1 **Syn depositional diagenetic control of molybdenum isotope variations in**
2 **carbonate sediments from the Bahamas**

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25 **Abstract**

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

35 Here, we focus on the role of early diagenesis in determining the Mo isotopic
36 composition preserved in shallow-water carbonate sediments from four push
37 cores collected in different shallow-water depositional environments in the
38 Bahamas. In contrast with carbonate primary precipitates, which generally contain
39 <0.2 ppm Mo, we find that carbonate sediments deposited under fully oxic
40 shallow bottom water can experience extensive syndepositional authigenic
41 enrichment (1 to >10 ppm Mo). The extent of this authigenic enrichment appears
42 to be driven by high concentrations of hydrogen sulfide in the porewaters. In
43 cores with the least authigenic Mo enrichment and lowest pore water sulfide, Mo
44 isotopes are ~ 1 – 1.2% lighter than seawater, while cores with greater Mo
45 enrichments and higher pore water sulfide approach seawater Mo isotope values

46 (2.2-2.5‰), even under oxic bottom water conditions. However, the sensitivity of
47 bulk carbonate $\delta^{98}\text{Mo}$ to syndepositional diagenetic conditions potentially
48 complicates interpretation of a carbonate Mo isotope paleoredox proxy. Robust
49 reconstruction of seawater Mo isotopic composition from carbonates will thus
50 require the ability to place constraints on early diagenetic conditions of pore
51 waters at the time of deposition. We show that in order to record seawater Mo
52 isotopes values, carbonate pore waters must contain 50-100 $\mu\text{M H}_2\text{S}_{\text{aq}}$, which is
53 achieved only in organic- and sulfide-rich carbonate sediments.

54 **1 Introduction**

55 The marine geochemistry of molybdenum (Mo) is highly sensitive to the
56 redox state of seawater, making Mo concentrations in marine sediments an
57 attractive proxy for the reconstruction of paleoredox variations in the Earth's
58 ocean (Algeo and Lyons, 2006; Emerson and Huested, 1991; Scott et al., 2008).
59 Mo isotopes further strengthen this proxy by providing an additional constraint on
60 globally-averaged redox conditions (Anbar, 2004; Arnold et al., 2004; Dahl et al.,
61 2011; Duan et al., 2010; Kendall et al., 2009; Kendall et al., 2011; Siebert et al.,
62 2005; Wille et al., 2007). Because the residence time of Mo in seawater (~700 ka)
63 greatly exceeds ocean mixing timescales (~1500 yr), the isotopic composition of
64 Mo is uniform throughout the open ocean (Anbar, 2004; Nakagawa et al., 2012).
65 In theory, this allows global average paleoredox conditions to be constructed from
66 data at a single location, which is extremely useful when studying time periods

67 where it is difficult to locate and establish the contemporaneous deposition of
68 sediment in different depositional basins.

69 To date, most Mo isotope paleoredox reconstructions are based on black
70 shale lithologies that are thought to quantitatively capture seawater Mo and
71 directly record the Mo isotope composition of seawater (Erickson and Helz, 2000;
72 Gordon et al., 2009; Neubert et al., 2008). However, black shales are not
73 ubiquitous in the geologic record and so our conception of ocean redox evolution
74 may be biased by the conditions of restricted marginal basins in which such shales
75 are frequently deposited (Arthur and Sageman, 1994). Furthermore, quantitative
76 scavenging of Mo from the water column into sediments only occurs when the
77 water column concentration of $\text{H}_2\text{S}_{\text{aq}}$ greatly exceeds 11 μM . Above this switch
78 point, soluble molybdate ion (MoO_4^{2-}) is converted to the particle-reactive
79 tetrathiomolybdate (MoS_4^{2-}) on the time scale of several months (Erickson and
80 Helz, 2000). Under anoxic, weakly sulfidic, or seasonally varying conditions, Mo
81 isotopes can be fractionated during incorporation into sediments (Brucker et al.,
82 2009; Gordon et al., 2009; Neubert et al., 2008; Siebert et al., 2006). To avoid this
83 complication, shales are routinely screened using iron (Fe) speciation to identify
84 persistently euxinic conditions of deposition prior to Mo isotope analysis (Gordon
85 et al., 2009). However, while this screening process can identify euxinic
86 deposition conditions, it is difficult to prove that any particular threshold
87 guarantees sufficient $\text{H}_2\text{S}_{\text{aq}}$ to quantitatively scavenge Mo.

