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Tracking the spatial extent of redox variability in the mid-Proterozoic ocean

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ABSTRACT

Emerging geochemical evidence suggests considerable redox heterogeneity in the mid-Proterozoic ocean. However, quantitative estimates of the extent of different modes of anoxia remain poorly constrained. Due to their complementary redox-related behaviour, uranium and molybdenum isotopes can be combined to reconstruct ancient marine redox landscapes, but this approach has not been applied to the mid-Proterozoic. Here, we present new $\delta^{238}U$ and $\delta^{98}Mo$ data for marine rocks from the ~1.4 Ga Xiamaling Formation, North China Craton, together with independent redox indicators (Fe speciation and redox-sensitive trace metals). We find that most samples deposited under oxic or dysoxic conditions retain low U and Mo contents, with $\delta^{238}U$ and $\delta^{98}Mo$ values indistinguishable from continental crust, demonstrating a dominant detrital signal. By contrast, euxinic samples with authigenic enrichments in U and Mo record the highest authigenic $\delta^{238}U$ and $\delta^{98}Mo$ values, consistent with efficient reduction of U and Mo. Samples deposited under ferruginous conditions exhibit a wider range of intermediate $\delta^{238}U$ and $\delta^{98}Mo$ values that generally fall between the (dys)oxic and euxinic end-members. Using a coupled U-Mo isotope mass balance model, we infer limited euxinia (<0.5% of the global seafloor area) but extensive low-productivity (dys)oxic and ferruginous settings in ~1.4 Ga oceans. This redox landscape would have provided potentially habitable environments for eukaryotic evolution in the mid-Proterozoic.

INTRODUCTION

Reconstructing the oxygenation history of Earth's surface environment is crucial to understand the trajectory of Earth's habitability. The mid-Proterozoic (1.8–0.8 Ga) was a critical interval for early eukaryote evolution (Knoll and Nowak, 2017), and while emerging evidence suggests that biological innovation at this time occurred under heterogeneous ocean redox conditions (Sperling et al., 2014; Zhang et al., 2016; Luo et al., 2021; Song et al., 2023), the global extent of different modes of anoxia remains poorly constrained. As such, a quantitative assessment of the global redox landscape may provide critical insight into the spatial extent of potentially habitable conditions, thus ultimately enabling improved consideration of potential controls on early eukaryote evolution.

Uranium and molybdenum isotopes (δ^{238}U and δ^{98}Mo) are useful tools for reconstructing global redox conditions because of their redox sensitivity and long oceanic residence times (Andersen et al., 2017; Kendall et al., 2017). The largest U isotope fractionations occur during U reduction in anoxic environments, with heavy U isotopes preferentially sequestered in the sediments (Weyer et al., 2008). The largest Mo isotope fractionations occur during adsorption to Mn-Fe (oxyhydr)oxides under oxic conditions (Kendall et al., 2017). By contrast, minimal isotopic difference is expected between Mo in sediments and coeval seawater during near-quantitative drawdown under strongly euxinic conditions (Nägler et al., 2011). Since rapid Mo burial specifically requires relatively high dissolved sulfide concentrations, but U burial only requires anoxia, a particularly robust reconstruction of the extent of different ocean redox conditions can be achieved when considering δ^{238}U and δ^{98}Mo together (Andersen et al., 2020; Kendall et al., 2020). Although there are several studies using either δ^{238}U or δ^{98}Mo to investigate ocean redox variability in the mid-Proterozoic (Arnold et al., 2004; Yang et al., 2017; Gilleaudeau et al., 2019; Luo et al., 2021), there have been no studies of U-Mo isotope co-variation during this period.

Here, we present new U and Mo isotope data for drill core samples from the ~1.4 Ga Xiamaling Formation, North China Craton. In combination with new Re concentration data, which enables specific identification of dysoxic conditions (Crusius et al., 1996; Song et al., 2023; Li et al., 2025), and existing Fe speciation, δ^{98}Mo and U-Mo concentration data, we first explore δ^{238}U and δ^{98}Mo systematics in the context of the local redox state. We then utilize an isotope mass balance model to reconstruct the spatial extent of different redox conditions in the ~1.4 Ga ocean.

GEOLOGIC SETTING

The ~1.4 Ga Xiamaling Formation (Zhang et al., 2015) study site is located in the Xiahuayuan region of Hebei Province, north China (Fig. 1A), where the formation can be divided into six units (Wang et al., 2017; see Supplemental Material for detailed geologic background). Here, we focus on fresh drill core material from the upper four units (Fig. 1B), which are dominantly composed of low thermal maturity mudstones and black shales, representing deep-water deposition (Wang et al., 2017).

