**Article:**

Li, S., Wignall, P.B. and Poulton, S.W. orcid.org/0000-0001-7621-189X (2025) Co-application of rhenium, vanadium, uranium and molybdenum as paleo-redox proxies: Insight from modern and ancient environments. Chemical Geology, 674. 122565. ISSN 0009-2541

https://doi.org/10.1016/j.chemgeo.2024.122565

# Co-application of rhenium, vanadium, uranium and molybdenum as paleo-redox proxies: Insight from modern and ancient environments

Sen Li[1,2], Paul B. Wignall[2], Simon W. Poulton[2,3]

[1]State Key Laboratory of Biogeology and Environmental Geology,
China University of Geosciences, Wuhan, 430081, China
[2]School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK
[3]International Research Frontiers Initiative, Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo 152-8550, Japan

# ABSTRACT

Numerous approaches have been developed for determining past redox conditions in marine settings (e.g., Fe speciation, redox sensitive trace metal (RSTM) systematics, pyrite morphologies, I/(Ca+Mg) ratios), enabling a broad range of redox conditions, from fully oxic to euxinic, to be potentially identified. However, many points along this spectrum remain difficult to constrain, including dysoxic and highly versus weakly euxinic conditions. This limits the broader scale inferences that can be drawn from paleoredox studies, including links between oxygen availability and biological evolution, and the potential for isotope systems (e.g., Mo) to record water column signals. Here, we develop a new approach using RSTM ratios (Re/Mo, Re/U, Re/V, Mo/U), in combination with modified RSTM enrichment factors ($EF^*$) and $Mo_{EF}^*$-$U_{EF}^*$ cross-plots, that potentially enables a robust, highly resolved reconstruction of ancient water column redox conditions to be achieved. We initially document the differential behaviour of RSTM $EF^*$ values and ratios in modern settings that range from fully oxygenated, through weakly (30-90 µM $O_2$) and highly (<30 µM $O_2$) dysoxic, to anoxic non-sulfidic and euxinic conditions. This redox behaviour is further resolved when the drawdown mechanisms for Mo are evaluated by $Mo_{EF}^*$-$U_{EF}^*$ cross-plots. We subsequently ground-truth this approach by considering samples from the Carboniferous Bowland Basin, which have previously been studied for redox conditions via independent geochemical and mineralogical techniques, as well as the Jurassic Kimmeridge Clay Formation, where redox conditions have been defined based on paleoecological characteristics. A strong degree of consistency between RSTM behaviour in modern and ancient settings highlights that weakly to highly dysoxic conditions are characterised by increases in Re/Mo, Re/U and Re/V ratios, accompanied by RSTM $EF^*$ values that only become notably enriched under highly dysoxic conditions. Non-sulfidic water column anoxia is indicated by increased $U_{EF}^*$ values and low Re/Mo ratios, while euxinia is readily identified by high Mo/U, low Re/U and very low Re/Mo ratios, alongside high $Mo_{EF}^*$ values. In addition, highly euxinic conditions may be distinguished from weak euxinia by particularly high Mo/U ratios and $Mo_{EF}^*$ values. This combined approach has the potential to provide a hitherto unprecedented level of insight into paleodepositional redox conditions, and consequently the chemical evolution of the biosphere.

Keywords: enrichment factor; dysoxic; euxinic; redox sensitive trace metals

## 1. Introduction

Accurate reconstruction of water column redox conditions is essential for evaluating environmental controls on the evolution of the biosphere and atmosphere (e.g., Poulton and Canfield, 2011: Bennett and Canfield, 2020; Poulton, 2021). The development of proxies centred on Fe speciation and trace metal systematics has enabled refined reconstructions that potentially allow oxic, anoxic ferruginous ($Fe^{2+}$-containing) and euxinic ($H_2S$-containing) water column conditions to be distinguished (e.g., Algeo and Li, 2020; Bennett and Canfield, 2020; Poulton, 2021; Song et al., 2023; Li et al., 2024). Trace metal systematics may provide a particularly valuable measure of paleo-redox conditions, due to their differential behaviour under varying redox states (e.g., Anderson et al., 1989; Helz et al., 1996; Tribovillard et al., 2006; Robbins et al., 2006; Bennett and Canfield, 2020; Li et al., 2022; Paul et al., 2023b; Zhang et al., 2023; Song et al., 2023), although the full potential of this differential behaviour has rarely been explored.

Molybdenum (Mo), uranium (U), vanadium (V) and rhenium (Re) are amongst the most commonly utilized redox-sensitive trace metals (RSTMs) for reconstructing ancient water column redox conditions. Under oxic conditions, Mo accumulation is dependent upon adsorption of the molybdate ($MoO_4^{2-}$) anion onto Fe-Mn (oxyhydr)oxides, commonly resulting in limited enrichments in normal oxic marine sediments (Bertine and Turekian, 1973). Under dysoxic to ferruginous conditions, Mo may be drawn down via a particulate shuttle mechanism, due to uptake by minerals such as Fe- Mn (oxyhydr)oxides that may precipitate in the water column (e.g., Algeo and Tribovillard, 2009; Tribovillard et al., 2012; Paul et al., 2023b). In the presence of water column $H_2S$, however, the molybdate anion is converted to particle-reactive thiomolybdate (Helz et al., 1996), leading to significantly enhanced Mo accumulation in the sediments (Emerson and Huested, 1991;

Helz et al., 1996; Erickson and Helz, 2000). It is also worth noting that the Fe-Mn shuttle may persist in weakly euxinic bottom waters (e.g., the Cariaco Basin) and hence promote a degree of Mo accumulation (Algeo and Tribovillard, 2009).

The behaviour of U contrasts with that of Mo, in that the key process is the reduction of soluble carbonate complexes ($UO_2(CO_3)_3^{4-}$) to insoluble U(IV), which occurs in anoxic sediments rather than in the water column, and does not require dissolved sulfide (Anderson et al., 1989). Uranium may therefore be enriched in sediments accumulating beneath anoxic bottom waters (Anderson et al., 1989; Klinkhammer and Palmer, 1991; Partin et al., 2013), regardless of whether euxinic or ferruginous conditions dominate.

In the modern marine environment, V occurs in the quasi-conservative form of vanadate oxyanions ($HVO_4^{2-}$ and $H_2VO_4^{-}$ ). Under oxic water column conditions, V is commonly transported to sediments adsorbed to Mn oxides (Emerson and Huested, 1991). Under dysoxic porewater conditions, where Mn oxides are reduced to $Mn^{2+}$, V may be released from sediments and hence depleted (Emerson and Huested, 1991; Nameroff et al., 2002). Under anoxic conditions, however, reduction of V leads to different precipitation mechanisms under different redox conditions. First, the vanadate released following Mn oxide reduction is reduced to V(IV) and forms vanadyl ions ($VO_2^{-}$), which are highly surface-reactive and tend to be retained in the sediment (Emerson and Huested, 1991). Vanadium may also be reduced to V(IV) following uptake by Fe minerals (e.g., green rust), with the potential for further reduction to V(III) during the oxidation of green rust to lepidocrocite (Haase et al., 2023). In sulfidic settings, the Mn shuttle may still provide a flux of V to the sediment (Cui et al., 2023), and the V that is subsequently released during the reductive dissolution of Mn oxides can be reduced to V(III), resulting in precipitation as $V_2O_3$ or hydroxide

($V(OH)_3$) phases (Breit and Wanty, 1991; Wanty and Goldhaber, 1992), or adsorption to iron monosulfides (FeS) (Haase et al., 2024).

Rhenium has a higher redox potential than U, Mo and V, and may begin to become enriched under dysoxic conditions, where the oxygen penetration depth below the sediment-water interface is shallow (~1 cm; Morford and Emerson 1999; Morford et al., 2012). The mechanism for Re enrichment under dysoxic and anoxic non-sulfidic conditions involves the reduction of $ReO_4^-$ to an insoluble phase (Colodner et al., 1992; Crusius et al., 1996; Morford and Emerson, 1999). This may lead to significant enrichment in the sediments, with high Re concentrations (ranging from 5 to 130 ppb) reported for modern dysoxic and anoxic non-sulfidic sediments, compared to < 0.1 ppb for oxic sediments (Koide et al., 1986, Ravizza et al., 1991). Under euxinic conditions, Re sequestration also occurs, but does not appear to be linked to the formation of a sulfide phase, as there tends to be no correlation between Re and $HS^-$ concentrations in pore waters (Colodner et al., 1992). Instead, Re drawdown in the presence of sulfide is thought to be associated with pyrite precipitation, and/or coprecipitation as a discrete Mo-Re-S phase, such as $Fe(Mo,Re)S_4$ (e.g., Helz and Dolor, 2012; Akintomide et al., 2021; Helz, 2022; Živković et al., 2023).

The behaviour of RSTMs is commonly evaluated in terms of the extent of enrichment or depletion of a particular element in the deposited sediment, where the data are considered in terms of enrichment factors (EFs; Tribovillard et al., 2006) or after normalization to Al (e.g., Bennett and Canfield, 2020). In both cases a reference value is used, for example upper continental crust (UCC; McLennan, 2001), post-Archean Australian Shale (PAAS; Taylor and McLennan, 1985), or average shale (Turekian and Wedepohl, 1961). However, in addition to considering RTSM behaviour in this way, specific RSTM ratios may also aid in paleo-redox reconstructions. Indeed, the use of RSTM ratios may, at least in part, negate problems that commonly arise when proportional differences between the major (i.e., Al) and RSTM reference values for average shale do not match those of the source material being eroded into the particular basin being studied, which makes derivation of oxic baseline values particularly problematic (see Doyle et al., 2018; Li et al., 2024; Sánchez-Roda et al., 2024; Wang et al., 2024).

In particular, Mo/U ratios have been employed, alongside other redox proxies such as Fe speciation, to strengthen arguments for the presence of euxinia (e.g., He et al., 2022). However, while there are several commonly used paleo-redox proxies that may allow identification of water column euxinia or anoxic, non-sulfidic (i.e., ferruginous) conditions, the identification of settings that are depleted in oxygen, but not to the extent of full anoxia (i.e., dysoxic), has proven more challenging, as proxies such as Fe speciation and the most commonly applied RSTMs (e.g., Mo, U) are unable to distinguish such intermediate redox states (Raiswell and Canfield, 1998; Algeo and Tribovillard, 2009; Poulton, 2021). This lack of versatility in the geochemical toolbox limits the accuracy of environmental reconstructions, and particularly limits understanding of potential links between oxygen levels and biological evolution (e.g., Sperling et al., 2022).

Nevertheless, based on the RSTM behaviour outlined above, elevated Re/Mo ratios have sometimes been used to identify dysoxic settings (e.g., Crusius et al., 1996; Kendall et al., 2010; Schobben et al., 2020; Li et al., 2022), based on the accumulation of Re, but not Mo, under such conditions. The use of this proxy is also predicated on the fact that elevated Re/Mo ratios under dysoxic conditions should be distinct from those observed under euxinic conditions, whereby euxinic drawdown of both Re and Mo should result in much lower Re/Mo ratios (Crusius et al., 1996; Kendall et al., 2010; Helz, 2022). However, since Re is also sequestered under anoxic non-sulfidic conditions, but Mo specifically requires the presence of sulfide or a particulate shuttle draw down mechanism, elevated Re/Mo ratios may also potentially occur under anoxic non-sulfidic conditions. In fact, Re/U and/or Re/V ratios may potentially be more robust, or at least complementary, redox indicators for the identification of dysoxic conditions, but environmental calibration of different RSTM ratio proxies in modern and ancient environments has not been performed.

In order to improve the utility of Mo, U, V and Re as paleoredox proxies, we present and evaluate a compilation of published data for marine environments spanning a wide range of redox conditions. We subsequently build upon these findings by considering two ancient settings (the Carboniferous Bowland Shale and the Jurassic Kimmeridge Clay Formation), for which redox conditions have previously been constrained by independent techniques (Raiswell et al., 2001; Li et al., 2024). Our approach allows a comprehensive evaluation of the combined use of RSTM enrichment factors and ratios as a means to more accurately reconstruct paleoredox conditions, with a particular focus on the elusive dysoxic redox state.