88 Recent work suggests that non-skeletal carbonates may directly record the
89 Mo isotope composition of seawater, thus avoiding the need to demonstrate

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

99 However, in order to accurately interpret Mo isotope variations in the
 100 carbonate rock record, it is important to first evaluate the diagenetic processes that
 101 might alter Mo isotopes during sedimentation and subsequent burial. Shallow-
 102 water carbonates commonly preserved in the geologic record are produced on
 103 biologically productive platforms and margins. Although generally referred to as
 104 “carbonate factories,” these ecosystems also produce considerable organic matter
 105 which is remineralized during syndepositional diagenesis (Burdige and
 106 Zimmerman, 2002; Burdige et al., 2008; Hu and Burdige, 2007; Morse et al.,
 107 1987). Sulfate reduction is common in the pore waters of carbonate platform
 108 sediments. For example, in the Bahamas, pore water sulfide concentrations
 109 commonly reach 100-1000uM (Hu and Burdige, 2007; Romaniello et al., 2013).
 110 Furthermore, high rates of respiration in carbonate pore waters lead to low pH
 111 conditions (Burdige et al., 2010; Hu and Burdige, 2007; Romaniello et al., 2013;
 112 Walter et al., 1993). Low pH conditions increase the ratio of H_2S_{aq} to total sulfide

113 ($\Sigma\text{H}_2\text{S}$). In turn, $\text{H}_2\text{S}_{\text{aq}}$ reacts with the normally soluble MoO_4^{2-} anion to form
114 particle-reactive MoS_4^{2-} (Erickson and Helz, 2000). This species can be removed
115 to sediments via complexation with organic matter, pyrite or other Fe-bearing
116 minerals, or via further reduction to Mo(IV) species similar to molybdenite (Dahl
117 et al., 2013a; Erickson and Helz, 2000; Helz et al., 2011; Helz et al., 1996;
118 Tribovillard et al., 2004). While previous studies primarily focused on the
119 sequestration of Mo in euxinic water columns and muds, the purpose of this study
120 was to look for evidence of a similar process occurring in sulfidic carbonate pore
121 waters underlying well-oxygenated bottomwater in order to assess Mo isotope
122 variations in calcium carbonates as a potential paleoredox proxy.

123 **2 Materials and Methods**

124 Samples for this study were collected in the southern Exuma Islands,
125 Bahamas, between Lee Stocking and Little Darby Islands in January and July of
126 2011, and were previously described by Romaniello et al. (2013). The sample set
127 for this study consisted of a variety of primary carbonate precipitates collected
128 throughout the study region along with sediment and pore water samples from
129 four shallow push cores (~30-50 cm in length). Core 1 was collected in a shallow
130 turtle grass flat (*Thalassia testudium*), and consisted of 0.1 mm-1 mm carbonate
131 sand with abundant *Halimeda* fragments, and visible amounts of organic matter
132 including *T. testudium* rhizomes and leaves. The area included a large number of
133 shrimp (*Callinassa* sp.) mounds and burrows, although the core was collected to
134 avoid these features. Core 2 was collected approximately 100 meters 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 10mL syringes and sealed with a stopcock. pH and sulfide concentrations were determined in the field immediately following sample collection (< 3 hours). 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

157 to measurement. The concentration of $\text{H}_2\text{S}_{\text{aq}}$ was calculated using the apparent
158 equilibrium constant for seawater (Millero et al., 1988).