RESULTS

In total, 50 samples were analyzed for δ^{238}U compositions, while an additional 15 samples were analysed to augment existing δ^{98}Mo data (Zhang et al., 2019; see Supplemental Material for methods and data). Bulk δ^{238}U values show relatively constant values through unit 4 (-0.22 ± 0.04‰, 2SD; Fig. 2). An excursion to lower values (as low as -0.41‰) and then to higher values (up to 0.08‰) occurs in unit 3, followed by a progressive increase to values approaching 0.2‰ at the top of unit 2 (Fig. 2). Samples in unit 1 show more scatter, but with an initial drop to lower values, followed by a general increase up-section (Fig. 2). Calculated authigenic δ^{238}U ($\delta^{238}U_{auth}$) compositions (see Supplemental Material for detrital corrections; note that samples with low U and Mo contents were excluded from authigenic correction) range from -0.44‰ to +0.26‰, and exhibit a similar trend to bulk δ^{238}U values (Fig. 3). Our δ^{98}Mo data range from 0.15‰ to 1.26‰, with negligible difference relative to authigenic δ^{98}Mo ($\delta^{98}Mo_{auth}$) (Fig. 2; Table S1). In almost all cases, Re enrichment factors (Re_{EF}; see Supplemental Material for the enrichment factor (EF) calculation) are above 1 (Fig. 2).

DISCUSSION

Local Redox conditions

Previous detailed reconstructions have invoked a generally anoxic, but dynamic redox setting for the Xiamaling Formation (Zhang et al., 2016; Wang et al., 2017; Song et al., 2023). Based on mostly low but variable highly reactive Fe to total Fe (Fe_{HR}/Fe_T) ratios and U_{EF}-Mo_{EF} values, coupled with generally low pyritization (Fe_{py}) of the Fe_{HR} pool (Fig. 2), units 3 and 4 have been interpreted to record orbital-scale variability in the spatial extent of a ferruginous oxygen minimum zone (OMZ), which became more productive through unit 3 (Wang et al., 2017; Song et al., 2023). More expansive deeper water anoxia developed in unit 2, with a progression from ferruginous to euxinic conditions, while unit 1 documents continued euxinia, punctuated by more oxygenated conditions in the upper half of the unit (Fig. 2; Wang et al., 2017).

Persistent enrichments in Re (Fig. 2), including for samples with low Fe_{HR}/Fe_T ratios, further suggest that deeper waters below the OMZ in units 3 and 4 were likely dysoxic (Crusius et al., 1996; Song et al., 2023; Li et al., 2025), although intervals of fully oxygenated conditions (Zhang et al., 2016; Wang et al., 2017) cannot be discounted (hence we refer to such samples as being (dys)oxic).

Controls on U and Mo Isotope Compositions

To explore δ^{98}Mo-δ^{238}U variability, we plot δ^{98}Mo and δ^{238}U profiles in the context of local redox conditions (Fig. 2). The (dys)oxic samples have δ^{238}U values that are essentially indistinguishable from average continental crust (-0.3‰), consistent with generally low U contents and a dominant detrital contribution (Fig. 2; Fig. S1) (Andersen et al., 2017). Ferruginous samples have $\delta^{238}U_{auth}$ values that span a relatively wide range (Fig. 2), consistent with a previous $\delta^{238}U$ study of ferruginous lakes (Cole et al., 2020). In more detail, ferruginous samples with low TOC and U_{EF} values (termed F2 samples) tend to have $\delta^{238}U$ similar to the detrital composition, whereas higher $\delta^{238}U_{auth}$ values are observed for samples with higher TOC and U_{EF} (termed F1 samples) (Fig. 2). Euxinic samples are generally enriched in authigenic U and record the highest $\delta^{238}U_{auth}$ values (Fig. 2; see Supplemental Material for discussion of two euxinic samples with anomalously low $\delta^{238}U_{auth}$).

