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

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ABSTRACT

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

INTRODUCTION

Molybdenum (Mo) stable isotopes have emerged as a powerful proxy for marine redox evolution that is based on the redox sensitive nature of Mo sources and sinks. Under modern oxic conditions, seawater shows a homogenous value of 2.36‰ (Siebert et al., 2003; Figure DR1 in the GSA Data Repository[1]). Modern Mo seawater sources are principally derived from the oxidative weathering of continental crust sulfide minerals (~90%; mean δ^{98}Mo value of 0.20‰; Siebert et al., 2003; Voegelin et al., 2012) variably modified during transport to values as high as 2.39‰ (e.g., Voegelin et al., 2012). Modern Mo sinks are dominated by Mn(IV) and Fe(III) oxide minerals that sequester Mo by adsorption and co-precipitation. With an equilibrium Mo fractionation of 3.3‰ onto Mn(IV) oxides (Siebert et al., 2003, Barling and Anbar, 2004) and from 0.83 to 2.19‰ onto Fe(III) oxides (Goldberg et al. 2009), they constitute the isotopically lightest sink and are responsible for the heavy Mo isotope enrichment of seawater. The second most important sink is sedimentary Mo scavenging under suboxic, anoxic, and euxinic conditions, which also favor the lighter isotope but to a lesser degree (see Figure DR1). As sulfide increases, sediment isotope compositions approach that of seawater as Mo scavenging becomes near-quantitative (e.g., Neubert et al., 2008). This explains why black shales are used to track marine paleoredox using Mo isotopes.

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

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

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

SAMPLES AND METHODS

The newly acquired Mo isotopic data presented here include modern thrombolites and stromatolites from the Bahamas, 2.52 Ga stromatolites from the Gamohaan Formation (Ghaap Group, S. Africa), crystal fans and stromatolites from the 2.80 Ga Mosher Carbonate (Steep Rock Group, Canada) and 2.93 Ga Ball Assemblage (Red Lake Greenstone Belt, Canada), and 2.97 Ga stromatolitic and non-stromatolitic carbonates from the Chobeni Formation (Nsuze Group, S. Africa). See Figure 1 and Data Repository for descriptions and locations of each unit and sample. Major element concentrations were measured on a HORIBA Ultima 2 ICP-AES after HF-HNO_3 total digestion, trace elements on carbonate leaches (5% acetic acid) using a ThermoFisher Scientific Element2 HR-ICP-MS, and Mo isotopic compositions on a ThermoFisher Scientific Neptune MC-ICP-MS after 6N HCl digestion, double spike (DS, $^{97}Mo^{100}Mo$) addition, and chromatographic purification of Mo. Mo concentrations were calculated by isotope dilution. All analyses were performed at the Pôle Spectrometry Ocean, Brest, France. For all data (new and compiled), $\delta^{98}Mo$ values are reported relative to the NIST3134 standard set to 0.25‰ (Nägler et al., 2014; see Table DR1 for details), uncertainties are reported as two standard deviations (2SD), and datasets are tabulated in Tables DR2 to DR6. See Data Repository for extended methods.

RESULTS AND DISCUSSION

The Phanerozoic Mo Isotope Record

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

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

Mo Cycling in the Precambrian

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

From 2.50 to 2.60 Ga, maximum δ^{98}Mo values in shales and carbonates vary from 1.40‰ to 1.97‰, and their average places a lower limit on global seawater Mo isotopic composition of 1.63±0.48‰ during this period (Figure 2B). IF deposits analyzed during this period present a maximum value between 0.97‰ and 1.76‰. New data from 2.52 Ga carbonate samples from the Gamohaan Formation, Griqualand West basin, show a maximum δ^{98}Mo of 1.11‰, in line with elevated values observed for carbonates of the adjacent Transvaal basin (up to 1.97%; Eroglu et al., 2015; Figure 2B). The general agreement in maximum δ^{98}Mo values for available shale, carbonate, and IF records during this period is remarkable. All three archives appear to record seawater that is isotopically heavy due to sequestration of light Mo isotopes by Mn(IV)- and Fe(III)-oxide exit channels, consistent with evidence for increasing surface redox potential in the run-up to the GOE. Enhanced supply of sulfate (and likely Mo) to the oceans at this time and the development of euxinic conditions (e.g., Reinhard et al., 2009) would have promoted the authigenic enrichment of seawater Mo into organic-rich shales.