159 Molybdenum concentration and isotope measurements were made in the
160 W. M. Keck Laboratory for Environmental Biogeochemistry at Arizona State
161 University. Prior to analysis, sediments were dried at 100°C and homogenized
162 using a ball mill equipped with silicon carbide mortars. Sample aliquots (1.0 g)
163 were ashed at 750°C for 24 hours to remove organics and then dissolved in 10 mL
164 of 3 M nitric acid. Following dissolution, major and trace element concentrations
165 were determined on sample aliquots at 1:2000 dilution using an Thermo X-Series
166 2 quadrupole ICP-MS. Concentrations are reported in parts per million by mass
167 (i.e. 1 ppm = 1 mg/kg). Preliminary Mo concentrations were used to prepare
168 aliquots of core samples containing >75 ng Mo, spiked with a ^{97}Mo - ^{100}Mo double
169 spike at a spike:sample molar ratio of ~2. Spiked samples were dried down,
170 reconstituted in 2 mL of 0.5 M HCl and loaded onto cation exchange columns
171 containing 2 mL of previously-cleaned cation exchange resin (BioRad AG
172 50WX8, 200-400 mesh). The initial eluate was collected, and residual Mo was
173 eluted using additional 4 ml of 0.5 M HCl, leaving behind Fe on the column.
174 Following cation columns, the HCl molarity of the samples was brought up to 4
175 M with the addition of 2.6 mL of 12.1 M HCl. The resulting solution was loaded
176 onto anion exchange columns containing 1 ml of previously cleaned anion
177 exchange resin (BioRad AG 1X8, 200-400 mesh). Matrix elements were eluted in
178 an additional 5 ml 4 M HCl. Residual Fe and Zr were eluted using 2 mL of 2 M
179 HNO_3 , and finally the Mo was eluted and collected in an additional 6 mL of 2 M

180 HNO₃. Following column chemistry, samples were treated with a mixture of 0.5
181 mL concentrated HNO₃ and 0.2 mL 32% H₂O₂ repeatedly (3X) to oxidize any
182 organic materials leached from the ion exchange resins. Mo isotopes (⁹⁸Mo/⁹⁵Mo)
183 and final Mo concentrations (via double-spike isotope dilution) were determined
184 on a Thermo Neptune MC-ICP-MS equipped with an ESI Apex Q desolvating
185 nebulizer. The double spike equations were solved using a non-linear
186 optimization approach coded in MATLAB. Isotope data are reported as:

$$187 \quad \delta^{98/95}\text{Mo} (\text{‰}) = 1000 \times [({}^{98}\text{Mo}/{}^{95}\text{Mo}_{\text{sample}}) / ({}^{98}\text{Mo}/{}^{95}\text{Mo}_{\text{standard}}) - 1] \quad \text{Eq. 1}$$

188 relative to the “RochMo2” in-house laboratory standard (Johnson Matthey
189 Specpur, Lot #802309E). Seawater has a $\delta^{98/95}\text{Mo}$ of 2.3‰ on this scale (Arnold
190 et al., 2004; Barling and Anbar, 2004; Goldberg et al., 2013; Neubert et al., 2008;
191 Siebert et al., 2003). During the analytical session, USGS SDO-1 shale and NIST
192 SRM 3134 molybdenum were run repeatedly as secondary standards and yielded
193 values of $+1.15 \pm 0.02 \text{‰}$ (2sd, N = 17) and $+0.33 \pm 0.02 \text{‰}$ (2sd, N = 20)
194 respectively, in very good agreement with previous published values (e.g.
195 Goldberg et al., 2013). Analytical precision for samples was determined as $\pm 2\sigma$ of
196 three repeat measurements of a single solution and averaged 0.05‰.

