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2 Global importance of oxic molybdenum sinks prior to 2.6
3 Ga revealed by the Mo isotope composition of Precambrian
4 carbonates

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16

17 **ABSTRACT**

18 Sedimentary molybdenum (Mo) isotope compositions are a promising paleoredox
19 indicator as the Mo isotope composition of seawater reflects the balance between anoxic
20 and oxic sinks. Most available data are from shales, however the Mo isotope composition
21 of carbonates also reflects the composition of ancient seawater. Here we provide an
22 expanded dataset of carbonate Mo isotope compositions, including the first data for
23 carbonates older than 2.64 Ga, which we evaluate against a compilation of published data
24 for carbonates, shales, and iron formations spanning geological time. Archean carbonate
25 samples reveal maximum $\delta^{98}\text{Mo}$ values that are generally above 1‰. These heavy values
26 indicate that Mn(IV)- or Fe(III)-oxide sinks were sufficiently important to influence the
27 Mo isotope composition of seawater as far back as 2.93 Ga. Comparison of Mo isotope
28 and rare earth element data, as well as residence time considerations, indicates that this
29 metal oxide influence was likely global. Available Mo isotope data for shales over the
30 same time period generally show crustal values, which we attribute to negligible
31 authigenic enrichment of Mo from seawater due to low ambient concentrations and a
32 paucity of euxinic conditions. Our work demonstrates that the carbonate record provides
33 important new insights into marine paleoredox, especially when shale records are absent
34 or unsuitable, and re-enforces the emerging paradigm that oxic Mo sinks were important
35 in the marine realm prior to 2.7 Ga.

36

37 **INTRODUCTION**

38 Molybdenum (Mo) stable isotopes have emerged as a powerful proxy for marine
39 redox evolution that is based on the redox sensitive nature of Mo sources and sinks.
40 Under modern oxic conditions, seawater shows a homogenous value of 2.36‰ (Siebert et
41 al., 2003; Figure DR1 in the GSA Data Repository¹). Modern Mo seawater sources are
42 principally derived from the oxidative weathering of continental crust sulfide minerals
43 (~90%; mean $\delta^{98}\text{Mo}$ value of 0.20‰; Siebert et al., 2003; Voegelin et al., 2012) variably
44 modified during transport to values as high as 2.39‰ (e.g., Voegelin et al., 2012).
45 Modern Mo sinks are dominated by Mn(IV) and Fe(III) oxide minerals that sequester Mo
46 by adsorption and co-precipitation. With an equilibrium Mo fractionation of 3.3‰ onto
47 Mn(IV) oxides (Siebert et al., 2003, Barling and Anbar, 2004) and from 0.83 to 2.19‰
48 onto Fe(III) oxides (Goldberg et al. 2009), they constitute the isotopically lightest sink
49 and are responsible for the heavy Mo isotope enrichment of seawater. The second most
50 important sink is sedimentary Mo scavenging under suboxic, anoxic, and euxinic
51 conditions, which also favor the lighter isotope but to a lesser degree (see Figure DR1).
52 As sulfide increases, sediment isotope compositions approach that of seawater as Mo
53 scavenging becomes near-quantitative (e.g., Neubert et al., 2008). This explains why
54 black shales are used to track marine paleoredox using Mo isotopes.

55 The Mo isotope proxy has been used to provide critical insights into the relative
56 importance of oxic and anoxic marine waters through geological time. Arnold et al.
57 (2004) reported $\delta^{98}\text{Mo}$ values ~-0.69‰ for mid-Proterozoic euxinic sediments of the
58 Velkerri (1.40 Ga) and Wollogorang (1.70 Ga) formations, implying significant areas of
59 seafloor anoxia at the time. Heavy Mo isotope signatures in shales extend back to 2.60

60 Ga. Conversely, prior to 2.60 Ga, shales generally show crustal Mo isotope values
61 (Siebert et al., 2005; Wille et al., 2007), suggesting that either oxic Mo sinks were
62 minimal prior to the Great Oxygenation Event (GOE) ca. 2.45 Ga, or that Mo in shales is
63 a poor proxy for Archean oxygenation. Interestingly, Planavsky et al. (2014)
64 demonstrated that iron formation (IF) as old as 2.95 Ga show highly fractionated $\delta^{98}\text{Mo}$
65 values ranging from -0.71‰ to 2.32‰, which vary as a function of Fe/Mn ratio. The
66 lightest values are best explained by syndepositional adsorption of Mo to Mn(IV) oxides,
67 implying that sufficient O_2 for Mn(II) oxidation, and thus the evolution of oxidative
68 photosynthesis, had already occurred by 2.95 Ga.