## 2. The marine redox ladder

In comparing data from modern and ancient environments, redox terminology first needs to be constrained. Tyson and Pearson (1991) suggested that oxic conditions should be defined where bottom water $O_2$ concentrations are >2 ml/L (90 µM), whereas dysoxic conditions range from 0.2–2 ml/L (9–90 µM), suboxic conditions reflect $O_2$ concentrations <0.2 ml/L (<9 µM), and anoxia essentially refers to functionally oxygen-free conditions (noting here that trace oxygen can generally be detected in ‘anoxic’ bottom waters with advanced technology; Canfield and Thamdrup, 2009). However, the application of such subtle distinctions is difficult for ancient settings where direct measurements of oxygen concentrations are not possible, and sediments record average conditions whereby fluctuating oxygen levels may have influenced the redox chemistry of a single sample (e.g., Wignall and Myers, 1988; Dahl et al., 2019; Poulton, 2021). Recently, Algeo and Li (2020) used an alternative redox terminology (oxic, dysoxic, suboxic and euxinic) and noted that there tends to be a range of temporal redox variability, from large basins (e.g., the Black Sea) with relatively stable redox conditions, to small basins (e.g., Saanich Inlet) with highly variable redox conditions (Anderson and Devol, 1973).

Here, noting the importance of distinguishing anoxic non-sulfidic conditions (i.e., ferruginous) from euxinic conditions (Poulton and Canfield, 2011), we apply a redox scheme in which the oxic field is marked by an oxygen content of >90 µM, the dysoxic field has a seafloor-bearing oxygen content ranging from 90 µM to very low oxygen (~1 µM), anoxic non-sulfidic conditions occur where oxygen is below ~1 µM $O_2$ and free $H_2S$ is absent, and euxinia reflects the presence of $H_2S$ in the water column. However, noting additional distinct RSTM behaviour, we further divide oxic settings into >200 µM $O_2$ and 90-200 µM $O_2$ zones, while dysoxic settings are divided into weakly (30-90 µM) and highly (<30 µM) oxygen-depleted zones.

## 3. Study sites

### *3.1. Modern case studies*

Our data compilation from modern environments (see Table 1) includes permanently euxinic basins, which are usually silled with poor connection to the open ocean, seasonally euxinic basins with episodic ventilation, oxygen minimum zones (OMZs) on continental margins, and well-oxygenated open ocean settings. The euxinic basins have a large degree of variation in terms of $H_2S$

concentrations below the chemocline (12–4000 µM), while the OMZs document a diverse range in oxygen depletion at the seafloor (generally 0.1–90 µM $O_2$, noting that samples collected above or below the OMZ may reflect fully oxygenated bottom waters; Table 1). Oxic conditions are characterised by well-ventilated seafloor with high oxygen contents (bottom water $O_2$ usually beyond 200 µM), through to somewhat depleted $O_2$ levels of 90-200 µM (Table 1). However, we note here that even in fully oxygenated settings, sediment pore waters can be oxygen poor, especially under conditions of enhanced organic carbon burial and rapid sedimentation rate (e.g., Crusius et al., 1996; Morford and Emerson 1999).

### *3.2. Ancient case studies*

Our focus is on two well-characterized formations from England that show evidence for fluctuating redox conditions, namely the Carboniferous Bowland Shale Formation and the Late Jurassic Kimmeridge Clay Formation. The Bowland Shale Formation accumulated in the Bowland Basin, northern England, during the Early Carboniferous Visean–Serpukhovian stages, and succeeded the ramp carbonates of the Pendleside Limestone Formation (Gawthorpe, 1986). The Bowland Shale records variable redox conditions, based on a combined evaluation of multiple redox proxies, including U and Mo systematics, Fe speciation and framboidal pyrite petrography (Emmings et al., 2020; Li et al., 2024), and we augment these published data with new V and Re analyses. Our focus is on two sections, Tory Log Clough (TLC) and Dinckley Hall (DH) (Li et al., 2024). The TLC section includes the upper part of the Pendleside Limestone, which consists of alternating beds of calcareous mudstone and deep-water limestone (micritic mudstone and calcarenites of turbiditic origin), and the lower part of the Bowland Shale Formation. The DH section is dominated by dark grey, organic-rich shales of the Bowland Shale Formation (Li et al., 2024).

The Late Jurassic Kimmeridge Clay Formation has an extensive outcrop over England and is best known from the coastal exposures of the Wessex Basin in southern England (Cox and Gallois, 1981). The frequent alternations of organic-rich shale and mudstone that characterize the Kimmeridge Clay Formation have received detailed attention in terms of their paleontology, sedimentology and geochemistry (e.g., Myers and Wignall, 1987; Wignall, 1990; Tribovillard et al., 1994; Raiswell et al., 2001). Whereas our focus on the Bowland Basin is to use our new RSTM approach to test the potential to refine existing redox interpretations based on geochemistry (e.g., Li et al., 2024), for the Kimmeridge Clay Formation we take a different approach, whereby we compare our new RSTM data to paleoecological characteristics. Specifically, we present new Mo, U, V and Re data for samples that have previously been investigated in terms of an oxygen-restricted biofacies (ORB) scheme, which is based on the abundance and diversity of fossils (Wignall and Hallam, 1991), thereby providing an independent (i.e., non-geochemical) framework for interpreting depositional redox conditions. The ORB scheme documents a general decrease in the severity of redox conditions from ORB 1 to ORB 6, where ORB 1-2 represent anoxic water column conditions lacking benthos, and ORB 3-6 document progressively higher oxygen contents, from highly dysoxic (ORB 3) with few benthic species, through to weakly dysoxic (ORB 6) conditions with higher diversity (Wignall and Hallam, 1991).

## 4. Methods

### *4.1 Total digestion procedure*

Redox sensitive trace metals were determined for the Bowland Shale (V and Re) and Kimmeridge Clay (Mo, U, V and Re) formations by inductively coupled plasma–mass spectrometry in the Cohen Laboratories at the University of Leeds. Rock powders were first ashed at 550°C for 8 h, before a quantitative digestion using concentrated $HNO_3$, HF and $HClO_4$. Additional $H_3BO_3$ was then added to avoid the formation of Al hexafluorate complexes, and the samples were subsequently heated to dryness. The residues were then re-dissolved with near-boiling $HNO_3$ and diluted with ultrapure 18.2 MΩ $H_2O$. Accuracy and precision, estimated from repeat analyses of United State Geological Survey standard SGR-1b (Green River Shale), were better than 5% for all elements of interest. Previously published Mo and U data for the Bowland Shale Formation were determined using the same approach and instrumentation (Li et al., 2024).

*4.2 Enrichment factor calculations*

Here, we adopt the approach of calculating enrichment factors when normalizing our RSTM data, since this allows direct comparison with calibrated trends in the co-behaviour of elements such as Mo and U (e.g., Tribovillard et al., 2006; 2012; Algeo and Tribovillard, 2009). Enrichment factors are commonly calculated as:

$$\text{Element}_{\text{EF}} = \frac{\text{Element/Al}}{\text{Element}_{\text{UCC}}/\text{Al}_{\text{UCC}}} \qquad (1)$$

Here, we use the UCC database (McLennan, 2001) to normalize the elemental data, but with an updated Re concentration value of 0.29 ppb (Chen et al., 2016). However, a limitation when calculating EFs in this way arises from the highly variable degree of detrital sediment dilution by chemical sedimentation (e.g., carbonate, silica) in different environmental settings. For example, variable dilution by carbonate results in average Al contents of 7.6 wt% for northwest US margin sediments, whereas the average Al content for Black Sea sediments is 3.2 wt% (Crusius et al., 1996;

Morford and Emerson, 1999). The low detrital Al component typical for (bio)chemical sediments leads to artificially elevated EF values relative to siliciclastic sediments (Tribovillard et al., 2006; Van der Weijden, 2002), which clearly compromises direct comparison of different environmental settings required for the current study. Variable sedimentation rates also affect EFs, whereby rapid sedimentation decreases EF values, either because of enhanced dilution of phases precipitating in the water column, or because of more rapid development of closed system porewater conditions. However, variable sedimentation rates will generally have much less impact on RSTM ratios, which is why they are potentially more robust redox indicators and the principal focus of this study.

Given these considerations, we adopt the approach of Krewer et al. (2024), which eliminates the problem of variable dilution by chemical sediments. We initially calculate excess element concentrations as:

$$\mathrm{Element_{excess}} = \mathrm{Element_{sample}} - \left(\mathrm{Al_{sample}} \times \frac{\mathrm{Element_{UCC}}}{\mathrm{Al_{UCC}}}\right) \qquad (2)$$

To convert the excess concentration of an element (i.e., the redox-promoted drawdown concentration) to a form that is consistent with the original derivation of EFs (Eqn 1), we need to adopt the assumption used in Eqn 1 that the source material supplied to the basin had an elemental concentration equivalent to average upper continental crust (i.e., the $\mathrm{Element_{UCC}}$ value). The addition of the $\mathrm{Element_{UCC}}$ value to the calculated $\mathrm{Element_{excess}}$ value therefore gives the equivalent concentration used in the traditional EF calculation, but accounts for any dilution by, for example, carbonate or silica. To convert this to a relative enrichment value (i.e., EF*), the total element concentration is then divided by the $\mathrm{Element_{UCC}}$ value, to give (Eqn 3).

$$\mathrm{Element_{EF}}^{*} = \frac{\mathrm{Element_{excess}} + \mathrm{Element_{UCC}}}{\mathrm{Element_{UCC}}} \qquad (3)$$

For consistency, and because the extent of dilution by chemical sedimentation is generally not known for many of the samples included in this study, we calculate EF* values for all samples, including those dominated by siliciclastics (although generally this only has a limited impact for such samples). In some rare cases, where Al is higher than the UCC value and the element of interest has a very low concentration, this may result in negative element$_{EF}{}^{*}$ values, indicating a particularly high level of element depletion relative to the average UCC value. However, this affected only 2 samples in our entire database of modern and ancient samples. Furthermore, since these samples return EF values of <1 when calculated in the traditional way (indicating element depletion), redox interpretations remain entirely unaffected. Thus, in terms of a uniform approach that overcomes the problem of low Al contents in chemical sediments, hence allowing the degree of element enrichment in different settings to be directly compared, the approach of calculating EF$^{*}$ is highly beneficial (see Supplementary Information for an example of the impact of sediment dilution on enrichment factor calculations).

### *4.3 Statistical analysis*

We use independent *t*-test with a confidential interval of 95% to determine whether there are significant differences between RSTM EF$^{*}$ values and ratios under different redox conditions. Since *t*-test can only determine the significance between two groups of data, we apply this approach to adjacent redox fields of particular interest (see Supplementary Information). All statistical analyses were performed using IBM SPSS Statistic software.

## 5. Results

### *5.1. RSTM variability in modern environments*

#### *5.1.1. Enrichment factors*

The broad $EF^*$ characteristics for the different RSTMs are compiled in Table 2. Average $U_{EF}^*$ values progressively increase through each redox zone, with values that are consistently low in oxic (> 200 µM $O_2$ = 1.1 ± 0.3; 90- 200 µM $O_2$ zone = 1.2 ± 0.3) and weakly dysoxic (1.3 ± 0.6) settings, giving little evidence for any significant degree of enrichment. This is consistent with a *t*-test showing no significant difference between these redox settings (see Supplementary Information, Table S1). Average highly dysoxic (2.0 ± 2.0) and anoxic (2.2 ± 0.6) values are higher and overlap (with a $p$ value > 0.05), with highly dysoxic values being particularly variable between different settings (Fig. 1). However, higher $EF^*$ values in highly dysoxic settings uniquely occur in Peru margin sediments, which also have unusually high $Mo_{EF}^*$ and $V_{EF}^*$ values (Fig. 1; note that when the Peru margin sediments are excluded, the average $U_{EF}^*$ value (1.5 ± 0.5) for highly dysoxic settings remains slightly elevated relative to oxic and weakly dysoxic values).

