α) observed in CaCO_3 coprecipitation experiments A_1 , A_1^* , A_3 and C_3 at $\text{pH} \sim 8.5$ versus $\{f_{\text{neutral}}(f_1-1)/(f_{\text{neutral}}-1)\}$. The isotope fractionation factor in C_1 at $\text{pH} \sim 8.5$ (0.99979 +0.00021/-0.00027) is not included in Fig. 7 because of its large magnitude of fractionation and large uncertainty, due to the narrow range of f in Rayleigh model fitting. The inferred value of $\Delta^{238}\text{U}_{2-1}$ is 0.32 ± 0.06 ‰, which indicates $\delta^{238}\text{U}$ of Group 2 is about 0.32 ± 0.06 ‰ heavier than that of Group 1. The magnitude of U isotope fractionation between these U species is similar to the range of U isotope fractionation resulting from coordination changes during U adsorption to birnessite, goethite, illite, quartz and aquifer sediments (0.01 - 0.25 ‰, Brennecka et al., 2011b; Jemison et al., 2014) and U isotope fractionation of $\text{UO}_2(\text{CO}_3)_3^{4-}$ during ion-exchange chromatography (0.34 ± 0.05 ‰; Aoyama et al., 1989).

Using the estimated value of $\Delta^{238}\text{U}_{2-1}$, Eq. 8 can be used to predict the U isotope fractionation factor (α) as a function of the fraction of neutral U species (Fig. 8). This requires that the relationship between the fraction of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ (f_1) and the fraction of U species in Group 1 (f_{neutral}) should be known.

The relationship between f_1 and f_{neutral} can be derived from U chemical equilibrium. The chemical equilibrium equations of the U species are:

$$K_2 = \frac{\gamma_{\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})} [\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})]}{(\gamma_{\text{UO}_2^{2+}} [\text{UO}_2^{2+}]) (\gamma_{\text{CO}_3^{2-}} [\text{CO}_3^{2-}])^3 (\gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}])^2} \quad \text{Eq. 10}$$

$$K_3 = \frac{(\gamma_{\text{CaUO}_2(\text{CO}_3)_3^{2-}} [\text{CaUO}_2(\text{CO}_3)_3^{2-}])}{(\gamma_{\text{UO}_2^{2+}} [\text{UO}_2^{2+}]) (\gamma_{\text{CO}_3^{2-}} [\text{CO}_3^{2-}])^3 (\gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}])^2} \quad \text{Eq. 11}$$

$$K_4 = \frac{(\gamma_{\text{MgUO}_2(\text{CO}_3)_3^{2-}} [\text{MgUO}_2(\text{CO}_3)_3^{2-}])}{(\gamma_{\text{UO}_2^{2+}} [\text{UO}_2^{2+}]) (\gamma_{\text{CO}_3^{2-}} [\text{CO}_3^{2-}])^3 (\gamma_{\text{Mg}^{2+}} [\text{Mg}^{2+}])} \quad \text{Eq. 12}$$

where K_1 , K_2 , K_3 and K_4 are equilibrium constants for chemical equilibrium in Eq. 9, 10, 11 and 12; γ_i is activity coefficient of chemical species (i represents chemical species, for example, UO_2^{2+}); and chemical species in square brackets represent the concentration of those species (e.g., $[\text{UO}_2^{2+}]$ is the concentration of UO_2^{2+}). The activity coefficient of the neutral U species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ is assumed to be 1.