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

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

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

If both carbonates (this study) and iron formations (Planavsky et al., 2014) are characterized by Mo isotope compositions reflecting an important role for metal oxide-based Mo sinks prior to 2.7 Ga, then with the exception of recently analyzed shales from the Pongola Supergroup (Ossa Ossa et al., 2018), why has this not been detected in the larger shale record? Several possible explanations for this discrepancy exist, notably the possibility of spatial heterogeneity in seawater δ^{98}Mo (see below and supplementary discussion). However, considering that nearly all available data for shales older than 2.64 Ga show δ^{98}Mo values in the crustal range, we suggest that the most parsimonious explanation is that most shales simply did not experience authigenic Mo enrichment prior to 2.64 Ga. Indeed, shales older than ~2.64 Ga rarely show signs of enrichment in Mo above crustal values (Figure 2B) and generally reflect detrital Mo sources. This can be explained by the fact that euxinic conditions that strongly promote Mo enrichment in shales were generally absent, whereas after 2.63 Ga, when the first euxinic conditions were established (e.g., Reinhard et al., 2009), carbonates and shales show comparable δ^{98}Mo records. Moreover, shales deposited under anoxic but non-euxinic conditions today still become authigenically enriched in Mo; it would appear that lower marine Mo concentrations rendered this process less effective in the Archean. In this context, carbonates that contain a smaller Mo contribution from detrital components, and do not depend on local euxinia or a large marine Mo reservoir for authigenic enrichment, provide unique insight into the upper limit of δ^{98}Mo evolution of seawater prior to 2.63 Ga that is otherwise cryptic in the shale sedimentary record. The rare cases where authigenic signals are recorded in shales (e.g., Ossa Ossa et al., 2018) point to the intriguing possibility of localized Mo isotope responses to local redox conditions.

The new carbonate δ^{98}Mo data presented here show no relation with Mn content or Mn/Fe ratio, and considered in light of other redox indicators such as the presence of negative Ce anomalies (represented here as Pr/Pr* > 1; see Data Repository), it becomes apparent that interpretation of carbonate δ^{98}Mo data may not always be straightforward. Simple mixing calculations reveal that the Mo isotope composition of carbonates is more resistant to dilution by detrital material than REE-based signatures (Figure 3). However, paired δ^{98}Mo – Ce anomaly data from the 2.97 Ga Chobeni Formation (Figure 3) reveal the presence of significant negative Ce anomalies, as reported elsewhere (Siahi et al., 2018), yet show no sign of Mo isotope fractionation outside of the crustal range. This apparent contradiction may be reconciled by the significantly shorter residence times of light REE (<300 years; see Data Repository) compared to Mo (likely greater than 17 ky during the Archean; Asael et al., 2015), making REE signals a local proxy, and as a result, the two proxies are necessarily recording redox at different spatial and temporal scales. Thus, one interpretation of the paired Chobeni δ^{98}Mo-Ce anomaly data is that the basin experienced oxidative Ce cycling at a local scale, while oxic sinks for Mo remained minor in seawater at a global scale. The reverse is true for Red Lake samples, while the Mosher carbonate shows evidence for both local Mn(IV) oxide precipitation (positive Pr/Pr*, consistent with Riding et al., 2014, Fralick and Riding, 2015) as well as global Mn(IV) oxide precipitation (positive δ^{98}Mo). For the Chobeni, another possibility is that mixing occurred between authigenic Mo from seawater and oxide sources, with the resulting mixture falling within the crustal δ^{98}Mo range. Some points fall below the crustal δ^{98}Mo range, supporting this possibility. While caution is warranted as late oxidative alteration of surface samples may be difficult to detect (Albut et al., 2018), our Chobeni dataset is consistent with at least some O_2 present locally in the basin, similar to recent findings based on REE data (Siahi et al., 2018) and Fe, Mo and S isotope data (Eickmann et al., 2018; Ossa Ossa et al., 2018).