Integrating our new $\delta^{98}Mo$ analyses with previously published data (Zhang et al., 2019) shows that (dys)oxic and F2 samples are dominantly characterized by low $\delta^{98}Mo$ values (0.34 ± 0.14‰), close to continental crust (~0.3‰) (Voegelin et al., 2014), while the highest $\delta^{98}Mo$ values are observed for euxinic and F1 sediments (Fig. 2). It is noteworthy that euxinic samples have $\delta^{98}Mo$ values spanning a wide range, possibly suggesting variable, and relatively low, water column sulfide levels (Neubert et al, 2008). In addition, sulfidic pore waters may also have exerted an important control on the observed $\delta^{98}Mo$ variability (Kendall et al., 2017).

While $\delta^{238}U$ systematics are commonly used to evaluate global ocean redox changes, the potential impact of local redox conditions and organic carbon loading on fractionations recorded in the sediments needs to be considered (Lau et al., 2022; Rutledge et al., 2024). Although bulk $\delta^{238}U$ values show a general positive correlation with TOC (when OMZ samples are excluded) and U contents, $\delta^{238}U_{auth}$ values display no such correlation (Fig. 3), suggesting a negligible local environmental control on $\delta^{238}U_{auth}$ fractionations. We also note that our $\delta^{238}U_{auth}$ values are generally comparable to shale $\delta^{238}U_{auth}$ data (-0.27‰ to 0.16‰) from the ~1.36 Ga Velkerri Formation, northern Australia (Yang et al., 2017), suggesting a consistent isotopic offset from global seawater and a relatively stable seawater $\delta^{238}U$ composition.

Neither $\delta^{98}Mo$ or $\delta^{98}Mo_{auth}$ compositions show a systematic covariation with TOC or Mo contents (Fig. 3), therefore local changes in productivity or sedimentation rate appear to have exerted minimal impact on the observed $\delta^{98}Mo$ variability. Diamond et al. (2018) and Zhang et al. (2019) reported two distinct $\delta^{98}Mo$ maxima for euxinic sediments of the Xiamaling Formation at two different localities, which likely suggests heterogenous sulfide availability in the relatively low-sulfate mid-Proterozoic ocean (Fakhraee et al., 2019). Nevertheless, a combined evaluation of $\delta^{238}U$-$\delta^{98}Mo$ data can be used to estimate global ocean redox variability (Andersen et al. 2020; Kendall et al., 2020).

Reconstructing Global Redox Conditions

Generally, fluctuating $\delta^{238}U$ and $\delta^{98}Mo$ values in the Xiamaling Formation are consistent with local redox dynamics, and their ranges across different redox conditions are relatively constant throughout the formation (Fig. 2), suggesting relatively stable oceanic U-Mo inventories and isotopic compositions. To quantitatively evaluate the global oceanic redox distribution at this time, we employ a stochastic isotope mass balance model, assuming that both U and Mo are dominantly sourced from rivers and are buried under (dys)oxic, ferruginous and euxinic conditions. In this model, U-Mo burial is a function of the areal proportion of each redox sink, and seawater $\delta^{238}U$ and $\delta^{98}Mo$ are calculated from U-Mo burial and corresponding isotope fractionations for each redox sink, utilising specific fractionation factors from previous studies (Table S2; see Supplemental Material for details of the modelling approach). By running the model 10,000 times from a modern-day initialization through a random selection of ferruginous and euxinic areal fractions, model outputs (i.e., U and Mo isotope compositions for each redox sink) are produced that fit both the $\delta^{238}U$ and $\delta^{98}Mo$ data for the Xiamaling Formation (Fig. 4). An advantage of our model is that specific isotope compositions for ~1.4 Ga seawater are not required, as the model calculates coeval seawater isotope compositions in association with randomly selected isotope compositions and fractionation factors for each sink.

The resultant area that intersects all coloured areas (area b in Fig. 4) suggests that, at most, ~0.5% of the global seafloor was overlain by euxinic waters at ~1.4 Ga, while the areal fraction of ferruginous conditions was at least 20%, leaving the rest of the seafloor in a (dys)oxic state. Our estimate of more expansive ferruginous conditions is consistent with ferruginous-dominated redox models proposed for the mid-Proterozoic (Poulton et al., 2010; Planavsky et al., 2011; Poulton and Canfield, 2011). By contrast, our estimate for the extent of euxinia at ~1.4 Ga is relatively small compared to estimates for other intervals of the mid-Proterozoic (<10%), which were constrained by either $\delta^{238}U$ or $\delta^{98}Mo$ alone (Gilleaudeau et al., 2019; Luo et al., 2021). This may reflect either temporal variability in water column euxinia, or model limitations when considering one isotope system in isolation.