Combining Eq. 9, 10, 11 and 12, the fractions of $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, and $\text{MgUO}_2(\text{CO}_3)_3^{2-}$ are derived as:

$$f_{\text{UO}_2(\text{CO}_3)_3^{4-}} = \left(\frac{K_1}{K_2} \times \frac{1}{\gamma_{\text{UO}_2(\text{CO}_3)_3^{4-}} (\gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}])^2} \right) \times f_{\text{neutral}} \quad \text{Eq. 13}$$

$$f_{\text{CaUO}_2(\text{CO}_3)_3^{2-}} = \left(\frac{K_3}{K_2} \times \frac{1}{\gamma_{\text{CaUO}_2(\text{CO}_3)_3^{2-}} (\gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}])} \right) \times f_{\text{neutral}} \quad \text{Eq. 14}$$

$$f_{\text{MgUO}_2(\text{CO}_3)_3^{2-}} = \left(\frac{K_4 \times \frac{(\gamma_{\text{Mg}^{2+}} [\text{Mg}^{2+}])}{\gamma_{\text{MgUO}_2(\text{CO}_3)_3^{2-}} (\gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}])^2}}{K_2} \right) \times f_{\text{neutral}} \quad \text{Eq. 15}$$

Thus, the relationship between f_1 and f_{neutral} can be described by (see Supplementary Information for derivation):

$$f_1 = \left(1 + \frac{K_1}{K_2} \times \frac{1}{\gamma_{\text{UO}_2(\text{CO}_3)_3^{4-}} (\gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}])^2} \right) \times f_{\text{neutral}} \quad \text{Eq. 16}$$

Plugging f_1 in Eq. 16 into Eq. 8, the isotope fractionation factor (α) can be derived as a function of $[\text{Ca}^{2+}]$ and f_{neutral} below:

$$\alpha = \frac{\Delta^{238}\text{U}_{2-1}}{1000} \times \frac{(f_{\text{neutral}})^2}{f_{\text{neutral}} - 1} \left(1 + \frac{K_1}{K_2} \times \frac{1}{\gamma_{\text{UO}_2(\text{CO}_3)_3^{4-}} (\gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}])^2} \right) + 1 \quad \text{Eq. 17}$$

There are two variables in this function. Thus, it is necessary to determine the relationship between $[\text{Ca}^{2+}]$ and f_{neutral} . If we restrict the model to $\text{pH} > 8$, there are only four significant U species (in Group 1 and Group 2), whose abundances sum to unity:

$$1 = f_{\text{neutral}} + f_{\text{UO}_2(\text{CO}_3)_3^{4-}} + f_{\text{CaUO}_2(\text{CO}_3)_3^{2-}} + f_{\text{MgUO}_2(\text{CO}_3)_3^{2-}} \quad \text{Eq. 18}$$

Combine Eq. 13, 14, 15 and 18, we can get the fraction of neutral U species as:

$$f_{\text{neutral}} = \left(1 + \frac{K_1}{K_2 \gamma_{\text{UO}_2(\text{CO}_3)_3^{4-}} (\gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}])^2} + \frac{K_3}{K_2 \gamma_{\text{CaUO}_2(\text{CO}_3)_3^{2-}} \gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}]} + \frac{K_4 (\gamma_{\text{Mg}^{2+}} [\text{Mg}^{2+}])}{K_2 \gamma_{\text{MgUO}_2(\text{CO}_3)_3^{2-}} (\gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}])^2} \right)^{-1} \quad \text{Eq. 19}$$

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This equation shows that, at $\text{pH} > 8$, constant ionic strength, and fixed $[\text{Mg}^{2+}]$, f_{neutral} varies only as a function of $[\text{Ca}^{2+}]$. Thus, combining Eq. 17 and 19, the isotope

fractionation factor (α) as a function of the fraction of neutral U species (f_{neutral}) can be described.

To predict the relationship between f_{neutral} and the U isotope fractionation factor (α), the following experimental conditions are assumed: (1) $[\text{Mg}^{2+}] = 50 \text{ mM}$ and ionic strength = 0.65 M (A_1 and A_1^*); (2) $[\text{Mg}^{2+}] = 100 \text{ mM}$, and ionic strength = 0.80 M (A_3); (3) $[\text{Mg}^{2+}] = 0 \text{ mM}$ and ionic strength = 2.0 M (C_3). The activity coefficients of all chemical species are calculated using the software PHREEQC (Parkhurst and Appelo, 2004). With all these conditions, and using equilibrium constants (K_1 , K_2 , K_3 and K_4) from Grenthe et al. (1992) and Dong and Brooks (2006), the U isotope fractionation factor (α) as a function of f_{neutral} at different $[\text{Mg}^{2+}]$ is calculated and displayed in Fig. 8.

