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Syndepositional diagenetic control of molybdenum isotope variations in carbonate sediments from the Bahamas

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ABSTRACT

Molybdenum (Mo) isotope variations recorded in black shales provide important constraints on marine paleoredox conditions. However, suitable shales are not ubiquitous in the geologic record. Moreover, reliable reconstruction of Mo isotope records from shales requires deposition from a water column containing very high concentrations of sulfide—a condition which is both rare and difficult to verify with certainty when examining preserved sediments. The utility of Mo isotopic records could be improved if reconstructions were possible using alternative lithologies, such as marine carbonates, which are more abundant in the geologic record.

Here, we focus on the role of early diagenesis in determining the Mo isotopic composition preserved in shallow-water carbonate sediments from four push cores collected in different shallow-water depositional environments in the Bahamas. In contrast with carbonate primary precipitates, which generally contain <0.2 ppm Mo, we find that carbonate sediments deposited under fully oxic shallow bottom water can experience extensive syndepositional authigenic Mo enrichment (1 to >10 ppm Mo). The extent of this authigenic enrichment appears to be driven by high concentrations of hydrogen sulfide in the porewaters. In cores with the least authigenic Mo enrichment and lowest pore water sulfide, Mo isotopes are ~1–1.2‰ lighter than seawater, while cores with greater Mo enrichments and higher pore water sulfide approach seawater Mo isotope values (2.2–2.5‰), even under oxic bottom water conditions. However, the sensitivity of bulk carbonate δ^{98}Mo to syndepositional diagenetic conditions potentially complicates interpretation of a carbonate Mo isotope paleoredox proxy. Robust reconstruction of seawater Mo isotopic composition from carbonates will thus require the ability to place constraints on early diagenetic conditions of pore waters at the time of deposition. We show that in order to record seawater Mo isotope values, carbonate pore waters must contain 50–100 μM H_2S_{aq}, which is achieved only in organic- and sulfide-rich carbonate sediments.

1. Introduction

The marine geochemistry of molybdenum (Mo) is highly sensitive to the redox state of seawater, making Mo concentrations in marine sediments an attractive proxy for the reconstruction of paleoredox variations in the Earth's ocean (Algeo and Lyons, 2006; Emerson and Huested, 1991; Scott et al., 2008). Mo isotopes further strengthen this proxy by providing an additional constraint on globally-averaged redox conditions (Anbar, 2004; Arnold et al., 2004; Dahl et al., 2011; Duan et al., 2010; Kendall et al., 2009, 2011; Siebert et al., 2005; Wille et al., 2007). Because the residence time of Mo in seawater (~700 ka) greatly exceeds ocean mixing timescales (~1500 yr), the isotopic composition of Mo is uniform throughout the open ocean (Anbar, 2004; Nakagawa et al., 2012). In theory, this allows global average paleoredox conditions to be constructed from data at a single location, which is extremely useful when studying time periods where it is difficult to locate and establish the contemporaneous deposition of sediment in different depositional basins.

To date, most Mo isotope paleoredox reconstructions are based on black shale lithologies that are thought to quantitatively capture seawater Mo and directly record the Mo isotope composition of seawater (Erickson and Helz, 2000; Gordon et al., 2009; Neubert et al., 2008). However, black shales are not ubiquitous in the geologic record and so our conception of ocean redox evolution may be biased by the conditions of restricted marginal basins in which such shales are frequently deposited (Arthur and Sageman, 1994). Furthermore, quantitative scavenging of Mo from the water column into sediments only occurs when the water column concentration of H_2S_{aq} greatly exceeds 11 μM. Above this switch point, soluble molybdate ion (MoO_4^{2-}) is converted to the particle-reactive tetrathiomolybdate (MoS_4^{2-}) on the time scale of several months (Erickson and Helz, 2000). Under anoxic, weakly sulfidic, or

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seasonally varying conditions, Mo isotopes can be fractionated during incorporation into sediments (Brucker et al., 2009; Gordon et al., 2009; Neubert et al., 2008; Siebert et al., 2006). To avoid this complication, shales are routinely screened using iron (Fe) speciation to identify persistently euxinic conditions of deposition prior to Mo isotope analysis (Gordon et al., 2009). However, while this screening process can identify euxinic deposition conditions, it is difficult to prove that any particular threshold guarantees sufficient H_2S_{aq} to quantitatively scavenge Mo.