197 **3 Results**

198 **3.1 Mo Concentrations in Primary Precipitates**

199 Compared to the average composition of the upper crust, which contains ~
200 1.1 ppm Mo (Rudnick and Gao, 2003), Mo concentrations in primary precipitates

201 were generally low, ranging between 0.08-0.18 ppm (Fig. 1, Table S1).
202 Concentrations were lower in clean carbonate samples containing little associated
203 organic matter (corals, mollusk shells, ooids) and were elevated in algae samples
204 containing visible associated organic matter. Al and Ti concentrations were
205 variable, ranging from 4 - 644 ppm and 2 – 15 ppm, respectively. In all cases
206 however, detrital Mo, calculated from measured Al concentrations and assuming a
207 crustal Mo:Al₂O₃ ratio of 1.1 ppm/15.4 wt%, was <4% of measured Mo
208 concentrations. Our results are similar to the << 1 ppm Mo concentrations
209 previously reported for skeletal and non-skeletal precipitates measured by
210 Voegelin et al. (2009).

211 **3.2 Pore Water Chemistry**

212 Pore water sulfide profiles indicated significant (27-1500 µM) total sulfide
213 concentrations ($\sum H_2S = [H_2S_{aq}] + [HS^-]$) in all cores (Fig. 2, Table S2). Total
214 sulfide concentrations generally increased down core, with some evidence for a
215 local sulfide maximum between 10-15 cm. Extensive respiration was also
216 indicated by a decrease in pore water pH from bottom water values of ~8.0 to 7.0-
217 7.1 at >10 cm depth.

218 Over this pH range, Mo speciation is strongly influenced by the
219 equilibrium between hydrogen sulfide (H₂S_{aq}) and the bisulfide ion (HS⁻)
220 (Erickson and Helz, 2000). As a result of the high $\sum H_2S$ concentrations and
221 relatively low pH, calculated H₂S_{aq} concentrations were generally high, ranging
222 between ~20-300 µM in Cores 1, 3 and 4 (Table S2). H₂S_{aq} concentrations in

223 excess of 11 μM are important for the conversion of soluble MoO_4^{2-} to particle
224 reactive MoS_4^{2-} , suggesting that Mo scavenging should be an important process in
225 Cores 1, 2, and 4 (Erickson and Helz, 2000). Core 2, taken in a tidal flat, has the
226 lowest $\text{H}_2\text{S}_{\text{aq}}$ ranging between 3-30 μM , suggesting that Mo scavenging is
227 expected to be less pronounced in this core.

228 **3.3 Mo Concentrations and $\delta^{98/95}\text{Mo}$ in Core Samples**

229 Mo concentrations in core samples were quite variable between cores (Fig.
230 3, Table S3). Core 2 samples were similar to primary carbonate precipitates (0.10-
231 0.17 ppm), while samples from cores 1, 3, and 4 have Mo concentrations 10-100 $\times$
232 higher (1.8-28 ppm). Al and Ti concentrations in core samples were 120 – 8900
233 ppm and 9-250 ppm respectively. Detrital Mo estimated from measured Al
234 concentrations accounted for <1% of total Mo, implying that elevated Mo
235 concentrations in Cores 1, 2, and 4 were due to authigenic enrichment of Mo.

236 $\delta^{98/95}\text{Mo}$ varied between 1.1 and 2.5‰, with strong variations between
237 sites and more modest variations within cores. In general, cores with elevated Mo
238 concentrations also display $\delta^{98/95}\text{Mo}$ values closer to seawater (2.3‰), while Core
239 2 with the lowest Mo concentrations is significantly lighter (1.1-1.2‰). This
240 pattern is most clearly seen by comparing the results from Cores 2 and 3 where
241 down core variation in $\delta^{98/95}\text{Mo}$ is negligible. Cores 1 and 4 generally have heavy
242 Mo isotope compositions approaching that of seawater (1.6-2.5‰) but there is
243 significant down core variation that may reflect time-dependent variations in

244 depositional conditions or post-depositional alteration of $\delta^{98/95}\text{Mo}$ by processes
245 such as bioturbation.