Fig. 8 predicts that α always increases as the fraction of neutral U species increases at different Mg concentrations. This prediction is consistent with our experimental results at pH ~ 8.5 . Larger fractionation was observed in experiments A_1 ($1.00007 \pm 0.00002/-0.00003$) and A_1^* (1.00005 ± 0.00001), in which 27 % and 24 %, respectively, of the dissolved U was present as $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$, while smaller U isotope fractionation was seen in experiment A_3 (1.00003 ± 0.00001), which had a fraction of 9 % $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$. Calcite experiment C_3 showed unresolvable U isotope fractionation with a fraction of 5 % $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ in the aqueous solution. All these isotope fractionation factors lie on their corresponding isotope fractionation factor lines (Fig. 8).

The agreement between the model and data in Figures 7 and 8 support the hypothesis that differences in aqueous U speciation prior to incorporation is a likely mechanism to explain our results in these experiments.

One limitation of the model discussed above is that it is limited to $\text{pH} > 8$, where only the four U species in Group 1 and 2 are present. At lower pH (i.e., < 7.5), the U species in Group 3 and 4 become significantly abundant but are not accounted for by the model. Further experiments would be required to constrain the average U isotopic composition of all charged U species and total dissolved U species ($\Delta^{238}\text{U}_{\text{charged-total}}$) in the presence of these new U species. However, even without knowing this value, Eq. 8 qualitatively predicts that the fractionation in such experiments should be small, because f_{neutral} is small (13 % for A_2 and 5 % for C_2). This is qualitatively consistent with the unresolvable U isotope fractionation factor observed in aragonite experiment A_2 (1.00001 ± 0.00002).

4.2 Implications for marine carbonates as a paleoredox proxy

In order to extrapolate the U isotope fractionation in our abiotic carbonate experimental results to that occurring in marine carbonates in nature, it is necessary to consider the effect of experimental conditions (U concentration and crystal growth rates) on the U isotope fractionation. Although we did not specifically examine the effect of crystal growth rate, we argue that our results are probably representative of natural systems because the estimated growth rates of carbonates in our experiments fall within the range of natural carbonate growth rates in natural marine systems. Likewise,

geochemical modeling using PHREEQC (Parkhurst and Appelo, 2004) showed that the U speciation should remain constant at U concentrations below 50 μM , suggesting that our results should be comparable to U speciation in seawater at much lower [U].

In order to predict the U isotope fractionation for U coprecipitation with carbonate minerals in natural seawater, we used U speciation modeling using the software PHREEQC (Parkhurst and Appelo, 2004) to estimate the abundances of the four main U species expected to be present in modern seawater: $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ (36 %), $\text{MgUO}_2(\text{CO}_3)_3^{2-}$ (14 %), $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ (45 %), and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (5 %) at pH 8.22. Notably, seawater is predicted to have more neutrally charged $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ than was present in our experiments (27 % as the maximum percentage in A_1). By using the relationships inferred from our study (e.g., Fig. 8), we can extrapolate to seawater conditions. This extrapolation suggests that abiotic CaCO_3 precipitation in modern seawater may result in an isotope fractionation factor of 1.00009 - 1.00013, and therefore that the U isotopic composition in abiotically precipitated marine carbonates may be 0.11 $\pm$ 0.02 ‰ heavier than that of total dissolved U in seawater.