Modern euxinic environments show a high degree of variability, largely due to highly U-enriched sediments on the Namibian margin (Fig. 1), giving an overall average of (4.4 ± 3.4). However, as discussed below, the Namibian margin sediments appear to be anomalous, and when these samples are excluded, euxinic settings have a lower $U_{EF}^*$ value of 3.4 ± 1.8. Furthermore, similar to $Mo_{EF}$ and $Re_{EF}$ values, when Namibian samples are excluded, $U_{EF}$ values show a progressive increase as sulfide concentrations initially increase, but values then decrease in Kyllaren Fjord samples, where very high concentrations of sulfide (~4 mM) are recorded (Fig. 1). As discussed below, Kyllaren Fjord has distinct characteristics that may explain the deviation from the trend of increasing RSTM enrichments as sulfide concentrations increase.

Molybdenum shows limited enrichment in two oxic groups with very low $Mo_{EF}^*$ values (> 200 µM $O_2$ = 0.94 ± 0.27; 90-200 µM $O_2$ = 1.0 ± 0.2), and there is no obvious difference between two groups (supported by a $p$ value > 0.05; Table S1). Weakly (1.6 ± 1.8) and highly (4.7 ± 12.4) dysoxic settings have progressively elevated average values, but highly dysoxic samples have a particularly variable range, again driven by Peru margin sediments (Fig. 1). In anoxic sediments, average $Mo_{EF}^*$ values are similar to dysoxic settings (5.2 ± 2.1, $p$ value > 0.05; Table S1), but with less variability. In euxinic settings, $Mo_{EF}^*$ values are generally highly enriched (29 ± 17, or 32 ± 16 when the anomalously low Kyllaren Fjord samples are excluded) and show a similar trend to $U_{EF}^*$ values (Fig. 1), with increasing values as sulfide concentrations initially increase (note that unlike $U_{EF}^*$ values, Namibian margin samples follow this $Mo_{EF}^*$ trend).

Rhenium displays the largest overall variability in $EF^*$ values (Fig. 1). Although the data show a relatively high degree of variability through the oxic zone, it is notable that most settings have significantly elevated (i.e., >>1) $Re_{EF}^*$ values, giving average values of 20 ± 22 for the > 200 µM $O_2$ zone, and higher average values of 54 ± 19 for the 90-200 µM $O_2$ zone. These features may be a consequence of (variable) Re drawdown due to the development of dysoxic porewaters in surficial sediments beneath oxic bottom waters, potentially coupled with inadequacy in terms of the utility of the updated Re value for UCC to represent the Re content of typical oxic marine sediments (giving high overall values). In the weakly and highly dysoxic zones, $Re_{EF}^*$ values are again highly variable, but moderate average levels (31 ± 24) occur in weakly dysoxic settings, while average values increase considerably (94 ± 100) in highly dysoxic settings (Fig. 1). High $Re_{EF}^*$ values (117 ± 24) are maintained in anoxic settings, while through the euxinic zone, $Re_{EF}^*$ values show similar behaviour to $Mo_{EF}^*$ values, with an initial progressive increase as sulfide concentrations increase, giving an average value of 92 ± 96 (103 ± 99 when the anomalously low Kyllaren Fjord samples are excluded).

The extent of variability in $V_{EF}^*$ values is considerably less than for the other RSTMs (Fig. 1). However, in the oxic zone, $V_{EF}^*$ values are relatively high at the highest $O_2$ concentrations (1.7 ± 0.2 in Svalbard sediments), with generally lower values throughout the rest of the oxic zone (including depleted values in African margin samples), giving an average value for all > 200 µM $O_2$ samples of 1.3 ± 0.4, and an average value for 90-200 µM $O_2$ samples of 1.1 ± 0.1. Vanadium enrichments persist at low values throughout the subsequent dysoxic zone (weakly dysoxic = 1.3 ± 0.1; highly dysoxic = 1.3 ± 0.3), with enhanced variability in the highly dysoxic zone again being largely due to Peru margin sediments, while similar average values (1.2 ± 0.1) occur for anoxic settings (Fig. 1). In euxinic settings, average $V_{EF}^*$ values are slightly increased to moderate levels (1.5 ± 0.1; note that no V data were available for Kyllaren Fjord).

### *5.1.2. RSTM ratios*

The broad characteristics of different RSTM ratios are compiled in Table 3. Re/Mo ratios are generally highly elevated relative to UCC values ($Re/Mo_{UCC}$ = 0.17 ppb/ppm) in oxic and dysoxic settings, while ratios are commonly lower in anoxic and euxinic settings, with values that straddle the average UCC ratio, particularly in euxinic settings (Fig. 2). There are, however, additional distinct differences in Re/Mo ratios under different redox conditions. In the highest [$O_2$] marine settings (> 200 µM; Table 1), Re/Mo ratios are relatively low, but the data show considerable variability (4.2 ± 4.4 ppb/ppm; Fig. 2). As oxygen decreases from ~200 to ~90 µM, Re/Mo ratios show less variability, with moderate enrichments overall (8.2 ± 2.3 ppb/ppm, $p$ value < 0.05; Table S1). Under dysoxic conditions down to ~30 µM $O_2$, Re/Mo ratios fluctuate considerably, but overall, average values are high (15 ± 19 ppb/ppm), and even higher values with somewhat diminished variability (21 ± 16 ppb/ppm) are evident in dysoxic settings with $O_2$ concentrations <30 µM (Fig. 2). Anoxic settings show a clear decline to low (4.7 ± 2.4 ppb/ppm) Re/Mo ratios (see *t*-test in Table S1), and very low ratios then occur (0.57 ± 0.50 ppb/ppm) under euxinic conditions, with a significant statistical difference between the two redox groups (Table S1).

In contrast to Re/Mo ratios, Re/U ratios are generally higher than UCC values ($Re/U_{UCC}$ = 0.09 ppb/ppm) across all redox states (Fig. 2). In detail, Re/U ratios are relatively constant and low overall in the oxic (> 200 µM $O_2$ = 1.8 ± 1.7 ppb/ppm; 90-200 µM $O_2$ = 3.8 ± 0.7 ppb/ppm) and 30-90 µM dysoxic (2.8 ± 1.7 ppb/ppm) zones (Fig. 2). However, an increase to relatively high, but variable, Re/U ratios (8.1 ± 8.2 ppb/ppm) is apparent in the <30 µM $O_2$ dysoxic zone, which is also supported by a *t*-test (Table S1). There is then a shift to moderate Re/U ratios (5.3 ± 1.9 ppb/ppm, with a statistical difference relative to data in the dysoxic field, see Table S1) in the anoxic zone, followed by low values (1.8 ± 1.5 ppb/ppm) in euxinic settings (Fig. 2). Similar to Re/U ratios, Re/V ratios are generally elevated relative to UCC values ($Re/V_{UCC}$ = 0.002 ppb/ppm) across all redox states (Fig. 2). Variability in Re/V ratios is also similar to that observed for Re/U ratios (Fig. 2) through the oxic zone (> 200 µM $O_2$ = 0.05 ± 0.06 ppb/ppm; 90-200 µM $O_2$ = 0.11 ± 0.04 ppb/ppm) and into the 30-90 µM $O_2$ dysoxic zone (0.08 ± 0.06). There is then a similar relative increase to high ratios (0.31 ± 0.24 ppb/ppm) in the <30 µM $O_2$ dysoxic field, with a clear statistical difference compared to oxic samples (Table S1), and although the data continue to show a high degree of variability (Fig. 2), the range in Re/V ratios remains similar through the anoxic (0.34 ± 0.26 ppb/ppm) and euxinic (0.24 ± 0.22 ppb/ppm) zones (*p* value > 0.05; Table S1).

Mo/U ratios (Fig. 2) are persistently low and statistically indistinguishable (Table S1) through the oxic zone (> 200 µM $O_2$ = 0.58 ± 0.36 ppb/ppm; 90-200 µM $O_2$ = 0.50 ± 0.14 ppb/ppm), and while average values are higher in the dysoxic zones (weakly dysoxic = 1.0 ± 1.7 ppb/ppm; highly dysoxic = 0.84 ± 1.37 ppb/ppm), Mo/U ratios are highly variable. Similar moderate Mo/U ratios (1.3 ± 0.5 ppb/ppm) persist in anoxic settings, while euxinic settings are characterized by high ratios (5.1 ± 3.5 ppb/ppm, with a significant statistical difference between euxinic and anoxic data, $p < 0.001$; Table S1).

### *5.2. RSTMs in the Bowland Shale Formation*

All new geochemical data for the ancient case studies are provided in Supplementary Information Tables S2-S5. Based on Fe speciation, U and Mo systematics, and pyrite framboid size ranges, oxic conditions have been suggested during deposition of the Pendleside Limestone (note that our samples are from the calcareous mudstones of this formation) and the lower part of the Bowland Shale Formation (0–66.8 m at TLC). There was then a transition to conditions that fluctuated between ferruginous, weakly euxinic and highly euxinic (with weakly and highly euxinic conditions being broadly defined based on pyrite framboid size ranges, and relatively low and high $Mo_{EF}$ enrichment factors, respectively) through the overlying Bowland Shale Formation (Fig. 3; Li et al., 2024). Broadly speaking, the new $Re_{EF}^*$ and $V_{EF}^*$ data show similar behaviour to the $Mo_{EF}^*$ and $U_{EF}^*$ data, with low values in the lower part of the succession and generally higher, but fluctuating, values above the basal part of the Bowland Shale Formation (Fig. 3). However, enrichments in V are relatively muted above a height of ~70 m in the upper part of the Bowland Shale Formation (DH section; Fig. 3).

Re/Mo ratios show a large degree of variability through the TLC and DH sections, with overall high, but fluctuating values in the Pendleside Limestone and lowermost Bowland Shale in the TLC section (31 ± 24 ppb/ppm; Fig. 3). However, above the upper part of the $P_{1c}$ ammonoid zone, Re/Mo ratios are low and relatively constant (2.8 ± 2.2 ppb/ppm) through both sections, until the $E_{1b}$ zone, where there is a slight increase (7.8 ± 6.0 ppb/ppm) in the DH section (Fig. 3). Re/U ratios are relatively low and stable (4.0 ± 1.9 ppb/ppm) in the Pendleside Limestone, but the degree of variability increases considerably as redox conditions become more reducing through the Bowland Shale Formation (6.0 ± 5.0 ppb/ppm), with peaks in Re/U commonly occurring in weakly or highly euxinic intervals (Fig. 3).

The Re/V profile is similar to the Re/U profile, with relatively low and stable values (0.08 ± 0.05 ppb/ppm) through the Pendleside Limestone (Fig. 3). This is followed by generally higher and more variable values (0.34 ± 0.24 ppb/ppm) through the remainder of the succession, although Re/V ratios are commonly low (0.24 ± 0.17 ppb/ppm) in the lower part of the Bowland Shale Formation in the DH section, with a distinct transition to higher and more variable values (0.61 ± 0.24 ppb/ppm) through the prolonged highly euxinic interval in the middle to upper Bowland Shale Formation (Fig. 3). Mo/U ratios show distinct behaviour relative to the other RSTM ratios (Fig. 3). In the Pendleside Limestone, Mo/U ratios are persistently low (0.17 ± 0.10 ppb/ppm), with values that fall below the average UCC value. Similar low values are also found in overlying ferruginous intervals in both sections (0.39 ± 0.39 ppb/ppm). By contrast, euxinic samples commonly have ratios that plot above the UCC value, with a distinct overall increase in samples interpreted to record highly euxinic (3.4 ± 1.4 ppb/ppm) relative to weakly euxinic (1.9 ± 1.1 ppb/ppm) conditions (Fig. 3). This is supported by a *t*-test ($p < 0.001$), showing a significant difference between weakly and highly euxinic samples (Table S1).