246 **4 Discussion**

247 Compared with organic-rich mudrocks, limestone is often considered to be
248 low in organic matter and reduced sulfur, with trace metal concentrations
249 determined by co-precipitation of metals with the primary carbonate phase
250 (Gehman, 1962). However, the results presented here demonstrate that a diverse
251 range of depositional conditions exist at 10-1000 m spatial scales on the modern
252 Bahamas carbonate platform which strongly influence the distribution of Mo in
253 the bulk carbonate sediment. Although the number of cores is relatively small,
254 sediments range from organic-lean white carbonate sand (represented by Core 2)
255 to dark-colored, organic-rich carbonate muds and sands containing abundant
256 skeletal debris, ooids, peloids, and grapestones (Cores 1 and 3). In many areas, sea
257 grass can contribute significant amounts of macroscopic organic detritus to the
258 sediments (Burdige and Zimmerman, 2002; Morse et al., 1987). Although
259 laterally-restricted, tidal and evaporative ponds are also common features of
260 Bahamian islands. These environments range from fresh to hypersaline and are
261 often rich in organic matter sourced from cyanobacterial microbial mats and local
262 terrestrial and aquatic plants. Core 4 represents a tidally-influenced marine end-
263 member of these ponds.

264 As shown in Fig. 2, sulfate-reducing pore water conditions are common
265 across the range of sites sampled here. Measured pore water sulfide

266 concentrations are spatially variable, ranging from 27-1500 μM , and are similar to
267 previously published ranges in this area (Burdige et al., 2010; Burdige et al.,
268 2008; Hu and Burdige, 2007). High-rates of pore water respiration lead to low
269 pore water pH (7.0-7.5). Under these conditions, between 10-20% of $\Sigma\text{H}_2\text{S}$ is
270 present as $\text{H}_2\text{S}_{\text{aq}}$, which is able to complex molybdate (MoO_4^{2-}) to form a series of
271 particle-reactive thiomolybdate species ($\text{MoO}_x\text{S}_{4-x}^{2-}$) (Erickson and Helz, 2000;
272 Helz et al., 1996; Millero et al., 1988).

273 High concentrations of $\text{H}_2\text{S}_{\text{aq}}$ are present in Cores 1, 3, and 4 where
274 sediment Mo concentrations demonstrate significant authigenic enrichment (2-28
275 ppm) representing a 10-100 fold enrichment above concentrations found in
276 primary carbonate precipitates. In contrast, Core 2 with the lowest $\text{H}_2\text{S}_{\text{aq}}$
277 concentration displays background levels of Mo similar to measured primary
278 precipitates (0.10-0.17 ppm). This behavior is consistent with the suggestion of
279 the geochemical switch point where the speciation of dissolved MoO_4^{2-} rapidly
280 switches to MoS_4^{2-} at a $\text{H}_2\text{S}_{\text{aq}}$ concentration close to 11 μM (Erickson and Helz,
281 2000). Unlike MoO_4^{2-} , MoS_4^{2-} is thought to be readily scavenged to sediments,
282 leading to the high observed Mo concentrations in sulfidic cores (Fig. 4a). These
283 results demonstrate that a large amount of authigenic Mo can accumulate in
284 shallow water carbonate sediments, with concentrations approaching or exceeding
285 those typically associated with siliciclastic sediments (McManus et al., 2006;
286 Morford et al., 2005; Neubert et al., 2008).

287 Mo isotopes co-vary with Mo concentrations in core samples (Fig. 4b).

288 The lowest values are found in Core 2, where $\delta^{98/95}\text{Mo} = 1.07\text{-}1.24\text{‰}$,

289 approximately 1.2‰ lower than average seawater. $\delta^{98/95}\text{Mo}$ increases in Cores 1,
290 3, and 4, ranging between 1.60‰ to values reaching or even slightly exceeding
291 seawater (up to 2.51‰). The simplest explanation for this increase would be a
292 two end-member mixture between a carbonate-bound Mo component with
293 $\delta^{98/95}\text{Mo} \approx 1.1\text{‰}$ (similar to Core 2) and an authigenic Mo component similar to
294 seawater (2.3-2.5‰). However, a simple two end-member model fails to explain
295 the range of $\delta^{98/95}\text{Mo}$ values observed in Cores 1, 2, and 4 (Fig. 5).