To date, almost all measurements of primary calcium carbonate precipitates show U isotopic compositions similar to seawater (Weyer et al., 2008; Romaniello et al., 2013; Stirling et al., 2007; Tissot and Dauphas, 2015). However, almost all of these samples are biological precipitates (e.g., coral and calcifying green and red algae). If our prediction of the U isotope fractionation during U incorporation into abiotic calcium carbonate in seawater is right, then biological processes may lead to smaller U isotope fractionation during U uptake by biotic CaCO_3 than during abiotic precipitation. Such processes include those that cause changes in $[\text{Mg}^{2+}]$, $[\text{Ca}^{2+}]$, $[\text{CO}_3^{2-}]$, or pH at the calcification

sites. For example, in situ pH microelectrode and B isotope analyses have demonstrated that some biological calcifiers elevate pH as much as ~ 1 unit above the seawater pH (8.2) in the calcification sites, facilitating CaCO_3 precipitation with high oversaturation (Zeebe et al., 2003; Trotter et al., 2011; Rollion-Bard and Erez, 2009; Nooijer et al., 2009; Al-Horani et al, 2003). The elevation of pH by ~1 unit can lead to significant increase in $[\text{CO}_3^{2-}]$ (~ 90 %, Nooijer et al., 2009). Additionally, $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ in the calcification fluids are lower than in seawater (Weiner and Dove, 2003). The decreased $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ and elevated $[\text{CO}_3^{2-}]$ in the calcification sites should reduce the fraction of U present as the neutral U species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$. This change may reduce U isotope fractionation during U coprecipitation with CaCO_3 .

However, primary calcium carbonates are metastable aragonite and/or calcite, and are subsequently converted into stable low-Mg calcite and/or dolomite (Knauth and Kennedy, 2009; Morse and Mackenzie, 1990). During diagenesis, CaCO_3 will be dissolved and recrystallized, releasing original U within the crystal and incorporating new U from the ambient pore fluids which might be quite different in chemical composition from original carbonate precipitating fluids (Land, 1986). In this scenario, the U isotope composition in marine carbonates might change in two ways. One is the incorporation of U with different U isotope composition in the recrystallizing fluids. The other is the change in chemical composition of the recrystallizing fluids (pH, P_{CO_2} , and Ca^{2+} and Mg^{2+} concentrations), leading to variation in the magnitude of U isotope fractionation during U incorporation into calcium carbonates. Thus, it is essential to assess the effects of diagenetic processes on U isotope fractionation during application of U isotopes in marine calcium carbonates as a paleoredox proxy.

5. Conclusions

Our experiments revealed small fractionations of U isotopes (fractionation factor < 1.00009) during coprecipitation with aragonite. Based on equilibrium speciation modeling, we hypothesize that the magnitude of the fractionation depends on the U speciation. When the fraction of neutral U species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ in the aqueous solution was larger than 24 %, detectable fractionation was observed. When the fraction of this neutral species was < 13 %, fractionation was either not detectable or barely detectable. No resolvable U isotope fractionation was observed in any calcite coprecipitation experiments, all of which had < 11 % of U present as $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$. When fractionation was observed, Rayleigh-type behavior was seen, with heavier U isotopes preferentially incorporated into aragonite at pH 8.5.

Equilibrium isotope fractionation between different aqueous U species prior to incorporation is proposed as the most likely mechanism to explain these results. Specifically, we hypothesize a fractionation between the uncharged species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ and most of the dissolved charged species, favoring light U isotopes in $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$. Fractionation arises because charged U species are more readily incorporated into calcite and aragonite during precipitation. The relative abundance of the uncharged species was greatest in our aragonite experiments, potentially explaining why fractionation was seen in these experiments. Further work is needed to test this hypothesis, such as by quantum chemical modeling of U isotope fractionation between $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ and other U species.

796 Our results suggest that U speciation in seawater may be the key factor
797 controlling U isotope fractionation during incorporation into abiotic carbonates. Although
798 the similarity of $\delta^{238}\text{U}$ between seawater and modern biogenic carbonates suggests that U
799 isotopes in biotic marine carbonates might be a reliable paleoredox proxy, our result
800 show that interpretation of marine $\delta^{238}\text{U}$ records from abiotic carbonates might require
801 corrections which would depend on the U speciation in seawater at the time of
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FIGURE CAPTIONS

Figure 1. Illustration of experimental setup for the constant addition method.