Recent work suggests that non-skeletal carbonates may directly record the Mo isotope composition of seawater, thus avoiding the need to demonstrate highly euxinic depositional conditions in shales (Voegelin et al., 2009). As carbonates are abundant in the geologic record and are often deposited along open marine settings, a well-established Mo isotope proxy based on variations in carbonate rocks would be highly complementary to existing black-shale based records. Several authors have already attempted to apply this concept to Archean carbonates (Czaja et al., 2012; Voegelin et al., 2010). In these studies, similarities between Mo isotope variations measured in carbonates and coeval shale intervals suggest that Mo isotopes in carbonates may provide a useful proxy for the Mo isotopic composition of seawater (Voegelin et al., 2010; Wille et al., 2007).

However, in order to accurately interpret Mo isotope variations in the carbonate rock record, it is important to first evaluate the diagenetic processes that might alter Mo isotopes during sedimentation and subsequent burial. Shallow-water carbonates commonly preserved in the geologic record are produced on biologically productive platforms and margins. Although generally referred to as "carbonate factories," these ecosystems also produce considerable organic matter which is remineralized during syndepositional diagenesis (Burdige and Zimmerman, 2002; Burdige et al., 2008; Hu and Burdige, 2007; Morse et al., 1987). Sulfate reduction is common in the pore waters of carbonate platform sediments. For example, in the Bahamas, pore water sulfide concentrations commonly reach 100–1000 μM (Hu and Burdige, 2007; Romaniello et al., 2013). Furthermore, high rates of respiration in carbonate pore waters lead to low pH conditions (Burdige et al., 2010; Hu and Burdige, 2007; Romaniello et al., 2013; Walter et al., 1993). Low pH conditions increase the ratio of H_2S_{aq} to total sulfide (ΣH_2S). In turn, H_2S_{aq} reacts with the normally soluble MoO_4^{2-} anion to form particle-reactive MoS_4^{2-} (Erickson and Helz, 2000). This species can be removed to sediments via complexation with organic matter, pyrite or other Fe-bearing minerals, or via further reduction to Mo(IV) species similar to molybdenite (Dahl et al., 2013; Erickson and Helz, 2000; Helz et al., 2011, 1996; Tribovillard et al., 2004). While previous studies primarily focused on the sequestration of Mo in euxinic water columns and muds, the purpose of this study was to look for evidence of a similar process occurring in sulfidic carbonate pore waters underlying well-oxygenated bottomwater in order to assess Mo isotope variations in calcium carbonates as a potential paleoredox proxy.

2. Materials and methods

Samples for this study were collected in the southern Exuma Islands, Bahamas, between Lee Stocking and Little Darby Islands in January and July of 2011, and were previously described by Romaniello et al. (2013). The sample set for this study consisted of a variety of primary carbonate precipitates collected throughout the study region along with sediment and pore water samples from four shallow push cores (~30–50 cm in length). Core 1 was collected in a shallow turtle grass flat (*Thalassia testudium*), and consisted of 0.1 mm–1 mm carbonate sand with abundant *Halimeda* fragments, and visible amounts of organic matter including *T. testudium* rhizomes and leaves. The area included a large number of shrimp (*Callianassa* sp.) mounds and burrows, although the core was collected to avoid these features. Core 2 was collected approximately 100 m southeast of Core 1 on a tidal flat devoid of vegetation. Sediment consisted of <1 mm carbonate sand that was homogenous throughout the core. Core 3 was collected in a *T. testudium* flat similar to Core 1, but in deeper water (~4 m) and in the absence of *Callianassa* burrows. Sediment at this site was similar to that of Core 1 but lacked *Halimeda* fragments. Core 4 was collected in a tidal pond on Norman's Pond Cay, which is connected to the ocean through a 1 m deep manmade channel that was used to facilitate salt production from the 17th–19th centuries (Hein and Winsborough, 2001; Wicklund et al., 1991). Sediment in Core 4 consisted of fine dark-colored carbonate mud, interspersed with larger carbonate sand skeletal fragments and intervals of buried microbial laminates.