296 A second possible explanation is that the isotopic composition of the
297 carbonate bound-Mo component is variable. Previous work has suggested primary
298 skeletal carbonate precipitates may have $\delta^{98/95}\text{Mo}$ ranging from 0.07-2.2‰
299 (Voegelin et al., 2009). However, the steep mixing line implied by Fig. 5 would
300 require an unreasonably low $\delta^{98/95}\text{Mo}$ for the carbonate end-member ($< -10\text{‰}$),
301 ruling out this explanation.

302 A third possibility is that the isotopic signature of authigenic Mo in
303 carbonate sediments is controlled by the stepwise conversion of MoO_4^{2-} to MoS_4^{2-}
304 via a series of intermediates, $\text{MoO}_{4-x}\text{S}_x^{2-}$. Dahl et al. (2010a) proposed similar
305 control to explain Mo isotope fractionation in meromictic Lake Cadagno. *Ab*
306 *initio* modeling results suggest that as MoO_4^{2-} undergoes stepwise sulfidization,
307 each step is accompanied by a $\sim 1.25\text{‰}$ fractionation (Dahl et al., 2010a; Tossell,
308 2005). Figure 6 depicts the equilibrium speciation of thiomolybdate species and
309 the expected equilibrium isotope partitioning for seawater as a function of $\text{H}_2\text{S}_{\text{aq}}$
310 concentration. An important result of this calculation is that although the switch
311 between MoS_4^{2-} and MoO_4^{2-} occurs at $11\text{ }\mu\text{M H}_2\text{S}_{\text{aq}}$, the equilibrium isotope

312 composition of MoOS_3^{2-} and MoS_4^{2-} only approach the $\delta^{98/95}\text{Mo}$ of seawater at
313 much higher concentrations of $\text{H}_2\text{S}_{\text{aq}}$, 20 μM and $>80 \mu\text{M}$ respectively. Because
314 the kinetics of sulfidization slow by an order of magnitude with each step,
315 conversion of MoO_4^{2-} to MoOS_3^{2-} can occur quickly (~days), while the formation
316 of MoS_4^{2-} requires weeks to months. As a result, these two species are probably
317 the dominant form of Mo(VI) in sulfidic pore waters given an average porewater
318 residence time of 3-10 days for the upper 30 of bank top carbonate sediments
319 (Burdige et al., 2008). Figure 7 demonstrates that a mixture of these species at
320 isotopic equilibrium under pore water conditions could potentially explain the
321 observed sediment $\delta^{98/95}\text{Mo}$ trends if these species dominated the authigenic
322 enrichment of Mo in these sediments. Subsequent isotope fractionation during
323 absorption of thiomolybdates to authigenic solids, reduction to Mo(IV), or
324 formation of Fe-Mo-S complexes could further modify these expected trends, but
325 additional data will be required to fully assess these effects in carbonate sediments
326 (Dahl et al., 2013b; Helz et al., 2011; Nägler et al., 2011).

327 **4.1 Implications for the interpretation of $\delta^{98/95}\text{Mo}$ in carbonates**

328 In order to reconstruct seawater $\delta^{98/95}\text{Mo}$ from measured variations in
329 carbonate sediments, it is essential to understand what processes, if any,
330 fractionate $\delta^{98/95}\text{Mo}$ during early diagenesis. Although the number of cores
331 sampled in this study is relatively small, the results clearly indicate that
332 syndepositional diagenesis of carbonate sediments on the modern Bahamas
333 carbonate platform can result in authigenic enrichment of up to 10s of ppm Mo.

334 Both the magnitude of authigenic enrichment and the resulting $\delta^{98/95}\text{Mo}$ of bulk
335 carbonate sediments appear to depend on the concentration of pore water H_2S ,
336 which in turns depends on the local production of organic matter from algae, sea
337 grasses, and microbial mats. In the Bahamas, these parameters can vary on spatial
338 scales of 100 m or less, for example Core 1 and 2 were collected in the same
339 embayment, but differ in local sea grass vegetation, Mo content, and $\delta^{98/95}\text{Mo}$.