69 Here we turn here to another sedimentary proxy capable of recording ancient Mo
70 cycling: the molybdenum isotope composition of Mo hosted in carbonates ($\delta^{98}\text{Mo}_{\text{carb}}$;
71 Voegelin et al., 2009; 2010; Wen et al., 2011; Eroglu et al., 2015; Romaniello et al.,
72 2016). Although carbonates are a negligible Mo sink, they may record the $\delta^{98}\text{Mo}$
73 signature of seawater from which they were formed (Voegelin et al., 2009; Romaniello et
74 al., 2016). Our study provides an expanded dataset for modern and Archean carbonate
75 Mo isotopic compositions, which we compare to published data from carbonate, shale,
76 and iron formation records to shed new light on marine Mo cycling in the Archean.

77

78 **SAMPLES AND METHODS**

79 The newly acquired Mo isotopic data presented here include modern thrombolites
80 and stromatolites from the Bahamas, 2.52 Ga stromatolites from the Gamohaan
81 Formation (Ghaap Group, S. Africa), crystal fans and stromatolites from the 2.80 Ga
82 Mosher Carbonate (Steep Rock Group, Canada) and 2.93 Ga Ball Assemblage (Red Lake
83 Greenstone Belt, Canada), and 2.97 Ga stromatolitic and non-stromatolitic carbonates
84 from the Chobeni Formation (Nsuze Group, S. Africa). See Figure 1 and Data Repository
85 for descriptions and locations of each unit and sample. Major element concentrations
86 were measured on a HORIBA Ultima 2 ICP-AES after HF-HNO₃ total digestion, trace
87 elements on carbonate leaches (5% acetic acid) using a ThermoFisher Scientific
88 Element2 HR-ICP-MS, and Mo isotopic compositions on a ThermoFisher Scientific
89 Neptune MC-ICP-MS after 6N HCl digestion, double spike (DS, ⁹⁷Mo¹⁰⁰Mo) addition,
90 and chromatographic purification of Mo. Mo concentrations were calculated by isotope
91 dilution. All analyses were performed at the Pôle Spectrometry Ocean, Brest, France. For
92 all data (new and compiled), δ⁹⁸Mo values are reported relative to the NIST3134 standard
93 set to 0.25‰ (Nägler et al., 2014; see Table DR1 for details), uncertainties are reported as
94 two standard deviations (2SD), and datasets are tabulated in Tables DR2 to DR6. See
95 Data Repository for extended methods.

96

97 **RESULTS AND DISCUSSION**

98 **The Phanerozoic Mo Isotope Record**

99 The modern seawater $\delta^{98}\text{Mo}$ value of 2.36‰ ($\pm 0.1\%$, Siebert et al., 2003) is
100 reflected in the maximal $\delta^{98}\text{Mo}$ values of both modern black shales and carbonates (See
101 Figure 2A, Tables DR3 and DR4). With a maximum value of 1.76‰, our new data from
102 modern Bahamian microbialites fall within the range observed for contemporaneous
103 carbonates, but due to detrital impurities, or local production of sulfide, they do not reach
104 the modern seawater value (see sample description in the DR; Figure 2A and Table
105 DR2). For all available carbonate data, $\delta^{98}\text{Mo}$ values are never heavier than modern
106 seawater and are thus useful for constraining the minimum value of seawater at any given
107 time (Figure 2A).

108 During the Phanerozoic, carbonates record a range of $\delta^{98}\text{Mo}$ values from 2.42‰
109 to -0.91‰ (see Figure 2A), with maximum values universally attaining the modern
110 seawater value of $2.36 \pm 0.1\%$ (Figure 2A). Shales record a range of $\delta^{98}\text{Mo}$ values similar
111 to carbonates (from 2.44‰ to -1‰), but also include the few outliers lower than -1‰.
112 Only about one-fifth of compiled Phanerozoic shale values fall within 1‰ of the modern
113 seawater value, in part due to non-quantitative Mo removal. Carbonates are also limited
114 in their ability to record seawater signatures, notably by their low Mo contents that make
115 them susceptible to diagenetic resetting or dilution by detrital materials, by the presence
116 of organic matter or porewater sulfide during diagenesis that may alter whole-rock
117 values, and/or their pervasive re-crystallization at even low metamorphic grades.
118 Nonetheless, carbonates provide complimentary insight into Mo cycling during periods
119 when shale records fall short.