### *5.3. RSTMs in the Kimmeridge Clay Formation*

Our dataset for the Kimmeridge Clay Formation includes sporadic samples for which ORB have been defined (comprising samples that range from ORB 1 to ORB 6; Table S2), in addition to a continuous section that comprises ~40 m of stratigraphy through the late *scitilus*, *wheatleyensis* and early *hudlestoni* ammonite biozones of the Upper Kimmeridgian (Fig. 4). The biofacies of this section comprises ORB 3-6, and RSTMs show consistent behaviour in terms of enrichment factors, with relatively muted overall variability for $Mo_{EF}^*$, $U_{EF}^*$ and particularly $V_{EF}^*$, with values that are commonly close to 1 or slightly elevated. There are, however, occasional peaks to much higher values for these elements, and these uniquely occur in samples from the most reducing ORB (ORB 3) present in this section, while there is only subtle variability between ORB 4–6, with generally lower $EF^*$ values as the ORB level increases (Fig. 4). Rhenium $EF^*$ values show similar trends to the other RSTM values, but values are commonly highly elevated by comparison. Samples that document ORB 1 and 2 biofacies in the more complete dataset (Table S3) have considerably elevated $Mo_{EF}^*$ and $U_{EF}^*$ values relative to ORB 3–6 samples. By contrast, $Re_{EF}^*$ and $V_{EF}^*$ values for ORB 1 and 2 biofacies samples have a similar range to those observed for ORB 3 and 4 (Table S3).

Re/Mo, Re/U and Re/V ratios also show similar trends, with values that are generally elevated relative to UCC (to a lesser degree for Re/V), and a large degree of overall variability in response to changes in ORB levels (Fig. 4), which we evaluate in more detail in the discussion below. However, Mo/U ratios show highly contrasting behaviour, and while Mo/U ratios show significant variability, they are persistently lower than the UCC value across all of the ORB present in Fig. 4. This is commonly the case in terms of the complete dataset (Table S3), although there are occasional samples that have Mo/U ratios above the UCC value. By contrast, Mo/U ratios in samples of ORB 1 and ORB 2 are persistently elevated relative to the UCC value (Table S3).

## 6. Discussion

### *6.1. RSTM behaviour in modern environments*

### *6.1.1. Enrichment factors*

Our compilation of modern environmental data generally shows RSTM behaviour consistent with expectations for different redox conditions (see summaries in Tribovillard et al., 2006; Robbins et al., 2006; Bennett and Canfield, 2020; Algeo and Li, 2022; Paul et al., 2023b), but with novel insight and nuance arising from our consideration of both enrichment factors and RSTM ratios. Uranium generally becomes progressively enriched as reducing conditions intensify, with very low $U_{EF}^*$ values in oxic and weakly dysoxic settings, moderate values in highly dysoxic and anoxic settings (see discussion below for a detailed evaluation of the Namibian samples), and high values in euxinic settings (Fig. 5; Table 2). This is also in general agreement with a recent study focusing on U accumulation in coastal environments (Paul et al., 2023b). However, euxinic settings with low sulfide concentrations show a high degree of overlap with both anoxic and highly dysoxic settings (Fig. 1). These characteristics highlight that, when applied in isolation, $U_{EF}^*$ values do not adequately distinguish dysoxic to euxinic sediments (Table 2), although values close to 1 provide a strong indication of conditions that are not fully anoxic, while high values generally indicate euxinia.

The behaviour of Mo is similar to U, with a general progressive increase as redox conditions become more reducing (Table 2; Fig. 5). However, the particularly variable $Mo_{EF}^*$ values that occur under dysoxic conditions warrant further consideration in terms of potential controls on Mo drawdown to the sediments. As discussed above, it is well-established that Mo drawdown may occur via enhanced sulfide availability and/or via a particulate shuttle mechanism, which are commonly distinguished using a $Mo_{EF}$-$U_{EF}$ cross-plot (e.g., Algeo and Tribovillard, 2009; Tribovillard et al., 2012).

Here, we take this approach and distinguish our modern environmental data in terms of oxic, dysoxic and anoxic depositional settings (Fig. 6). Although a significant proportion of dysoxic samples follow the redox variation trajectory (Fig. 6b), consistent with dysoxic, rather than oxic, depositional conditions (Algeo and Tribovillard, 2009; Tribovillard et al., 2012), a large degree of overlap is apparent between oxic and dysoxic settings (cf. Figs. 6a and 6b), clearly highlighting a key limitation in the use of such cross-plots to distinguish oxic and dysoxic depositional conditions.

When considered in detail, a clear array of dysoxic samples from the Arabian Sea and Peru margin follow the particulate shuttle pathway (Fig. 6b). However, a proportion of the dysoxic Peru margin samples plot in the upper region of the redox trajectory pathway, in an area that would normally be considered to indicate euxinic depositional conditions (cf. Figs. 6b and c). This suggests a combined drawdown influence from the particulate shuttle mechanism and from progressive anoxia (see also Scholz et al., 2017; Vollebregt et al, 2023), with the latter likely reflecting non-sulfidic anoxia (and hence enhanced U drawdown) close to the sediment-water interface. This would have augmented the U content of samples that were already enriched in Mo due to drawdown via the particulate shuttle pathway. Hence, it is the combined effect of these processes on samples from the Arabian Sea and Peru margin that are responsible for the relatively high degree of $Mo_{EF}$ variability observed in the weakly and highly dysoxic zones (Fig. 1).

Anoxic and euxinic samples show particularly complex behaviour in terms of controls on Mo and U drawdown. While anoxic samples plot closest to the redox trajectory, euxinic samples commonly plot between the redox and particulate shuttle trends (Fig. 6c). In detail, the euxinic Saanich Inlet and Cariaco Basin show a particularly strong influence from the particulate shuttle pathway, consistent with a lasting impact from the Fe-Mn particulate shuttle in weakly euxinic bottom waters (Algeo and Tribovillard, 2009; see Table 1), which may relate to the slower sulfidation kinetics of Fe (oxyhydr)oxides at lower sulfide concentrations (Canfield et al., 1992; Poulton et al., 2004). In addition, apart from the Nambian margin samples, the remaining euxinic samples plot between the anoxic samples and the particulate shuttle trajectory (Fig. 6c), suggesting a combined influence from drawdown due to progressive anoxia and via a particulate shuttle mechanism.

These characteristics are perhaps not unexpected, since while U drawdown is promoted by redox conditions in sediment porewaters close to the sediment-water interface (Anderson et al., 1989; Klinkhammer and Palmer, 1991), Mo drawdown under euxinic conditions is initiated in the water column, via two pathways. The first pathway occurs via the aforementioned uptake to Fe-Mn (oxyhydr)oxides, while the second pathway reflects the formation of particle reactive thiomolybdates within the euxinic water column itself, followed by scavenging by transition metal particles and organic matter (Helz et al., 1996; Vorlicek et al., 2004; Nägler et al., 2011). Following deposition, subsequent drawdown of Mo likely occurs in sulfidic porewaters, further augmenting the sequestration of Mo. However, since our modern sample suite documents near-surface sediments, the influence of diagenetic Mo drawdown may be incomplete. Thus, while anoxic samples plot relatively close to the redox trajectory, most euxinic samples document the variable influence of Mo drawdown via the two different water column pathways, combined with subsequent drawdown in sulfidic porewaters.

The euxinic $Mo_{EF}^{*}$–$U_{EF}^{*}$ cross-plot also highlights the distinct nature of the Namibian margin sediments (Fig. 6c). These samples have unusually elevated $U_{EF}^{*}$ values relative to $Mo_{EF}^{*}$ values, and the U data also contrast with the other RSTMs, which follow the general trend of increasing RSTM $EF^{*}$ values as sulfide concentrations initially increase (Fig. 1). This may be associated with the particular hydrography, plus Mo and U accumulation mechanisms, on the margin. Redox variability on the Namibian margin is characterized by highly fluctuating redox conditions controlled by diverse water masses (e.g., Brüchert et al., 2003; He et al., 2021). Although the sediment experiences conditions that fluctuate from weakly euxinic to dysoxic, unlike other seasonally euxinic basins (e.g., Sannich Inlet), Mo delivery via the particulate Fe and Mn (oxyhydr)oxide shuttle is generally not observed (He et al., 2021; Kossack et al., 2023), and Mo accumulation is dominated by diffusive Mo influxes into the sediment (Kossack et al., 2023). By contrast, U enrichment is almost exclusively delivered in particulate form, and 50-90% of the particulate U supply is buried in the sediment (Borchers et al., 2005; Kossack et al., 2023). In addition, U accumulation is promoted by the deposition of phosphorite (Lachkar and Gruber, 2012; Kossack et al., 2023). Given this, we exclude data from the Nambian margin from further consideration.

Overall, the above discussion highlights difficulties in using Mo enrichment factors, in isolation, as a robust tool for reconstructing oceanic redox conditions, since high values may occur in dysoxic and euxinic settings (and likely in anoxic settings as well). However, our approach reinforces the utility of $Mo_{EF}^{*}$-$U_{EF}^{*}$ cross-plots for providing key information in terms of the pathways influencing

Mo and U enrichments in marine sediments (e.g., Algeo and Tribovillard, 2009; Tribovillard et al., 2012).

Re accumulation is particularly sensitive to oxygen levels, with low average $Re_{EF}^{*}$ values in the >200 µM $O_2$ zone, moderate enrichments in the 90- 200 µM $O_2$ and weakly dysoxic zones, and a high average degree of enrichment in the highly dysoxic and anoxic zones (Fig. 1; Table 2). However, variability in $Re_{EF}^{*}$ values is high throughout each redox zone (Fig. 5), with variability in the extent of drawdown in oxic and dysoxic settings likely reflecting variable levels of oxygen depletion in the sediment, which is regulated by sedimentation rate and organic carbon burial (Morford and Emerson, 1999). Rapid sedimentation rates combined with enhanced organic carbon input stimulates oxygen depletion in porewaters close to the sediment-water interface, promoting reduction of Re(VII) to Re(IV) and accumulation in the sediment (Crusius et al., 1996; Morford and Emerson, 1999). These controls are clearly important on the African and northwest US margins, where a high organic carbon flux promotes oxygen-depletion in near-surface porewaters (Morford and Emerson, 1999), resulting in relatively enhanced Re drawdown (Fig. 1). Similarly, Arabian Sea samples are organic-rich, promoting relatively high enrichments in Re under weakly dysoxic conditions (Goswami et al., 2012). The progressive enrichment in Re as the intensity of dysoxia increases is well documented (Crusius et al., 1996; Morford and Emerson, 1999; Yamashita et al., 2007), and high $Re_{EF}^{*}$ values generally persist in anoxic and euxinic settings, although there is considerable variability and overlap (Fig. 1, Table 2). This clearly precludes definitive redox interpretations based on $Re_{EF}^{*}$ values alone.

Vanadium $EF^{*}$ values are particularly variable through the >200 µM $O_2$ zone, with an overall progressive (but fluctuating) decrease from 280-200 µM (Fig. 1). We speculate that this may be due to slightly enhanced dissolution of V-bearing phases in dysoxic porewaters and loss of V from the sediments as [$O_2$] decreases (Emerson and Huested, 1991; Nameroff et al., 2002). Generally speaking, however, $V_{EF}$ values are above 1 throughout most redox states (Table 2; Fig. 5), and hence show little discernible evidence for the proposed loss of V from sediments deposited under dysoxic conditions (cf. Emerson and Huested, 1991; Nameroff et al., 2002). This suggests that application of V depletion as a diagnostic tool for dysoxia is limited, and is restricted to the identification of dysoxic porewaters beneath well-oxygenated bottom waters. Thus, in intermediate redox settings, the behaviour of V appears more strongly controlled by the rapid development of anoxic porewaters beneath dysoxic bottom waters, giving rise to V enrichment in the sediments. Indeed, the similarity in $V_{EF}^{*}$ values under dysoxic and anoxic conditions suggests that it is primarily porewater anoxia that drives the extent of V enrichment in most redox settings. However, higher average V enrichments tend to occur in euxinic settings (Table 2), although there is considerable overlap with other redox zones (Fig. 5).