340 Comparison with published results suggests that the patterns of Mo
341 enrichment observed in the Bahamas may be typical of shallow water marine
342 carbonates. Voegelin et al. (2009) examined a series of Carboniferous-aged
343 marine carbonate micrites and cements from three sections in China and Spain
344 yielding Mo concentrations (<0.1- 0.5 ppm) and variable $\delta^{98/95}\text{Mo}$ values between
345 -0.6 and 2.3‰. Voegelin et al. (2010) examined bulk limestone and dolomite
346 samples from the late Archean Ghaap Group and found similar Mo concentrations
347 (<0.1 ppm – 1ppm), with variable $\delta^{98/95}\text{Mo}$ values between 0 and 1.5‰.
348 Tribovillard et al. (2004) compiled Mo concentrations in the extremely organic-
349 rich, Late Jurassic Orbagnoux and Akkuyu carbonates where concentrations of
350 10s of ppm were common and correlated with concentrations of sulfurized
351 organic matter. Hua et al (2013) reported Mo contents from the 1.56Ga
352 Gaoyuzhuang Formation limestone to be 0.1-3.5 ppm, with approximately 45% of
353 the measured values exceeding 1 ppm Mo.

354 Taken together, these studies suggest that authigenic accumulation of Mo in
355 marine carbonate sediments is likely to be an important process in shallow-water
356 carbonate environments. In settings like the Bahamas, spatial and temporal

357 variability in the productivity of localized depositional environments is likely to
358 result in variable Mo enrichment and $\delta^{98/95}\text{Mo}$ in carbonate rocks, similar to
359 results reported in several of the studies above. This is likely to significantly
360 complicate the interpretation of $\delta^{98/95}\text{Mo}$ in carbonates, unless strategies can be
361 developed to avoid or correct for diagenetic effects.

362 With relatively high Mo concentrations (1-10's of ppm), Mo-enriched
363 carbonates should be relatively easy to identify. Although altered, when deposited
364 under high concentrations of pore water H_2S , these samples may record $\delta^{98/95}\text{Mo}$
365 values approaching that of seawater as seen in Core 3. However, similar samples
366 in Cores 1 and 4 are up to 0.7‰ lower than seawater, highlighting the potential
367 limitation of this approach. This offset is similar in magnitude and direction to the
368 offset observed for anoxic but non-euxinic siliciclastic sediments (Poulson et al.,
369 2006). Similar to shales, future development of proxy criteria for pore water
370 sulfide concentrations such as organic content or iron speciation might be useful
371 tools for distinguishing carbonate samples which directly record seawater
372 $\delta^{98/95}\text{Mo}$ (Gordon et al., 2009).

373 **5 Conclusions**

374 The purpose of this study was to examine the potential for early diagenetic
375 fractionation during the preservation of $\delta^{98/95}\text{Mo}$ records in shallow marine
376 carbonate sediments. A comprehensive understanding of these processes is
377 essential to properly interpret $\delta^{98/95}\text{Mo}$ variation in ancient carbonate sediments
378 (e.g. Czaja et al., 2012; Voegelin et al., 2010).

379 The results demonstrate that direct incorporation of Mo during primary
380 carbonate precipitation is likely the dominant process controlling down core Mo
381 concentrations and isotopes at low levels of pore water sulfide ($< 20\mu\text{ M H}_2\text{S}_{\text{aq}}$).
382 Under these conditions, measured Mo concentrations were $<0.2\text{ ppm}$ and $\delta^{98/95}\text{Mo}$
383 values were 1.6‰, within the range of ooids and carbonate sands reported by
384 Voegelin et al (2009).

385 In contrast, in cores with higher levels of pore water sulfide ($20 - 300\mu\text{M}$
386 $\text{H}_2\text{S}_{\text{aq}}$) sediment Mo concentrations were increased 10-100 fold and $\delta^{98/95}\text{Mo}$
387 shifted toward the value of seawater, even under oxic bottom water conditions.
388 These measurements are consistent with the authigenic accumulation of Mo via
389 the formation of thiomolybdate species and subsequent scavenging to sediments.
390 The spatially- and temporally-variable nature of Mo enrichment and the $[\text{H}_2\text{S}_{\text{aq}}]$ -
391 dependent fractionation associated with this process is likely to significantly
392 complicate the interpretation of $\delta^{98/95}\text{Mo}$ variations in marine carbonates unless
393 strategies can be developed to avoid or correct for diagenetic effects.