120

121 **Mo Cycling in the Precambrian**

122 For the Proterozoic, no Mo isotope data are available for carbonate rocks.
123 Maximum values for shales are highly variable, ranging from -0.09‰ to 1.98‰ and
124 averaging 0.81 ± 1.31 ‰; Arnold et al. (2004) inferred a Proterozoic $\delta^{98}\text{Mo}_{\text{sw}}$ value of
125 1.08‰. Available IF data during this period are limited, but universally heavy in $\delta^{98}\text{Mo}$,
126 with maximum values for each deposit ranging from 1.03‰ to 2.08‰ (n=3). Archean
127 Mo isotope data are more abundant in literature for all three lithologies, and a significant
128 contrast in Mo isotope compositions between the three lithologies appears to occur prior
129 to ~2.6 Ga. Maximum shale values range from 1.72‰ to 1.76‰ and average
130 1.73 ± 0.05 ‰ from 2.50 Ga to 2.60 Ga, yet are universally low (ranging from -0.46‰ to
131 0.89‰, averaging 0.31 ± 0.52 ‰) before 2.64 Ga. In contrast, and with the exception of the
132 Chobeni carbonates, maximum values for carbonates and IF are consistently positive
133 from 2.50 Ga to 2.97 Ga (0.82‰ to 1.97‰ with an average of 1.31 ± 0.72 ‰ for
134 carbonates; 0.97‰ to 1.87‰ with an average of 1.52 ± 0.79 ‰ for IF; see Figure 2B). As
135 discussed below, this contrast likely relates to the chemical conditions that enable the
136 capture of seawater molybdenum in shale records.

137 From 2.50 to 2.60 Ga, maximum $\delta^{98}\text{Mo}$ values in shales and carbonates vary from
138 1.40‰ to 1.97‰, and their average places a lower limit on global seawater Mo isotopic
139 composition of 1.63 ± 0.48 ‰ during this period (Figure 2B). IF deposits analyzed during
140 this period present a maximum value between 0.97‰ and 1.76‰. New data from 2.52 Ga
141 carbonate samples from the Gamohaam Formation, Griqualand West basin, show a
142 maximum $\delta^{98}\text{Mo}$ of 1.11‰, in line with elevated values observed for carbonates of the

143 adjacent Transvaal basin (up to 1.97‰; Eroglu et al., 2015; Figure 2B). The general
144 agreement in maximum $\delta^{98}\text{Mo}$ values for available shale, carbonate, and IF records
145 during this period is remarkable. All three archives appear to record seawater that is
146 isotopically heavy due to sequestration of light Mo isotopes by Mn(IV)- and Fe(III)-oxide
147 exit channels, consistent with evidence for increasing surface redox potential in the run-
148 up to the GOE. Enhanced supply of sulfate (and likely Mo) to the oceans at this time and
149 the development of euxinic conditions (e.g., Reinhard et al., 2009) would have promoted
150 the authigenic enrichment of seawater Mo into organic-rich shales.

151 In several carbonate samples measured by others (Voegelin et al., 2010; Eroglu et
152 al., 2015), $\delta^{98}\text{Mo}$ compositions are isotopically light (as low as -0.82‰), indicating the
153 former presence of Mn(IV)- or Fe(III)-oxides in the samples. As chemical sediments that
154 often contain little detrital material, Precambrian carbonates are generally characterized
155 by low Mo concentrations (<200 ppb), with average isotope-dilution whole rock Mo
156 concentrations of 140 ± 470 ppb for the period 2.50 to 2.97 Ga (Voegelin et al., 2010;
157 Eroglu et al., 2015; this study). By contrast, shales generally reflect crustal Mo
158 abundances (1.1 ppm; Rudnick and Gao, 2003), unless authigenic enrichment from
159 seawater occurs. Accordingly, detritus-poor carbonate rocks should be more sensitive to
160 the addition of small amounts of isotopically light Mo associated with Mn(IV)- or
161 Fe(III)-oxide sedimentary inputs.