Recent studies have suggested increased ocean oxygenation at ~1.4 Ga, relating to enhanced nutrient-driven primary productivity (Cox et al., 2016). However, our results suggest that large expanses of the ocean were more likely dysoxic than oxic, and as such, elevated productivity was likely restricted to local settings experiencing increased nutrient availability, driven either by locally-enhanced nutrient influxes or recycling under euxinic conditions (Song et al., 2023). The limited extent of euxinia in ~1.4 Ga oceans would have diminished the specific 'toxicity' control of sulfide on eukaryote evolution (Anbar and Knoll, 2002), which together with the expansive extent of at least mildly oxygenated oceans (Heard et al., 2023), may have exerted a significant control on the evolution of the biosphere in the mid-Proterozoic.

CONCLUSIONS

Uranium and Mo isotope systematics in the ~1.4 Ga Xiamaling Formation provide constraints on global ocean redox evolution in the mid-Proterozoic. Our $\delta^{238}U$ and $\delta^{98}Mo$ data exhibit distinct ranges related to different redox conditions, with (dys)oxic samples having $\delta^{238}U$-$\delta^{98}Mo$ values indistinguishable from the detrital input. By contrast, the highest $\delta^{238}U_{auth}$-$\delta^{98}Mo_{auth}$ values are preferentially recorded in euxinic samples. Ferruginous sediments with low TOC tend to have low $\delta^{238}U$-$\delta^{98}Mo$ values, while higher-TOC ferruginous samples tend to have intermediate to high $\delta^{238}U$-$\delta^{98}Mo$ compositions. Coupled U-Mo modelling results suggest that eutrophic euxinic settings covered ~0.5% of the global seafloor at most, while less-productive ferruginous and (dys)oxic settings were much more extensive at ~1.4 Ga. This redox partitioning may account for the moderate diversification of eukaryotes observed in the Xiamaling Formation. Similar studies linking mid-Proterozoic isotopic and fossil records will help to determine whether the Xiamaling Formation documents a relatively static mid-Proterozoic redox environment, or one stage in a temporal progression towards increased, stable ecological niche space that promoted enhanced eukaryotic diversification.

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FIGURE CAPTIONS

Figure 1. A: Geological map of the North China Craton, after Zhao et al. (2005) and Wang et al. (2017). Red square shows the location of the study area. B: Simplified stratigraphy of the Xiamaling Formation, with age constraints from Zhang et al. (2015).

Figure 2. Stratigraphic geochemical profiles for the Xiamaling Formation. Total organic carbon (TOC), Fe speciation, U and Mo concentration data are from Wang et al. (2017). Re data are from this study (closed circles) and Song et al. (2023) (open circles). The bulk δ^{98}Mo profile comprises data from Diamond et al. (2018) (red open circles), Zhang et al. (2019) (dark open circles for core samples and grey open circles for outcrop rocks), and this study (closed circles). All δ^{238}U data are from this study. Blue shading on the $\delta^{98}Mo_{auth}$ and $\delta^{238}U_{auth}$ profiles represent isotope ranges for (dys)oxic and F2 samples, while grey shading indicates the euxinic isotope range. EF–enrichment factor. (U)CC–(upper) continental crust. F1–high-TOC ferruginous. F2–low-TOC ferruginous.

Figure 3. Cross-plots of δ^{238}U and δ^{98}Mo *versus* their respective elemental and TOC contents. $\delta^{238}U_{det}$ and $\delta^{98}Mo_{det}$ represent average continental crust values of -0.3‰ (Andersen et al., 2017) and 0.3‰ (Voegelin et al., 2014), respectively. Note that the regression line on the δ^{238}U *versus* TOC plot excludes the OMZ data (an R^2 of 0.12 is obtained when the OMZ data are included).

Figure 4. Simplified U-Mo isotope mass balance model outputs. Most likely isotope compositions are mapped as a function of the relative areal fraction in different redox sinks. Area (a) represents the solution space that satisfies the δ^{238}U data for the three sinks, while area (b) represents the solution

space that additionally satisfies the $\delta^{98}Mo$ data. Thus, area (b) represents the inferred spatial extent of ferruginous and euxinic conditions, as satisfied by both isotope systems.

[1]Supplemental Material. Detailed descriptions of the geological background, analytical methods, detrital corrections, further discussion, modelling approach and geochemical data. Please visit https://doi.org/10.1130/XXXX to access the supplemental material, and contact editing@geosociety.org with any questions.