Figure 2. Variations of pH in calcium carbonate coprecipitation experiments at pH 8.5 ± 0.1 (A_1 and C_1) and 7.5 ± 0.1 (A_2 and C_2). The variations of pH in other experiments A_1^* , A_3 and C_3 (pH ~ 8.5) were similar to those of A_1 and C_1 .

Figure 3. XRD spectra of calcium carbonate. A_1 (aragonite 1), A_2 (aragonite 2), A_{std} (aragonite standard), C_1 (calcite 1), C_2 (calcite 2), C_3 (calcite 3), C_{std} (calcite standard).

Figure 4. Aqueous U(VI) speciation as a function of pH (7-9) for aragonite and calcite experiments at $P_{\text{CO}_2} = 10^{-3.5}$ atm. The vertical dashed lines are pHs of different aragonite and calcite experiments. (a) U(VI) speciation in aragonite experiments A_1 , A_2 and A_1^* with ionic strength $I = 0.65$ M, total Ca^{2+} concentration 5 mM, Mg^{2+} concentration 50 mM. U speciation in A_1^* is slightly different from that in A_1 due to the lower concentration of Ca^{2+} (4.8 mM); (b) U(VI) speciation in aragonite experiment A_3 with ionic strength $I=0.8$ M, total Ca^{2+} concentration 4 mM, Mg^{2+} concentration 100 mM; (c) U(VI) calcite experiments C_1 and C_2 with ionic strength $I=0.5$ M, total Ca^{2+} concentration 2 mM; (d) U(VI) speciation in calcite experiment C_3 with ionic strength $I=2.0$ M, total Ca^{2+} concentration 3.5 mM.

Figure 5. U isotopic compositions of aqueous and solid samples versus fraction of U remaining in the aqueous solution for aragonite experiments A_1 , A_1^* , A_2 and A_3 . The

open triangles and filled rectangles represent the U isotopic compositions of aqueous samples and bulk solid samples, respectively. The black curves are Rayleigh fractionation curves in all aragonite experiments. The gray areas in (a), (b), (c) and (d) are confidence envelopes of the isotope fractionation factor α (95% confidence interval).

Figure 6. U isotopic composition in aqueous and solid samples versus fraction of U incorporated into calcite. The open triangles, filled triangles and filled rectangles are the U isotopic compositions of aqueous samples, daily solid samples and bulk solid samples, respectively.

Figure 7. Linear fitting for Rayleigh isotope fractionation factors (α) in CaCO_3 coprecipitation experiments at pH 8.5 versus $\{f_{\text{neutral}}(f_1-1)/(f_{\text{neutral}}-1)\}$. The filled rectangle, circle, triangle and diamond are Rayleigh isotope fractionation factors observed in experiments A_1 , A_1^* , A_3 , and C_3 .

Figure 8. U isotope fractionation factor (α) between U in instantaneous solid and total dissolved U vs. fraction of neutral U species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ at different concentrations of Mg^{2+} and ionic strengths. The red, blue and black curves correspond to experimental conditions in A_1 and A_1^* , A_3 and C_3 . The filled rectangle, circle, triangle and diamond are Rayleigh isotope fractionation factors observed in experiments A_1 , A_1^* , A_3 , and C_3 . The dashed line shows the fraction of neutral U species and the U isotopic composition fractionation predicted for the open ocean. The vertical dashed line is the

1204 fraction of neutral U species – $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ predicted from thermodynamic models
1205 using PHREEQC.
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Table 1. Summary and results of CaCO₃ coprecipitation experiments