162 Our dataset includes the first available Mo isotope data for carbonates older than
163 2.64 Ga. Microbialitic calcite and aragonitic crystal fans (now replaced by calcite) from
164 the 2.80 Ga Mosher Formation at Steep Rock (Canada) show a maximum $\delta^{98}\text{Mo}$ value of
165 1.22 ± 0.04 ‰, comparable to dolomitic stromatolites and dolomitized crystal fans from the

166 2.93 Ga Ball Assemblage at Red Lake (Canada) that display a maximum $\delta^{98}\text{Mo}$ value of
167 $1.03\pm 0.03\%$ (Figure 2B). Both of these values are remarkably heavy. While the low Mo
168 contents of these samples might make their $\delta^{98}\text{Mo}$ values more susceptible to diagenetic
169 alteration, multiple lines of evidence indicate this was not responsible for heavy isotope
170 enrichments prior to 2.64 Ga. Briefly, there is no relationship between $\delta^{98}\text{Mo}$ and
171 $\delta^{18}\text{O}_{\text{carb}}$, and $\delta^{98}\text{Mo}$ data tend toward crustal values as a function of degree of
172 silicification (see discussion in Data Repository and Figures DR4 and DR5).
173 Furthermore, burial of light Mo with organic carbon at concentrations typical of Archean
174 shale is unlikely to have affected the global marine Mo cycle (see Data Repository).
175 Instead, these heavy values suggest that Mn(IV)- and Fe(III)-oxide exit channels for Mo
176 were sufficiently important to impart a heavy Mo isotope signature on Mesoarchean
177 seawater. This conclusion is similar to that of Planavsky et al. (2014) and Ossa Ossa et al.
178 (2018), who also concluded that an Mn(IV)-oxide exit channel was in operation ca. 2.95
179 Ga. Crucially, the isotopically light data of these studies simply implies some unknown
180 degree of Mo removal by an oxide-based exit channel, while the isotopically heavy data
181 in our new dataset (also present in the IF examined by Planavsky et al., 2014) reflects the
182 composition of residual seawater.

183 If both carbonates (this study) and iron formations (Planavsky et al., 2014) are
184 characterized by Mo isotope compositions reflecting an important role for metal oxide-
185 based Mo sinks prior to 2.7 Ga, then with the exception of recently analyzed shales from
186 the Pongola Supergroup (Ossa Ossa et al., 2018), why has this not been detected in the
187 larger shale record? Several possible explanations for this discrepancy exist, notably the
188 possibility of spatial heterogeneity in seawater $\delta^{98}\text{Mo}$ (see below and supplementary

189 discussion). However, considering that nearly all available data for shales older than 2.64
190 Ga show $\delta^{98}\text{Mo}$ values in the crustal range, we suggest that the most parsimonious
191 explanation is that most shales simply did not experience authigenic Mo enrichment prior
192 to 2.64 Ga. Indeed, shales older than ~ 2.64 Ga rarely show signs of enrichment in Mo
193 above crustal values (Figure 2B) and generally reflect detrital Mo sources. This can be
194 explained by the fact that euxinic conditions that strongly promote Mo enrichment in
195 shales were generally absent, whereas after 2.63 Ga, when the first euxinic conditions
196 were established (e.g., Reinhard et al., 2009), carbonates and shales show comparable
197 $\delta^{98}\text{Mo}$ records. Moreover, shales deposited under anoxic but non-euxinic conditions
198 today still become authigenically enriched in Mo; it would appear that lower marine Mo
199 concentrations rendered this process less effective in the Archean. In this context,
200 carbonates that contain a smaller Mo contribution from detrital components, and do not
201 depend on local euxinia or a large marine Mo reservoir for authigenic enrichment,
202 provide unique insight into the upper limit of $\delta^{98}\text{Mo}$ evolution of seawater prior to 2.63
203 Ga that is otherwise cryptic in the shale sedimentary record. The rare cases where
204 authigenic signals are recorded in shales (e.g., Ossa Ossa et al., 2018) point to the
205 intriguing possibility of localized Mo isotope responses to local redox conditions.

206 The new carbonate $\delta^{98}\text{Mo}$ data presented here show no relation with Mn content
207 or Mn/Fe ratio, and considered in light of other redox indicators such as the presence of
208 negative Ce anomalies (represented here as $\text{Pr}/\text{Pr}^* > 1$; see Data Repository), it becomes
209 apparent that interpretation of carbonate $\delta^{98}\text{Mo}$ data may not always be straightforward.
210 Simple mixing calculations reveal that the Mo isotope composition of carbonates is more
211 resistant to dilution by detrital material than REE-based signatures (Figure 3). However,