A particular feature of the data concerns the relatively low $U_{EF}$, $Mo_{EF}$ and $Re_{EF}$ values in Kyllaren Fjord sediments, where EF*s deviate from the general trend of increasing values as sulfide concentrations increase (Fig. 1; see also Noordmann et al., 2015). This may be explained by a combination of basinal restriction, since Kyllaren Fjord is a 29 m deep basin with limited connection to the open ocean, and high sedimentation rates (1 mm/yr; Noordmann et al., 2015). Without sufficient resupply of RSTMs to the basin, and with high sedimentation rates diluting RSTM enrichments from the water column, sediment trace metal accumulation is restricted. This is similar to the Black Sea, where Mo drawdown is controlled by limited resupply from deep waters (Algeo and Lyons, 2006), although in the case of the Black Sea, this is not severe enough to dramatically reduce observed Mo enrichments (Fig. 1). Despite this limitation, the clear progressive trend, in terms of increasing $Mo_{EF}^*$ values as sulfide concentrations increase in the remaining euxinic settings (Fig. 1), highlights the utility of Mo enrichment factors as a potential means to distinguish highly and weakly euxinic conditions (e.g., Song et al., 2023; Li et al., 2024), particularly when resupply of Mo is not limited.

### *6.1.2. RSTM ratios*

In almost all cases, the variability in RSTM ratios is lower than variability in EF values, with the notable exception of Mo/U ratios in dysoxic settings (Tables 2 and 3). The clear progressive increase in Re/Mo ratios as water column oxygen levels decrease through the oxic and dysoxic zones (Fig. 5; Table 3) highlights the potential utility of Re/Mo ratios as a sensitive indicator of the degree of water column oxygen depletion. However, significant overlap between weakly and highly dysoxic settings, which as discussed above reflects variability in the strength of Mo drawdown via the particulate shuttle, highlights a limitation in the use of Re/Mo ratios alone. The dramatic and persistent decrease in Re/Mo ratios that then occurs in euxinic settings (Figs. 1 and 5) clearly reflects enhanced drawdown of Mo in the presence of water column sulfide (Emerson and Huested, 1991; Helz et al., 1996), and Re/Mo ratios may be particularly low in basins that fluctuate between euxinic and oxic (Helz, 2022). It is perhaps surprising, however, that Re/Mo ratios are low in anoxic non-sulfidic settings (Fig. 2), since as discussed above, high ratios might be expected under such conditions due to extensive Re drawdown but limited Mo drawdown in the absence of dissolved sulfide in the water column. These anoxic non-sulfidic settings do not appear to be appreciably impacted by Mo drawdown via the particulate shuttle mechanism (Fig. 6c), and hence it may be the development of sulfidic porewaters close to the sediment-water interface that is responsible for Mo sequestration in the sediments, and hence low Re/Mo ratios (Morford et al., 2005). The resultant significant overlap in average Re/Mo ratios between anoxic and fully oxic (i.e., >200 µM $O_2$) settings (Fig. 2) highlights that additional proxies are required for a robust redox interpretation.

The overall increase in Re/U and Re/V ratios through the oxic and dysoxic zones (Table 3; Fig. 5) reflects enhanced Re drawdown as oxygen is increasingly depleted, although the high degree of variability apparent in each redox zone highlights that porewater chemistry, specifically the relative development of dysoxic versus anoxic porewater conditions close to the sediment-water interface, exerts a strong control on these ratios. However, the increase in Re/U and Re/V ratios from the >200 µM to the 90-200 µM oxic zone (Table 3) is particularly noteworthy, and suggests that such ratios may be a particularly sensitive indicator of oxygen depletion through the oxic zone. The decrease in Re/U and Re/V ratios that then occurs as oxygen concentrations decrease further (i.e., in the dysoxic 30-90 µM zone) likely reflects generally more rapid development of anoxic porewaters, thus stimulating enhanced U and V drawdown.

It is perhaps unexpected that Re/U and Re/V ratios remain relatively high under anoxic conditions (Table 3; Fig. 5), since both U and V would be expected to be drawn down more extensively in the complete absence of oxygen (Anderson et al., 1989; Emerson and Huested, 1991). Instead, anoxia appears to promote a similar relative increase in Re sequestration, which is reflected by increased $Re_{EF}^*$ values under anoxic conditions (Fig. 5). Under euxinic conditions, Re/U ratios then decrease compared to anoxic settings, while Re/V ratios remain relatively constant. This suggests that, in these modern sediments at least, the intensity of reducing conditions may exert a particularly strong control on U drawdown.

The distinct behaviour of Mo/U ratios relative to the other RSTM ratios is particularly striking (Table 3; Fig. 5). Average ratios below the $UCC_{Mo/U}$ ratio in oxic and dysoxic settings clearly reflect enhanced drawdown of U as porewaters become anoxic, while the high degree of variability in dysoxic settings reflects drawdown of Mo via the particulate shuttle, as discussed above. The slight increase in Mo/U ratios in anoxic settings is likely due to enhanced Mo drawdown due to the development of sulfidic porewaters (Fig. 5). However, the key attribute of Mo/U ratios is the dramatic increase in euxinic sediments, which occurs in all settings except the Namibian margin, which as discussed above, have unusually high U contents, giving low Mo/U ratios. Thus, Mo/U ratios are a powerful tool for identifying euxinic conditions, particularly when combined with other techniques (e.g., Re/Mo ratios) that are able to distinguish Mo/U enrichments under euxinic conditions from those that may occur under dysoxic conditions (Fig. 5). It is worth noting that even in Kyllaren Fjord, where Mo and U resupply is strongly limited, high Mo/U ratios are still observed, consistent with other fjord settings (e.g., Paul et al., 2023a). This suggests that this ratio provides a robust indication of euxinia in settings with diverse hydrographic characteristics, redox variability and sedimentation rates.

### *6.2. Insight from Bowland Basin*

The Bowland Basin samples have previously been interpreted to reflect deposition under oxic, anoxic ferruginous, and weakly and highly euxinic conditions, based on Fe speciation, U and Mo enrichment factors, and pyrite framboid size ranges (Fig. 3; Li et al., 2024). Importantly, the distinction between weakly and highly euxinic settings is based on a combined evaluation of $Mo_{EF}$ values and pyrite framboid size ranges (Li et al., 2024), and is thus not predicated on RSTM systematics alone. As discussed below, our RSTM approach provides strong support for these redox groupings, but also provides an opportunity for refined interpretations.

In terms of RSTM enrichment factors, the Bowland Basin shows a high level of consistency with modern environments (cf. Figs. 5 and 7), with a clear increase in average RSTM enrichment factors as redox conditions become progressively more reducing. This progressive increase is particularly striking for $Mo_{EF}^*$, $U_{EF}^*$ and $Re_{EF}^*$ values, while $V_{EF}^*$ values show more muted behaviour, similar to modern environments. RSTM ratios also show a high degree of consistency with modern environments. In the Bowland Basin, Re/Mo ratios decline slightly in anoxic samples, with a further substantial decrease in euxinic samples (Fig. 7), as in modern environments (Fig. 5). Re/U and Re/V ratios in the Bowland Basin show similar (Re/U) or slightly increased (Re/V) ratios in anoxic samples, relative to better oxygenated samples (Fig. 7), which is again similar to modern settings (Fig. 5). There is then a slight divergence in behaviour, with both Re/U and Re/V progressively increasing through weakly and highly euxinic settings in the Bowland Basin (Fig. 7), while in modern settings, Re/U decreases slightly and Re/V remains relatively constant under euxinic conditions (Fig. 5).

Trends in Mo/U ratios are as striking in the Bowland Basin as they are in modern settings, with a dramatic increase to substantially elevated ratios in euxinic settings. In detail, Bowland Basin Mo/U ratios are below the UCC value in all redox settings except for samples deposited under euxinic conditions. This is similar to modern settings, with the exception that under anoxic conditions, modern settings have Mo/U ratios that are slightly above the UCC value (Fig. 5). This suggests that under ferruginous conditions in the Bowland Basin, sulfidic porewaters did not develop close to the sediment-water interface, thus limiting Mo drawdown and thereby resulting in relatively low Mo/U ratios. These observations further highlight how a detailed evaluation of RSTM ratios may provide insight into porewater redox conditions, in addition to water column redox systematics.

A particularly important feature of the data relates to the clear increase in Mo/U ratios from weakly to highly euxinic conditions (Fig. 7). This occurs alongside a substantial increase in $Mo_{EF}^{*}$ values, as well as moderate increases $U_{EF}^{*}$ and $Re_{EF}^{*}$ values, and Re/U and Re/V ratios (although given the divergent behaviour of Re/U and Re/V ratios relative to modern environments, we do not place particular emphasis on these ratio increases here). This clearly highlights the utility of Mo/U ratios, particularly when supported by increased $Mo_{EF}^{*}$ values, for distinguishing weakly and highly euxinic conditions. For example, Mo isotopes in siliciclastic sediments deposited under euxinic conditions are commonly used to reconstruct the isotopic composition of seawater Mo, which may then be used to model the global extent of different redox conditions (e.g., Kendall, 2021). However, this approach requires relatively high concentrations of dissolved sulfide in the water column, to give near-quantitative Mo drawdown and hence a water-column Mo isotope signal (e.g., Neubert et al., 2008). Our findings suggest that Mo/U ratios may be a useful tool for evaluating the likelihood that this requirement is met.

The techniques applied by Li et al. (2024) to the Bowland Basin redox reconstruction were not able to identify any degree of oxygen depletion from the water column, other than fully anoxic conditions. Thus, samples that did not show evidence for anoxic deposition were defined as ‘oxic’ (Fig. 3). However, our approach enables a refined interpretation for these samples, which are characterised by high Re/Mo ratios, moderate Re/U ratios and low Re/V ratios (Fig. 7), suggesting they were deposited under weakly dysoxic, rather than fully oxic, conditions (see Table 3). This refined redox interpretation is more consistent with the paleontological record for these horizons (e.g., the Pendleside Limestone; Fig. 3), where the benthos is characterised by a low diversity assemblage, comprising only a few thin-shelled brachiopods and bivalves, combined with small-scale burrowing. This further highlights the enhanced utility of our approach, which may provide a hitherto unprecedented level of insight into ancient redox conditions and links to the biotic record.

We also note that the redox interpretations outlined here are fully supported by a $Mo_{EF}^{*}$-$U_{EF}^{*}$ crossplot (Fig. 8), where the samples dominantly follow the redox trajectory pathway. However, a significant proportion of weakly euxinic samples (and perhaps some ferruginous samples), plot between the redox trajectory and particulate shuttle pathways, again highlighting the complex drawdown pathways for Mo from the water column, as suggested above for modern environments. In addition, the weakly dysoxic samples plot in a position that would previously have been assigned to oxic samples (see also Fig. 6a), again highlighting the limitations of such cross-plots for recognition of oxic to dysoxic settings, which instead requires detailed insight from Re-based RSTM ratios.