394 One such strategy is to take advantage the observation that $\delta^{98/95}\text{Mo}$ in
395 marine sediments is typically lighter than seawater, and approaches seawater
396 values only under the most reducing conditions. Thus, in a given population of
397 nearly contemporaneous samples deposited under euxinic conditions, the highest
398 $\delta^{98/95}\text{Mo}$ value gives the best approximation of seawater $\delta^{98/95}\text{Mo}$ (Dahl et al.,
399 2010b). A similar pattern holds for Bahamian carbonates— $\delta^{98/95}\text{Mo}$ approaches
400 seawater values only in the most organic- and sulfide-rich sediments. Thus,
401 paleoredox studies of $\delta^{98/95}\text{Mo}$ in marine carbonates might focus on a suite of

402 organic- and sulfide-rich carbonate samples and interpret the highest $\delta^{98/95}\text{Mo}$
403 values as a minimum estimate for coeval seawater.

404 Future work on $\delta^{98/95}\text{Mo}$ variations in modern carbonate sediments should
405 focus on expanding the spatial and temporal limits of this study, particularly with
406 a focus on deeper platform margin sediments and longer cores. With lower
407 organic content, some deeper water cores may not contain sufficient pore water
408 sulfide to result in authigenic Mo accumulation. Furthermore, this study covers
409 only the earliest phase of diagenesis to burial depths < 50 cm. The extent to which
410 $\delta^{98/95}\text{Mo}$ patterns are altered during later burial and diagenesis must be explored
411 before reliable conclusions can be drawn from the geological record.

412

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419

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 568

569

570 **Figure captions**

571 Fig. 1. Mo concentrations in a variety of biological and abiological primary
572 carbonate precipitates from the Bahamas. See Table S1 for specific sample
573 information.

574 Figure 2. Pore water pH, $\Sigma\text{H}_2\text{S}$ and concentrations.

575 Figure 3. Solid phase Mo concentrations and $\delta^{98/95}\text{Mo}$ variations in shallow
576 sediment cores. Except where visible, error bars are smaller than the symbol size.

577 Figure 4. (A) Cross plot of Mo concentrations in core samples with calculated
578 $\text{H}_2\text{S}_{\text{aq}}$ concentrations. (B) Correlation between $\delta^{98/95}\text{Mo}$ and Mo concentration.

579 Figure 5. $\delta^{98/95}\text{Mo}$ versus inverse Mo concentration depicting possible mixing
580 relationships between sediment Mo pools.

581 Figure 6. Thiomolybdate speciation diagram and equilibrium isotopic
582 composition in seawater. (A) Relative abundance of each Mo species as a
583 function of $\text{H}_2\text{S}_{\text{aq}}$ concentration at equilibrium based on equilibrium constants in
584 Erickson and Helz (2000). (B) Equilibrium isotopic composition of each Mo
585 species as a function of $\text{H}_2\text{S}_{\text{aq}}$ given a total Mo isotopic composition of 2.3‰
586 (gray horizontal line) and assuming a 1.25‰ offset between each species (Dahl et
587 al., 2010a; Nägler et al., 2011; Tossell, 2005). See Supplemental Section S1 for
588 the full model derivation.

589 Figure 7. Relationship between $\delta^{98/95}\text{Mo}$ of bulk carbonates sediments and pore
590 water $\text{H}_2\text{S}_{\text{aq}}$. The blue line indicates the Mo isotopic composition of open ocean
591 seawater. Dashed black lines indicated the calculated isotope composition of tri-
592 and tetrathiomolybdate, assuming that the isotopic composition of the total Mo
593 pool is 2.3‰ (see text for details). Error bars indicated the 2σ uncertainty of
594 replicate measurements.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7