212 paired $\delta^{98}\text{Mo}$ – Ce anomaly data from the 2.97 Ga Chobeni Formation (Figure 3) reveal
213 the presence of significant negative Ce anomalies, as reported elsewhere (Siahi et al.,
214 2018), yet show no sign of Mo isotope fractionation outside of the crustal range. This
215 apparent contradiction may be reconciled by the significantly shorter residence times of
216 light REE (<300 years; see Data Repository) compared to Mo (likely greater than 17 ky
217 during the Archean; Asael et al., 2015), making REE signals a local proxy, and as a
218 result, the two proxies are necessarily recording redox at different spatial and temporal
219 scales. Thus, one interpretation of the paired Chobeni $\delta^{98}\text{Mo}$ -Ce anomaly data is that the
220 basin experienced oxidative Ce cycling at a local scale, while oxic sinks for Mo remained
221 minor in seawater at a global scale. The reverse is true for Red Lake samples, while the
222 Mosher carbonate shows evidence for both local Mn(IV) oxide precipitation (positive
223 Pr/Pr*, consistent with Riding et al., 2014, Fralick and Riding, 2015) as well as global
224 Mn(IV) oxide precipitation (positive $\delta^{98}\text{Mo}$). For the Chobeni, another possibility is that
225 mixing occurred between authigenic Mo from seawater and oxide sources, with the
226 resulting mixture falling within the crustal $\delta^{98}\text{Mo}$ range. Some points fall below the
227 crustal $\delta^{98}\text{Mo}$ range, supporting this possibility. While caution is warranted as late
228 oxidative alteration of surface samples may be difficult to detect (Albut et al., 2018), our
229 Chobeni dataset is consistent with at least some O₂ present locally in the basin, similar to
230 recent findings based on REE data (Siahi et al., 2018) and Fe, Mo and S isotope data
231 (Eickmann et al., 2018; Ossa Ossa et al., 2018).

232

233 **CONCLUSION**

234 This study presents the first $\delta^{98}\text{Mo}$ data for carbonates older than 2.64 Ga, with
235 values ranging from -1.54‰ to 1.22‰. By contrast, Mo isotope compositions of shales of
236 similar age generally show crustal values. We suggest that this discrepancy results from
237 low concentrations of Mo in seawater as well as a general absence of euxinic conditions.
238 This, in turn, prevented widespread authigenic Mo enrichment in shales prior to the onset
239 of oxidative continental weathering, an increased Mo reservoir, and the first
240 establishment of localized euxinia ca. 2.7–2.6 Ga (e.g., Reinhard et al., 2009). Carbonate
241 rocks are not subject to these constraints, and along with IF, provide additional
242 perspective on the $\delta^{98}\text{Mo}$ composition of Mesoarchean seawater. Our dataset further
243 indicates minimum global seawater $\delta^{98}\text{Mo}$ values of 1.2‰ and 1.0‰ at 2.80 and 2.93 Ga,
244 respectively, consistent with the idea that Mn(IV)- and Fe(III)- oxide sinks for Mo were
245 globally important as far back as 2.95 Ga (Planavsky et al., 2014; Ossa Ossa et al, 2018).
246 Despite possible limitations stemming from detrital contamination and mixing of
247 different authigenic components in the same sample, the $\delta^{98}\text{Mo}$ composition of
248 carbonates is a promising proxy for understanding marine molybdenum cycling and
249 paleoredox evolution before conditions permitted widespread authigenic Mo enrichment
250 in shales.

251

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338

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351

352 **FIGURE CAPTIONS**

353 Figure 1. Maps showing (A) Canadian and (B) South African Archean carbonate
354 occurrences analyzed in this study. See Data Repository for additional details and GPS
355 coordinates.

356

357 Figure 2. New and compiled $\delta^{98}\text{Mo}$ data for shales, iron formations, and carbonates
358 through geological time: (A) data from 3.5 Ga to present; (B) focus on the period from
359 2.5 Ga to 3.0 Ga. See Data Repository for values and data sources. The dark grey area
360 represents modern continental crust values ($\pm 2\text{SD}$; Siebert et al., 2003) and the light grey
361 area represents the value of modern seawater ($\pm 2\text{SD}$; Siebert et al., 2003). (C) New and
362 compiled Mo concentration data for shales, iron formation, and carbonates through
363 geological time.

364 Figure 3. $\delta^{98}\text{Mo}$ data for carbonate samples analyzed in this study plotted against PAAS-
365 normalized Pr anomalies as a proxy for true Ce anomalies (see Data Repository). Grey
366 areas represent crustal ranges for both proxies, with the darker grey box indicating their
367 intersection; black lines represent mixing trajectories between crust ($\delta^{98}\text{Mo}\approx 0\text{‰}$ and
368 $\text{Pr}/\text{Pr}^*=1$) and different authigenic end-members, including modern seawater
369 ($\delta^{98}\text{Mo}=2.36\text{‰}$ and $\text{Pr}/\text{Pr}^*=1.4$) and different hypothetical $\delta^{98}\text{Mo}$ compositions of
370 ancient seawater and Mn- and Fe-oxides ($\delta^{98}\text{Mo}$ ranging from 1.5 to 0‰; Pr/Pr^* fixed at
371 1.2). Grey arrows show the trajectory of admixing of Mo associated with Mn- and Fe-
372 oxide sources.