### *6.3. Insight from the Kimmeridge Clay*

The Kimmeridge Clay samples provide an additional opportunity to assess the robustness of our RSTM approach, but in a way that is entirely independent of existing geochemical or mineralogical constraints on paleoredox interpretations. Oxygen-restricted biofacies 3-6 are considered to represent dysaerobic (i.e., dysoxic) conditions, with progressively increased levels of oxygen depletion from ORB 6 to ORB 3 (Wignall and Hallam, 1991; Wignall, 1994). As such, ORB 6 may overlap with the 90-200 µM $O_2$ zone, as indicated by the size range of pyrite framboid populations from this biofacies, which plot in the oxic-dysoxic field on a mean-standard deviation cross-plot (Wignall and Newton, 1998). Towards the other end of the redox spectrum, ORB 3 is comparable to our highly dysoxic zone, albeit with framboids plotting in the euxinic field on a mean-standard deviation plot, although values are slightly greater than for ORB 1 and 2 (Wignall and Newton, 1988). ORBs 1 and 2 lack benthos and are interpreted to be anoxic biofacies, with ORB 1 only containing fossils derived from the upper water column, thereby likely recording euxinic conditions (Wignall and Hallam, 1991; Wignall, 1994). Thus, in contrast to the Bowland Basin, which dominantly provides a window into differential RSTM behaviour under anoxic conditions, the Kimmeridge Clay Formation provides particularly enhanced resolution through the various zones of oxygen depletion, prior to the development of fully anoxic conditions.

Redox-sensitive trace metal $EF^*$ trends for the Kimmeridge Clay Formation (Fig. 9) are similar to those observed for modern environments (Fig. 5), with a significant increase in $U_{EF}^*$ and $Mo_{EF}^*$ values under anoxic/euxinic conditions, while $Re_{EF}^*$ values reach a relatively constant level under highly dysoxic and anoxic/euxinic conditions, and $V_{EF}^*$ values show an overall increase through the dysoxic zones, but with muted variability overall (Fig. 9). The RSTM ratios also show trends that are strikingly similar to those observed in modern environments. In detail, the clear progressive increase in Re/Mo, Re/U and Re/V ratios that occurs as the level of oxygen depletion intensifies from ORB 6 to ORB 3 (Fig. 9), highlights the major utility of these proxies for identifying different intensities of dysoxia. It is noticeable, however, that Re/Mo ratios show a large degree of variability, and although average Mo/U ratios through these dysoxic zones show consistent behaviour with modern environments (i.e., low average values that are below the $UCC_{Mo/U}$ ratio), the data also show considerable variability. The high degree of variability observed for these RSTM ratios is similar to that observed in modern environments (cf., Figs. 5 and 9), suggesting that the dysoxic Kimmeridge Clay Formation samples may have been similarly impacted by enhanced Mo drawdown via a particulate shuttle mechanism.

We evaluate this in Fig. 10, which shows a clear separation in terms of samples that follow the redox trajectory and those that follow the particulate shuttle pathway, which in turn explains the large degree of variability apparent in dysoxic Re/Mo and Mo/U ratios (Fig. 9). This again highlights the utility of considering Mo-based RSTM ratios alongside $Mo_{EF}$-$U_{EF}$ cross-plots, since this approach allows samples that have been clearly affected by enhanced particulate shuttle drawdown to be identified. Hence, exclusion of such samples when calculating average Re/Mo and Mo/U ratios would potentially provide a more robust and diagnostic assessment of the different oxygen-depleted zones.

The RSTM ratio characteristics of the anoxic/euxinic ORB 1 and 2 are also entirely consistent with the insight obtained from modern environments. Here, the substantial increase in Mo/U ratios, combined with elevated $Mo_{EF}^{*}$ values and low Re/Mo ratios (Fig. 9), is clearly highly characteristic of euxinic settings, with the progressive increase in Mo/U ratios from ORB 2 to ORB 1 supporting highly euxinic conditions in the latter case, which is consistent with independent constraints from pyrite framboid size range analyses (Wignall and Newton, 1998).

### *6.5. Improved application of RSTMs as paleoredox proxies*

Most reconstructions of paleoredox conditions over recent years have focussed on identifying oxic, anoxic (often ferruginous) and euxinic water column conditions, largely because commonly used techniques such as Fe speciation are not able to distinguish different levels of oxygen depletion prior to the development of anoxia (e.g., Poulton and Canfield, 2011; Raiswell et al., 2018; Poulton, 2021). Furthermore, as demonstrated here, Mo-U covariation (e.g., Algeo and Tribovillard, 2009; Tribovillard et al., 2012) does not adequately distinguish oxic and dysoxic depositional conditions (Fig. 6). Our approach of combining RSTM EF values with RSTM ratios provides heightened, robust nuance in terms of redox reconstructions in general, particularly allowing a range of oxygen-depleted settings to be recognised, while strengthening identification of weakly and highly euxinic conditions.

Noting the general move away from defining specific threshold values for universal application to different environmental settings, due to the likelihood for inherent regional variability (see Poulton and Canfield, 2011; Algeo and Li, 2020; Poulton, 2021), we specifically stop short of defining such values here. Nevertheless, the broad ranges observed for RSTM EF$^*$ values and ratios are reasonably consistent between modern and ancient settings, thereby providing a first approximation of different redox states. However, it is the combined consideration of relative changes in enrichment factors and ratios, combined with the additional insight afforded by $Mo_{EF}$-$U_{EF}$ cross-plots, that provides the most robust redox interpretation, particularly when applied alongside independent techniques such as Fe speciation (Poulton and Canfield, 2011; Poulton, 2021), I/(Ca+Mg) ratios (Lu et al., 2010) and/or pyrite framboid size ranges (Wilkin et al., 1996; Wignall and Newton, 1998).

Based on the combined characteristics of samples from modern settings, and from the Bowland Shale and Kimmeridge Clay formations, fully oxic (>200 µM $O_2$) conditions are commonly characterized by low EF$^*$ values and low RSTM ratios, although slightly elevated $Re_{EF}^*$ values and depleted (< 1) $V_{EF}^*$ values may indicate dysoxic porewaters close to the sediment-water interface. The 90-200 µM $O_2$ zone is also marked by variable development of dysoxic porewaters close to the sediment-water interface, but in general, Re enrichments tend to be at a moderate level, giving similarly elevated Re/Mo and Re/U ratios. Weakly dysoxic settings are characterized by the additional development of higher Re/Mo ratios and moderate Mo/U ratios, but in both cases, these ratios may be impacted by enhanced drawdown of Mo via the particulate shuttle pathway, which requires consideration in terms of a $Mo_{EF}$-$U_{EF}$ cross-plot. Highly dysoxic settings may also be significantly affected by Mo drawdown via the particulate shuttle pathway, however, this redox zone is characterized by moderate average $U_{EF}^*$ and $Mo_{EF}^*$ values, and high $Re_{EF}^*$ values, resulting in high Re/Mo, Re/U and Re/V ratios.

Anoxic non-sulfidic conditions are, perhaps surprisingly, rather difficult to resolve from RSTM systematics alone, since while U enrichment factors may be somewhat elevated (see Fig. 5), there is commonly a high degree of overlap with dysoxic settings. Similarly, most other RSTM enrichment factors and ratios also show significant overlap with other redox states. However, low Re/Mo ratios alongside elevated $U_{EF}^*$ values may be considered diagnostic of anoxic conditions (Figs. 5 and 7; Table 3). In addition, recognition of anoxic non-sulfidic conditions may be achieved via Fe speciation analyses (Poulton and Canfield, 2011; Poulton, 2021), which considered alongside RSTM systematics, can provide a particularly robust indication of anoxic, non-sulfidic water column conditions (e.g., He et al., 2022; Li et al., 2024).

A particularly useful aspect of our refined evaluation of RSTM systematics is the potential ability to distinguish weakly and high euxinic conditions. Euxinia in general may be identified by high Mo/U ratios, combined with high $Mo_{EF}^*$ values and low Re/Mo ratios (Table 3; Fig. 5; Fig. 9), but particularly elevated Mo/U ratios and $Mo_{EF}^*$ values are diagnostic of highly euxinic conditions (Fig. 7). One caveat here is that a low level of Mo resupply to a particular basin may result in depleted Mo drawdown, even under highly euxinic conditions, as appears to occur in the Kyllaren Fjord (Noordmann et al., 2015) and to an extent in the Black Sea (Algeo and Lyons, 2006). In addition, global RSTM drawdown under widespread anoxia/euxinia may also result in limited enrichment of Mo in the sediments (e.g., Algeo, 2004; Goldberg et al., 2016). Nevertheless, very high Mo/U ratios and $Mo_{EF}^{*}$ ratios, combined with low Re/Mo ratios, appear to provide a robust indication of highly euxinic conditions.

## 7. Conclusions

Our RSTM datasets from modern and ancient environments provide new insight into the utility of RSTMs for reconstructing ancient redox conditions. Modern settings have average $U_{EF}^{*}$ values that gradually increase from oxic to euxinic conditions, but this parameter alone does not adequately distinguish dysoxic to euxinic conditions due to a high degree of overlap between each redox field (Fig. 11). Similarly, enhanced Mo accumulation may occur under dysoxic, anoxic non-sulfidic and euxinic depositional conditions, due to drawdown either via a particulate shuttle mechanism under non-euxinic conditions (e.g., Arabian Sea, Peru margin) or due to water column euxinia (e.g., Black Sea). However, these pathways may be distinguished by $Mo_{EF}^{*}$-$U_{EF}^{*}$ cross-plots, thus aiding redox interpretations. Rhenium accumulation in oxic and dysoxic settings is highly variable, and is regulated by oxygen depletion in porewaters, which is related to organic carbon depositional fluxes and sedimentation rates. Under anoxic and euxinic conditions, $Re_{EF}^{*}$ values are also rather variable, with significant overlap with highly dysoxic settings, thus limiting robust redox reconstructions based Re enrichment factors alone (Fig. 11). Vanadium enrichments are highly dependent on porewater redox conditions, with enrichments commonly occurring across a wide spectrum of redox conditions.

Redox sensitive trace metal ratios provide heightened insight into paleoredox conditions. In modern settings, Re/Mo ratios are commonly high under dysoxic conditions and low under anoxic to euxinic conditions, with particularly low ratios occurring under euxinic conditions (Fig. 11). An overall progressive increase in Re/U and Re/V values from oxic to dysoxic conditions highlights the utility of these ratios for providing unprecedented insight into the degree of oxygen depletion in ancient marine settings (Fig. 11). Mo/U ratios are persistently low under oxic conditions, but elevated ratios may occur under dysoxic and euxinic conditions (Fig. 11). However, $Mo_{EF}^{*}$-$U_{EF}^{*}$ cross-plots can again distinguish these drawdown pathways, and euxinic conditions may also be identified by the combined consideration of Re/Mo ratios.

Our new data from the Bowland Basin and the Kimmeridge Clay Formation show a high degree of consistency with modern settings. The Bowland Basin data are particularly useful for demonstrating how weakly and strongly euxinic conditions may be distinguished using Mo/U ratios (Fig. 11). This approach should prove useful in future studies attempting to track the Mo isotope composition of ancient seawater, which requires quantitative drawdown of Mo under strongly euxinic conditions. Another important finding from the Bowland Shale study, is that weakly dysoxic conditions may be identified by high Re/Mo, moderate Re/U and low Re/V ratios. The Kimmeridge Clay RSTM data allow an independent calibration relative to the paleontological record, via the determination of oxygen-restricted biofacies. This approach demonstrates how RSTM ratios, particularly when combined with $Mo_{EF}^{*}$-$U_{EF}^{*}$ cross-plots, may be used to reconstruct different degrees of oxygen depletion under dysoxic conditions.