CONCLUSION

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

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FIGURE CAPTIONS

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

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

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

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

Figure 1

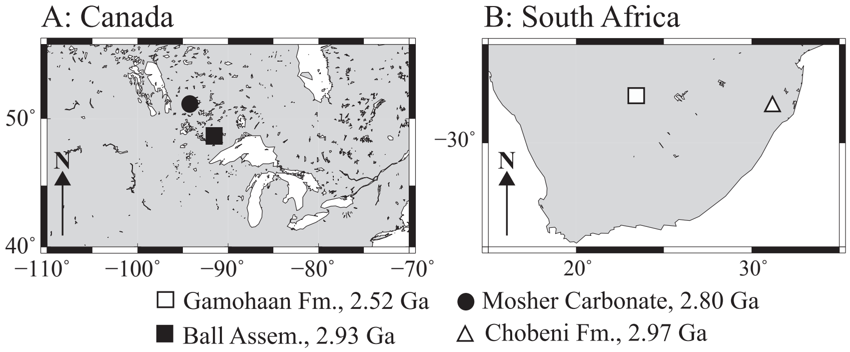


Figure 2

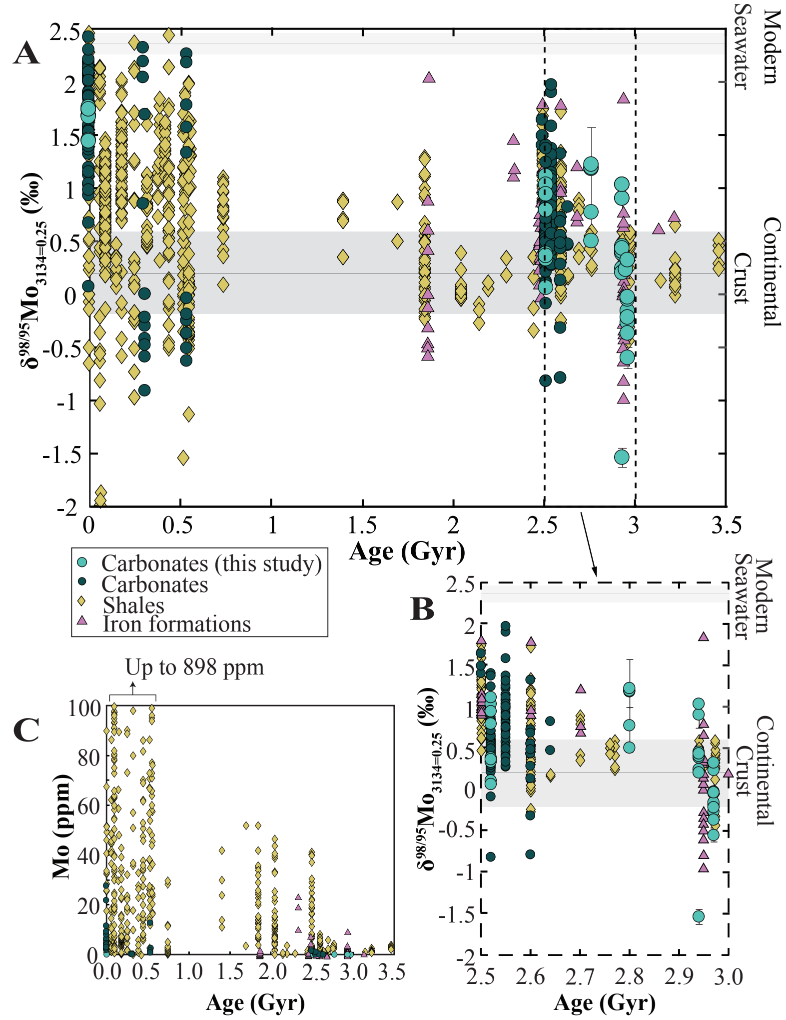
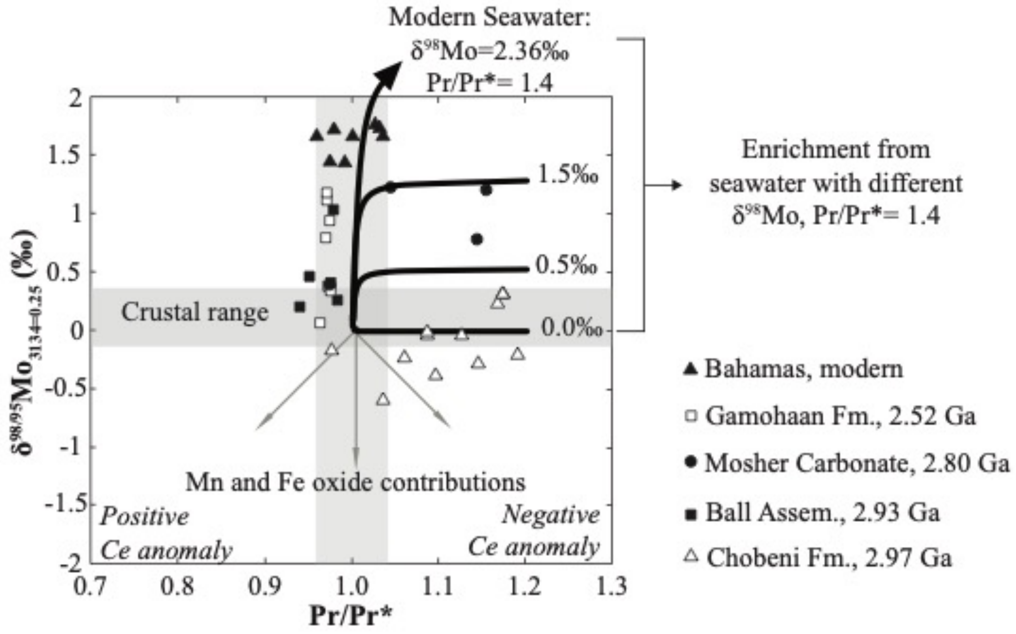


Figure 3


Modern Seawater:
δ98Mo=2.36‰
Pr/Pr*= 1.4
Enrichment from seawater with different δ98Mo, Pr/Pr*= 1.4
1.5‰
0.5‰
0.0‰
Crustal range
Mn and Fe oxide contributions
Positive Ce anomaly
Negative Ce anomaly
δ98/95Mo3134=0.25 (‰)
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0.7
0.8
0.9
1.0
1.1
1.2
1.3
Pr/Pr*
▲ Bahamas, modern
□ Gamohaan Fm., 2.52 Ga
● Mosher Carbonate, 2.80 Ga
■ Ball Assem., 2.93 Ga
△ Chobeni Fm., 2.97 Ga