373

374 ¹GSA Data Repository item 2018xxx, containing supplemental discussion on marine Mo
375 cycling and post-depositional modification, description of samples and their REE spectra,
376 detailed methods and compilation data sources, and data tables, is available online at
377 <http://www.geosociety.org/datarepository/2018/>, or on request from
378 editing@geosociety.org.

Figure 1

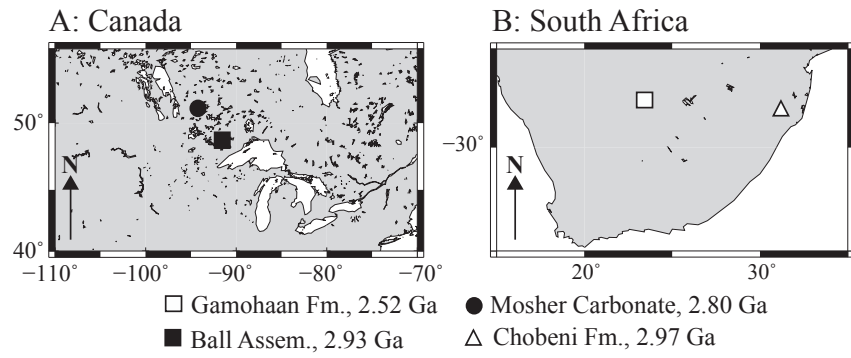


Figure 2

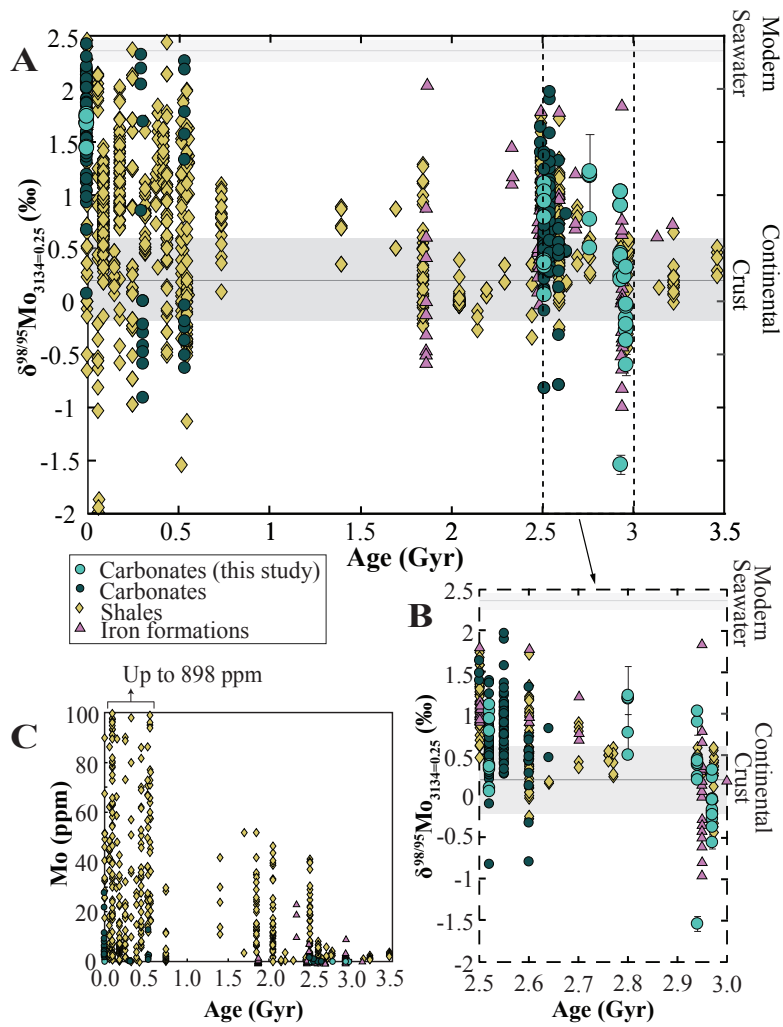


Figure 3