Consequently, our approach demonstrates how a combination of RSTM ratios, enrichment factors and $Mo_{EF}$-$U_{EF}$ cross-plots, particularly when applied alongside independent paleoredox indicators such as Fe speciation, I/(Ca+Mg) ratios and/or pyrite framboid size ranges, can be used to reconstruct a broad spectrum of redox conditions during deposition of ancient mudrocks. Fully oxic settings (> 200 µM $O_2$) record low RSTM ratios and $EF^*$ values, while slight increases in Re/Mo and Re/U ratios indicate a subtle decline in $O_2$ concentrations (90-200 µM). A transition from weakly (30-90 µM $O_2$) to highly (<30 µM $O_2$) dysoxic conditions may be revealed by increases in Re/Mo, Re/U and Re/V ratios, accompanied by RSTM $EF^*$ values that only become notably enriched under highly dysoxic conditions. Water column anoxia is indicated by enhanced $U_{EF}^*$ values and a sharp decline in Re/Mo ratios. Euxinic conditions are marked by high Mo/U, low Re/U and very low Re/Mo ratios, alongside high $Mo_{EF}^*$ values. Additionally, the increasing intensity of euxinia can be identified by exceptionally high Mo/U and $Mo_{EF}^*$ values. While further detailed studies of RSTM systematics under different redox conditions in the modern environment are clearly required, our new insight suggests that when applied appropriately and with consideration for potential local environmental controls, a hitherto unprecedented level of insight into paleodepositional redox conditions may be achieved.

## CRediT authorship contribution statement

Sen Li: Conceptualization, Writing - Original Draft, investigation; Paul Wignall: Writing - Review & Editing; Simon Poulton: Conceptualization, Writing - Review & Editing.

## Acknowledgements

We thank Jeffrey Peakall, Kaixuan Ji, Yafang Song, Zhen Xu and Yuxuan Wang for help with fieldwork in the Bowland Basin. This study was funded by a University of Leeds research training grant to SL. SWP acknowledges support from NERC grant NE/T008458/1, and from the World Research Hub (WRH) Program of the International Research Frontiers Initiative, Tokyo Institute of Technology. We thank George Helz and an anonymous reviewer for their constructive comments during the review process.

## Appendix A. Supplementary material

Geochemical data from Tory Log Clough (TLC) and Dinckley Hall (DH) section in Bowland Basin and from Kimmeridge Clay Formation.

## References

Akintomide, O.A., Adebayo, S., Horn, J.D., Kelly, R.P., Johannesson, K.H., 2021. Geochemistry of the redox-sensitive trace elements molybdenum, tungsten, and rhenium in the euxinic porewaters and bottom sediments of the Pettaquamscutt River estuary, Rhode Island. Chemical Geology, 584, 120499.

Algeo, T.J., 2004. Can marine anoxic events draw down the trace element inventory of seawater? Geology, 32(12), 1057-1060.

Algeo, T.J., Li, C., 2020. Redox classification and calibration of redox thresholds in sedimentary systems. Geochimica et Cosmochimica Acta, 287, 8-26.

Algeo, T.J., Lyons, T.W., 2006. Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions. Paleoceanography, 21(1).

Algeo, T.J., Tribovillard, N., 2009. Environmental analysis of paleoceanographic systems based on molybdenum–uranium covariation. Chemical Geology, 268(3-4), 211-225.

Anderson, J.J., Devol, A.H., 1973. Deep water renewal in Saanich Inlet, an intermittently anoxic basin. Estuarine and Coastal Marine Science, 1(1), 1-10.

Anderson, R.F., LeHuray, A.P., Fleisher, M.Q., Murray, J.W., 1989. Uranium deposition in saanich inlet sediments, vancouver island. Geochimica et Cosmochimica Acta, 53(9), 2205-2213.

Bennett, W.W., Canfield, D.E., 2020. Redox-sensitive trace metals as paleoredox proxies: A review and analysis of data from modern sediments. Earth Science Reviews, 204, 103175.

Bertine, K.K., Turekian, K.K., 1973. Molybdenum in marine deposits. Geochimica et Cosmochimica Acta, 37(6), 1415-1434.

Böning, P., Brumsack, H.J., Böttcher, M.E., Schnetger, B., Kriete, C., Kallmeyer, J., Borchers, S.L., 2004. Geochemistry of Peruvian near-surface sediments. Geochimica et Cosmochimica acta, 68(21), 4429-4451.

Borchers, S.L., Schnetger, B., Böning, P., Brumsack, H.J., 2005. Geochemical signatures of the Namibian diatom belt: Perennial upwelling and intermittent anoxia. Geochemistry, Geophysics, Geosystems, 6(6).

Breit, G.N., Wanty, R.B., 1991. Vanadium accumulation in carbonaceous rocks: a review of geochemical controls during deposition and diagenesis. Chemical Geology, 91(2), 83-97.

Brüchert, V., Jørgensen, B.B., Neumann, K., Riechmann, D., Schlösser, M., Schulz, H., 2003. Regulation of bacterial sulfate reduction and hydrogen sulfide fluxes in the central Namibian coastal upwelling zone. Geochimica et Cosmochimica Acta, 67(23), 4505-4518.

Calvert, S.E., Piper, D.Z., Thunell, R.C., Astor, Y., 2015. Elemental settling and burial fluxes in the Cariaco Basin. Marine Chemistry, 177, 607-629.

Canfield, D.E., Raiswell, R., Bottrell, S.H., 1992. The reactivity of sedimentary iron minerals toward sulfide. American Journal of Science, 292(9), 659-683.

Canfield, D.E., Thamdrup, B.O., 2009. Towards a consistent classification scheme for geochemical environments, or, why we wish the term ‘suboxic’ would go away. Geobiology, 7(4), 385-392.

Chen, K., Walker, R. J., Rudnick, R. L., Gao, S., Gaschnig, R. M., Puchtel, I. S., Hu, Z. C. 2016. Platinum-group element abundances and Re–Os isotopic systematics of the upper continental crust through time: Evidence from glacial diamictites. Geochimica et Cosmochimica Acta, 191, 1-16.

Colodner, D.C., Boyle, E.A., Edmond, J.M., Thomson, J., 1992. Post-depositional mobility of platinum, iridium and rhenium in marine sediments. Nature, 358(6385), 402-404.

Cox, B.M., Gallois, R.W., 1981. The stratigraphy of the Kimmeridge Clay of the Dorset type area and its correlation with some other Kimmeridgian successions. Report of the Institute of Geological Sciences, 80/4, 44 pp.

Crusius, J., Calvert, S., Pedersen, T., Sage, D., 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. Earth and Planetary Science Letters, 145(1-4), 65-78.

Cui, M., Luther III, G. W., Gomes, M. 2023. Constraining the major pathways of vanadium incorporation into sediments underlying natural sulfidic waters. Geochimica et Cosmochimica Acta, 359, 148-164.

Dahl, T.W., Connelly, J.N., Li, D., Kouchinsky, A., Gill, B.C., Porter, S., Bizzarro, M., 2019. Atmosphere– ocean oxygen and productivity dynamics during early animal radiations. Proceedings of the National Academy of Sciences, 116(39), 19352-19361.

Dellwig, O., Leipe, T., März, C., Glockzin, M., Pollehne, F., Schnetger, B., Yakushev, E., Böttcher, M., Brumsack, H.J., 2010. A new particulate Mn–Fe–P-shuttle at the redoxcline of anoxic basins. Geochimica et Cosmochimica Acta, 74(24), 7100-7115.

Doyle, K.A., Poulton, S.W., Newton, R.J., Podkovyrov, V.N., Bekker, A., 2018. Shallow water anoxia in the Mesoproterozoic ocean: Evidence from the Bashkir Meganticlinorium, Southern Urals. Precambrian Research, 317, 196-210.

Emerson, S.R., Huested, S.S., 1991. Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. Marine Chemistry, 34(3-4), 177-196.

Emmings, J.F., Poulton, S.W., Vane, C.H., Davies, S.J., Jenkin, G.R., Stephenson, M.H., Moss-Hayes, V., 2020. A Mississippian black shale record of redox oscillation in the Craven Basin, UK. Palaeogeography, palaeoclimatology, palaeoecology, 538, 109423.

Erickson, B.E., Helz, G.R., 2000. Molybdenum (VI) speciation in sulfidic waters: stability and lability of thiomolybdates. Geochimica et Cosmochimica Acta, 64(7), 1149-1158.

Gawthorpe, R.L., 1986. Sedimentation during carbonate ramp-to-slope evolution in a tectonically active area: Bowland Basin (Dinantian), northern England. Sedimentology, 33(2), 185-206.

Goldberg, T., Poulton, S.W., Wagner, T., Kolonic, S., Rehkämper, M., 2016. Molybdenum drawdown during Cretaceous Oceanic Anoxic Event 2. Earth and Planetary Science Letters. 440. 81-91.

Goswami, V., Singh, S.K., Bhushan, R., 2012. Dissolved redox sensitive elements, Re, U and Mo in intense denitrification zone of the Arabian Sea. Chemical Geology, 291, 256-268.

Haase, F. J., Vessey, C. J., Sekine, R., Doriean, N. J., Welsh, D. T., Otte, J. A., Bennett, W. W. 2024. Reductive sorption of vanadium by iron monosulfide in seawater. Chemical Geology, 649, 121983.

Haase, F. J., Vessey, C. J., Sekine, R., Welsh, D., Hamilton, J., Wang, Y., Bennett, W. W. 2023. Reductive sorption of vanadium by green rust in seawater. Geochimica et Cosmochimica Acta, 361, 171-182.

Häusler, K., Dellwig, O., Schnetger, B., Feldens, P., Leipe, T., Moros, M., Arz, H.W., 2018. Massive Mn carbonate formation in the Landsort Deep (Baltic Sea): Hydrographic conditions, temporal succession, and Mn budget calculations. Marine Geology, 395, 260-270.

He, T., Wignall, P.B., Newton, R.J., Atkinson, J.W., Keeling, J.F., Xiong, Y., Poulton, S.W., 2022. Extensive marine anoxia in the European epicontinental sea during the end-Triassic mass extinction. Global and Planetary Change, 210, 103771.

He, Z., Clarkson, M.O., Andersen, M.B., Archer, C., Sweere, T.C., Kraal, P., Guthausere, A., Huang, F., Vance, D., 2021. Temporally and spatially dynamic redox conditions on an upwelling margin: The impact on coupled sedimentary Mo and U isotope systematics, and implications for the Mo-U paleoredox proxy. Geochimica et Cosmochimica Acta, 309, 251-271.

Helz G.R., 2022. The Re/Mo redox proxy reconsidered. Geochimica et Cosmochimica Acta, 317, 507-22.

Helz, G.R., Dolor, M.K., 2012. What regulates rhenium deposition in euxinic basins? Chemical Geology, 304, 131-141.

Helz, G.R., Miller, C.V., Charnock, J.M., Mosselmans, J.F.W., Pattrick, R.A.D., Garner, C.D., Vaughan, D.J., 1996. Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. Geochimica et Cosmochimica Acta, 60(19), 3631-3642.

Kendall, B., 2021. Recent advances in geochemical paleo-oxybarometers. Annual Review of Earth and Planetary Sciences, 49(1), 399-433.

Kendall, B., Reinhard, C.T., Lyons, T.W., Kaufman, A.J., Poulton, S.W., Anbar, A.D., 2010. Pervasive oxygenation along late Archaean ocean margins. Nature Geoscience, 3(9), 647-652.

Klinkhammer, G.P., Palmer, M.R., 1991. Uranium in the oceans: where it goes and why. Geochimica et Cosmochimica Acta, 55(7), 1799-1806.

Koide, M., Hodge, V.F., Yang, J.S., Stallard, M., Goldberg, E.G., Calhoun, J., Bertine, K.K., 1986. Some comparative marine chemistries of rhenium, gold, silver and molybdenum. Applied Geochemistry, 1(6), 705-714.

Kossack, M., Scholz, F., Anderson, C. H., Vosteen, P., Su, C. C., Mohrholz, V., Zabel, M. 2023. Sedimentary molybdenum and uranium cycling under seasonally contrasting redox conditions on the Namibian Shelf. Geochimica et Cosmochimica Acta, 358, 174-191.

Krewer, C., Poulton, S.W., Newton, R.J., März, C., Mills, B.J., Wagner, T., 2024. Controls on the Termination of Cretaceous Oceanic Anoxic Event 2 in the Tarfaya Basin, Morocco. American Journal of Science, 324, 11.