Experiment	pH	Electrolyte NaCl (M)	Reagents	Flow rate (μ l/min)	Time (hrs)	Mg ²⁺ (mM)	Ca ²⁺ (mM)	CaCO ₃ (g)	U drawdown (%)	U in carbonate (μ g U/g CaCO ₃)
A ₁	8.5 $\pm$ 0.1	0.50	CaCl ₂ + NaHCO ₃ + MgCl ₂	4	160	50	5	1.94	94.9	2145
A ₂	7.5 $\pm$ 0.1	0.50	CaCl ₂ + NaHCO ₃ + MgCl ₂	40	16	50	5	1.71	98.6	2525
A ₃	8.5 $\pm$ 0.1	0.50	CaCl ₂ + NaHCO ₃ + MgCl ₂	4	160	100	4	1.96	98.2	2075
A ₁ *	8.5 $\pm$ 0.1	0.50	CaCl ₂ + NaHCO ₃ + MgCl ₂	4	160	50	4.8	1.95	93.7	2053
C ₁	8.5 $\pm$ 0.1	0.50	CaCl ₂ + NaHCO ₃	4	160	0	2	1.91	14.5	336
C ₂	7.5 $\pm$ 0.1	0.50	CaCl ₂ + NaHCO ₃	40	16	0	2	1.64	17.5	360
C ₃	8.5 $\pm$ 0.1	2.00	CaCl ₂ + Na ₂ CO ₃	10	168	0	3.5	19.44	90.5	250

Note: Mg²⁺ and Ca²⁺ were concentrations of Mg and Ca after pH was stable. Flow rate in the table is the flow rate of delivering CaCl₂ and NaHCO₃/Na₂CO₃ solutions into the reactor.

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1215 **Table 2.** Rayleigh isotope fractionation factors in aragonite and calcite experiments

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Experiment	pH	U uptake (%)	f_{neutral}	Rayleigh isotope fractionation factor (α)
A ₁	8.5 ± 0.1	94.9	0.27	1.00007 +0.00002/-0.00003
A ₁ *	8.5 ± 0.1	93.7	0.24	1.00005 +0.00001/-0.00001
A ₂	7.5 ± 0.1	98.6	0.13	1.00001 +0.00002/-0.00002
A ₃	8.5 ± 0.1	98.2	0.09	1.00003 +0.00001/-0.00001
C ₁	8.5 ± 0.1	14.5	0.11	0.99979 +0.00021/-0.00027
C ₂	7.5 ± 0.1	17.5	0.05	1.00043 +0.00011/-0.00050
C ₃	8.5 ± 0.1	90.5	0.05	1.00000 +0.00005/-0.00003

1217 Note: f_{neutral} is the fraction of neutral U species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$.

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Table 3. Coordination numbers and distances between U and its nearest atoms

	U(VI) species	Coordination number (U-O _{eq})	U-O _{ax} (Å)	U-O _{eq} (Å)	References
Group 1	UO ₂ (CO ₃) ₃ ⁴⁻	6.0	1.80	2.43	Docrat et al., 1999
	Ca ₂ UO ₂ (CO ₃) ₃ (aq)	6.0	1.80	2.44	Bernhard et al., 2001
Group 2	CaUO ₂ (CO ₃) ₃ ²⁻	6.0	1.80	2.40	Kerisit et al., 2010
	MgUO ₂ (CO ₃) ₃ ²⁻	6.0	1.80	2.39	Kerisit et al., 2010
Group 3	UO ₂ (CO ₃) ₂ ²⁻	4.0	1.81	2.36	Kerisit et al., 2010
Group 4	(UO ₂) ₂ (CO ₃)(OH) ₃ ⁻	1.3		2.36	Szabo et al., 2000
		3.9	1.80	2.45	
	Adsorbed-U on calcite (pH=8.3)	6.0	1.80	2.40	Elzinga et al., 2004
Calcite Bonding Environment	Adsorbed-U on calcite (pH=7.4)	3.0		2.25	Elzinga et al., 2004
		3.0	1.80	2.45	

Note: U-O_{ax} is the distance between U and axial O; U-O_{eq} is the distance between U and equatorial O. The uncertainty for the measurements the bond length is within ± 0.01 Å.

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