2.1. Analytical methods

Pore water samples were collected using trace-metal-clean Rhizon pore water samplers, both in situ by inserting the samplers directly into the sediment in the field, and ex situ via small holes drilled in the core liners upon return to the field laboratory. Pore water samples were stored in bubble- and headspace-free 10 mL syringes and sealed with a stopcock. pH and sulfide concentrations were determined in the field immediately following sample collection (<3 h). Sample pH was measured using an ISFET pH electrode (IQ Scientific), calibrated using NBS buffers, and converted to the seawater scale assuming a H^+ activity of $f_{H^+} = 0.729$ (Perez and Fraga, 1987). Total sulfide was determined using the traditional Cline assay measuring the absorption in a 1 cm cell at 670 nm (Cline, 1969). Sulfide samples were diluted 1:50 using deionized water immediately prior to measurement. The concentration of H_2S_{aq} was calculated using the apparent equilibrium constant for seawater (Millero et al., 1988).

Molybdenum concentration and isotope measurements were made in the W. M. Keck Laboratory for Environmental Biogeochemistry at Arizona State University. Prior to analysis, sediments were dried at 100 °C and homogenized using a ball mill equipped with silicon carbide mortars. Sample aliquots (1.0 g) were ashed at 750 °C for 24 h to remove organics and then dissolved in 10 mL of 3 M nitric acid. Following dissolution, major and trace element concentrations were determined on sample aliquots at 1:2000 dilution using an Thermo X-Series 2 quadrupole ICP-MS. Concentrations are reported in parts per million by mass (i.e. 1 ppm = 1 mg/kg). Preliminary Mo concentrations were used to prepare aliquots of core samples containing >75 ng Mo, spiked with a ^{97}Mo—^{100}Mo double spike at a spike:sample molar ratio of ~2. Spiked samples were dried down, reconstituted in 2 mL of 0.5 M HCl and loaded onto cation exchange columns containing 2 mL of previously-cleaned cation exchange resin (BioRad AG 50WX8, 200–400 mesh). The initial eluate was collected, and residual Mo was eluted using additional 4 mL of 0.5 M HCl, leaving behind Fe on the column. Following cation columns, the HCl molarity of the samples was brought up to 4 M with the addition of 2.6 mL of 12.1 M HCl. The resulting solution was loaded onto anion exchange columns containing 1 mL of previously cleaned anion exchange resin (BioRad AG 1X8, 200–400 mesh). Matrix elements were eluted in an additional 5 mL of 4 M HCl. Residual Fe and Zr were eluted using 2 mL of 2 M HNO_3, and finally the Mo was eluted and collected in an additional 6 mL of 2 M HNO_3. Following column chemistry, samples were treated with a mixture of 0.5 mL concentrated HNO_3 and 0.2 mL 32% H_2O_2 repeatedly (3×) to oxidize any organic materials leached from the ion exchange resins. Mo isotopes ($^{98}Mo/^{95}Mo$) and final Mo concentrations (via double-spike isotope dilution) were determined on a Thermo Neptune MC-ICP-MS equipped with an ESI Apex Q desolvating nebulizer. The double spike equations were solved using a non-linear optimization approach coded in MATLAB. Isotope data are reported as:

$$\delta^{98/95}\mathrm{Mo}(‰) = 1000 \times \left[\left(^{98}\mathrm{Mo}/^{95}\mathrm{Mo}_{\mathrm{sample}}\right)/\left(^{98}\mathrm{Mo}/^{95}\mathrm{Mo}_{\mathrm{standard}}\right) - 1\right] \quad (1)$$

relative to the "RochMo2" in-house laboratory standard (Johnson