Lachkar, Z., Gruber, N. 2012. A comparative study of biological production in eastern boundary upwelling systems using an artificial neural network. Biogeosciences, 9(1), 293-308.

Li, S., Wignall, P.B., Poulton, S.W., Hedhli, M., Grasby, S.E., 2022. Carbonate shutdown, phosphogenesis and the variable style of marine anoxia in the late Famennian (Late Devonian) in western Laurentia. Palaeogeography, Palaeoclimatology, Palaeoecology, 589, 110835.

Li, S., Wignall, P.B., Xiong, Y., Poulton, S.W., 2024. Calibration of redox thresholds in black shale: Insight from a stratified Mississippian basin with warm saline bottom waters. Geological Society of America Bulletin, 136(3-4), 1266-1286.

Lu, Z., Jenkyns, H.C., Rickaby, R.E., 2010. Iodine to calcium ratios in marine carbonate as a paleo-redox proxy during oceanic anoxic events. Geology, 38(12), 1107-1110.

Lüschen, H., 2004. Vergleichende anorganisch-geochemische Untersuchungen an phanerozoischen $C_{org}$-reichen Sedimenten: Ein Beitrag zur Charakterisierung ihrer Fazies (Doctoral dissertation, Universität Oldenburg).

McLennan, S.M., 2001, Relationships between the trace element composition of sedimentary rocks and upper continental crust: Geochemistry, Geophysics, Geosystems, v. 2, https://doi.org/10.1029/2000GC000109.

Morford, J.L., Emerson, S., 1999. The geochemistry of redox sensitive trace metals in sediments. Geochimica et Cosmochimica Acta, 63(11-12), 1735-1750.

Morford, J.L., Emerson, S.R., Breckel, E.J., Kim, S.H., 2005. Diagenesis of oxyanions (V, U, Re, and Mo) in pore waters and sediments from a continental margin. Geochimica et Cosmochimica Acta, 69(21), 5021-5032.

Morford, J.L., Martin, W.R., Carney, C.M., 2012. Rhenium geochemical cycling: Insights from continental margins. Chemical Geology, 324, 73-86.

Myers, K.J., Wignall, P.B., 1987. Understanding Jurassic organic-rich mudrocks—new concepts using gamma-ray spectrometry and palaeoecology: examples from the Kimmeridge Clay of Dorset and the Jet Rock of Yorkshire. Marine clastic sedimentology: Concepts and case studies, 172-189.

Nägler, T.F., Neubert, N., Böttcher, M.E., Dellwig, O., Schnetger, B., 2011. Molybdenum isotope fractionation in pelagic euxinia: Evidence from the modern Black and Baltic Seas. Chemical Geology, 289(1-2), 1-11.

Nameroff, T.J., Balistrieri, L.S., Murray, J.W., 2002. Suboxic trace metal geochemistry in the eastern tropical North Pacific. Geochimica et Cosmochimica Acta, 66(7), 1139-1158.

Neubert, N., Nägler, T.F., Böttcher, M.E., 2008. Sulfidity controls molybdenum isotope fractionation into euxinic sediments: Evidence from the modern Black Sea. Geology, 36(10), 775-778.

Noordmann, J., Weyer, S., Montoya-Pino, C., Dellwig, O., Neubert, N., Eckert, S., Paetzel, M., Böttcher, M.E., 2015. Uranium and molybdenum isotope systematics in modern euxinic basins: Case studies from the central Baltic Sea and the Kyllaren fjord (Norway). Chemical Geology, 396, 182-195.

Partin, C., Bekker, A., Planavsky, N.J., Scott, C.T., Gill, B.C., Li, C., Podkovyrov, V., Maslov, A., Konhauser, K., Lalonde, S.V., Love, G., Poulton, S.W., Lyons, T.W., 2013. Large-scale fluctuations in Precambrian atmospheric and oceanic oxygen levels from the record of U in shales. Earth and Planetary Science Letters, 369, 284-293.

Paul, K. M., Hermans, M., Jokinen, S. A., Brinkmann, I., Filipsson, H. L., Jilbert, T. 2023a. Revisiting the applicability and constraints of molybdenum and uranium-based paleo redox proxies: comparing two contrasting sill fjords. Biogeosciences, 2023, 1-39.

Paul, K. M., van Helmond, N. A., Slomp, C. P., Jokinen, S. A., Virtasalo, J. J., Filipsson, H. L., Jilbert, T. 2023b. Sedimentary molybdenum and uranium: Improving proxies for deoxygenation in coastal depositional environments. Chemical Geology, 615, 121203.

Poulton, S.W., 2021. The Iron Speciation Paleoredox Proxy. Elements in Geochemical Tracers in Earth System Science, Cambridge University Press, 1-24.

Poulton, S.W., Canfield, D.E. 2011. Ferruginous conditions: a dominant feature of the ocean through Earth's history. Elements,7(2), 107-112.

Poulton, S.W., Krom, M.D., Raiswell, R., 2004. A revised scheme for the reactivity of iron (oxyhydr) oxide minerals towards dissolved sulfide. Geochimica et cosmochimica acta, 68(18), 3703-3715.

Raiswell, R., Canfield, D.E., 1998. Sources of iron for pyrite formation in marine sediments. American Journal of Science, 298(3), 219-245.

Raiswell, R., Hardisty, D.S., Lyons, T.W., Canfield, D.E., Owens, J.D., Planavsky, N.J., Poulton, S.W., Reinhard, C.T., 2018. The iron paleoredox proxies: A guide to the pitfalls, problems and proper practice. American Journal of Science, 318(5), 491-526.

Raiswell, R., Newton, R., Wignall, P.B., 2001. An indicator of water-column anoxia: resolution of biofacies variations in the Kimmeridge Clay (Upper Jurassic, UK). Journal of Sedimentary Research, 71(2), 286-294.

Ravizza, G., Turekian, K.K., Hay, B.J., 1991. The geochemistry of rhenium and osmium in recent sediments from the Black Sea. Geochimica et Cosmochimica Acta, 55(12), 3741-3752.

Robbins, L.J., Lalonde, S.V., Planavsky, N.J., Partin, C.A., Reinhard, C.T., Kendall, B., Scott, C., Hardisty, D., Gill, B., Alessi, D., Dupont, C., Saito, M., Crowe, S., Poulton, S., Bekker, A., Lyons, T., Konhauser, K., 2016. Trace elements at the intersection of marine biological and geochemical evolution. Earth Science Reviews, 163, 323-348.

Sánchez-Roda, A., Wignall, P.B., Xiong, Y., Poulton, S.W., 2024. Redox changes in the Iapetus Ocean during the Late Ordovician extinction crises. Journal of the Geological Society, 181(5), jgs2023-195.

Schobben, M., Foster, W.J., Sleveland, A.R., Zuchuat, V., Svensen, H.H., Planke, S., Bond, DPG., Marcelis, F., Newton, R., Wignall P.B., Poulton, S.W., 2020. A nutrient control on marine anoxia during the end-Permian mass extinction. Nature Geoscience, 13(9), 640-646.

Scholz, F., Siebert, C., Dale, A.W., Frank, M., 2017. Intense molybdenum accumulation in sediments underneath a nitrogenous water column and implications for the reconstruction of paleo-redox conditions based on molybdenum isotopes. Geochimica et Cosmochimica Acta, 213, 400-417.

Song, Y., Bowyer, F.T., Mills, B. J., Merdith, A.S., Wignall, P.B., Peakall, J., Shuichang, Z., Xiaomei, W., Huajian, W., Canfield, D., Shields, G., Poulton, S.W. 2023. Dynamic redox and nutrient cycling response to climate forcing in the Mesoproterozoic ocean. Nature Communications, 14(1), 6640.

Sperling, E.A., Boag, T.H., Duncan, M.I., Endriga, C.R., Marquez, J.A., Mills, D. B., Monarrez, P.M., Sclafani, J.A., Stockey, R.G., Payne, J. L., 2022. Breathless through time: oxygen and animals across Earth's history. The Biological Bulletin, 243(2), 184-206.

Taylor, S.R., McLennan, S.M., 1985. The continental crust: its composition and evolution. United States.

Tribovillard, N., Algeo, T.J., Baudin, F., Riboulleau, A.J., 2012. Analysis of marine environmental conditions based on molybdenum–uranium covariation—Applications to Mesozoic paleoceanography. Chemical Geology, 324, 46-58.

Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. Chemical Geology, 232(1-2), 12-32.

Tribovillard, N.P., Desprairies, A., Lallier-Vergès, E., Bertrand, P., Moureau, N., Ramdani, A., Ramanampisoa, L., 1994. Geochemical study of organic-matter rich cycles from the Kimmeridge Clay Formation of Yorkshire (UK): productivity versus anoxia. Palaeogeography, Palaeoclimatology, Palaeoecology, 108(1-2), 165-181.

Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the earth's crust. Geological society of America bulletin, 72(2), 175-192.

Van der Weijden, C.H., 2002. Pitfalls of normalization of marine geochemical data using a common divisor. Marine Geology, 184(3-4), 167-187.

Vollebregt, A., van Helmond, N. A., Pit, S., Kraal, P., Slomp, C.P. 2023. Trace metals as a redox proxy in Arabian Sea sediments in and below the oxygen minimum zone. Chemical Geology, 618, 121300.

Vorlicek, T.P., Kahn, M. D., Kasuya, Y., Helz, G.R., 2004. Capture of molybdenum in pyrite-forming sediments: role of ligand-induced reduction by polysulfides. Geochimica et Cosmochimica Acta, 68(3), 547-556.

Wang, Y., Wignall, P.B., Xiong, Y., Loydell, D.K., Peakall, J., Baas, J.H., Mills B.J.W., Poulton, S.W., 2024. Marine redox dynamics and biotic response to the mid-Silurian Ireviken Extinction Event in a mid-shelf setting. Journal of the Geological Society, 181(4), jgs2023-155.

Wanty, R.B., Goldhaber, M.B., 1992. Thermodynamics and kinetics of reactions involving vanadium in natural systems: Accumulation of vanadium in sedimentary rocks. Geochimica et Cosmochimica Acta, 56(4), 1471-1483.

Wignall, P.B. 1990. Benthic palaeoecology of the late Jurassic Kimmeridge Clay of England. The Palaeontological Association, Special Papers in Palaeontology, 43, 1-74.

Wignall, P.B., 1994. Black shales. Geology and Geophysics Monograph Series 30, Oxford University Press, 136 pp

Wignall, P.B., Hallam, A., 1991. Biofacies, stratigraphic distribution and depositional models of British onshore Jurassic black shales. Geological Society, London, Special Publications, 58(1), 291-309.

Wignall, P.B., Myers, K.J. 1988. Interpreting benthic oxygen levels in mudrocks: a new approach. Geology, 16(5), 452-455.

Wignall, P.B., Newton, R.J., 1998. Pyrite framboid diameter as a measure of oxygen deficiency in ancient mudrocks. Ameircan Journal of Science, 298, 537-552.

Wilkin, R.T., Barnes, H.L., Brantley, S.L., 1996. The size distribution of framboidal pyrite in modern sediments: an indicator of redox conditions. Geochimica et Cosmochimica Acta, 60(20): 3897-3912.

Yamashita, Y., Takahashi, Y., Haba, H., Enomoto, S., Shimizu, H., 2007. Comparison of reductive accumulation of Re and Os in seawater–sediment systems. Geochimica et Cosmochimica Acta, 71(14), 3458-3475.

Zhang, B., Yao, S., Poulton, S.W., Wignall, P.B., He, T., Xiong, Y., Hu, W. 2023. Widespread marine euxinia along the western Yangtze Platform caused by oxygen minimum zone expansion during the Capitanian mass extinction. Global and Planetary Change, 230, 104273.

Živković, I., Bura-Nakić, E., Knežević, L., Helz, G.R., 2023. Deposition of Mo, Re and U under contrasting redox conditions; assessment of the [Re/Mo] sw redox proxy. Geochimica et Cosmochimica Acta, 359, 176-190.