**Molybdenum as a paleoredox proxy: past, present, and future**

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**Abstract:** Molybdenum (Mo) is a widely used trace metal for investigating redox conditions. However, traditional methods for analysis of the Mo paleoproxy still have room for improvement by combining new and cross disciplinary geochemical techniques. In this manuscript, we propose the refinement of Mo geochemistry within aquatic systems, ancient rocks, and modern sediments by applying molecular geochemistry (a systematic combination of concentration, isotope ratio, elemental mapping, and speciation analyses). There still, however, remain unanswered questions that concentration and bulk isotopic analysis cannot specially answer in a nuanced way. Specifically the role of intermediate sulfide concentrations governing Mo behavior below the so called switch-point (sulfide XXX), and dominant Mo sequestration pathways in low oxygen conditions. The aim of this work is to 1) aid and improve the breadth of Mo paleoproxy interpretations and 2) address outstanding research gaps concerning Mo systematics (cycling, partitioning, sequestration, etc.). The Mo paleoproxy continues to provide potential to solve ever complex research questions, while identifying the impacts varied redox conditions on geochemistry. However, we conclude that additional progress regarding Mo paleo proxy interpretations and reconstruction can be achieved using contemporary analytical recommendations through molecular geochemical.

**1. Introduction**

Molybdenum (Mo, Z = 42, Ar = 94.95 g mol-1) has been recognized as a versatile trace metal for investigating paleoredox settings ever since its chemical behavior in natural systems was described (*e.g.,* Goldschmidt, 1954). It has a high degree of chemical reactivity–both solid and dissolved phases–across a wide range of redox states leaving distinct geochemical signatures related to the depositional environment (Helz et al., 1996). As a paleoredox proxy, Mo has contributed to major breakthroughs regarding the ancient ocean and atmospheric chemistry of the early Earth (e.g., Anbar et al., 2007). Yet, despite considerable effort, the specifics on Mo cycling between dissolved, particulate, and solid phases are still controversial and actively debated (Chappaz et al., 2014, Wagner et al., 2017, Dahl et al., 2017, Vorlicek et al., 2018, Helz & Vorlicek, 2019). Molybdenum is widely distributed across the surface of the Earth, occurring in trace amounts within the crust, while juxtaposed as a highly concentrated transition metal in the ocean (Collier, 1985). It occupies a large range of oxidation states (-IV to VIII) with IV, VI most commonly found on the Earth’s surface. Additionally, Mo has seven naturally occurring stable isotopes (A ~ 92, 94, 95, 96, 97, 98, 100) with relatively similar abundances (*i.e.*, ~10–25%). In the lithosphere, Mo can be concentrated up to weight percent in ore porphyry deposits, igneous bodies, magma contacts, or residual melts (Fig. 1). However, the disseminated average upper crustal (non-ore deposits) concentrations of Mo range from 1 to 3 ppm and are associated with neoformation of solid phases minerals such as Powellite (CaMo(VI)O4), Wulfenite (PbMo(VI)O4), or weathering products of Molybdenite (Mo(IV)S2) (Ross & Sussman, 1955, Turekian & Wedepohl, 1961; Wedepohl, 1971; Bertine & Turekian, 1973; Erickson, 1973; Emerson and Huested, 1991). In the hydrosphere, Mo is supplied by oxidative weathering and hydrolysis of primary minerals (e.g., Mo(IV)S2), to form the highly soluble—in pH 6 to 8 waters—oxyanion molybdate (Mo(VI)O42-). In riverine and lacustrine systems total molybdenum (Σ[Mo]) averages ~5–10 nM; with a range in some cases up to ~80 nM (Miller et al., 2001; Chappaz et al., 2008; Rahaman et al., 2010; Reimann & de Caritat, 2012). Across the oxygenated oceans Mo is generally ubiquitous (~105 nM) with an average residence time of ~0.44 to 0.8 Ma (Fig. 1) (Collier, 1985; Miller et al., 2011; Nakagawa et al., 2012). The distinct concentration contrast of solid phase crustal Σ[Mo] and long-lived aqueous phase (Σ{Mo}) has fundamental redox and pH interpretations especially when Σ[Mo] is enriched (>> 1 ppm) in modern sediments or in the geological record. As a paleoredox proxy Mo has proven to be an invaluable “forensic” tool for geochemists, especially to identify strongly reducing episodes in sedimentary strata. Characterizing its chemical behavior in rocks, sediments, and pore waters has helped define the chemical composition of earth’s early oceans (*e.g.,* Lyons et al., 2009, Chappaz et al., 2017), identify changes in atmospheric oxygen concentration (*e.g.,* Lyons et al., 2014), measure pervasiveness of oceanic redox conditions and total sulfide (ΣS(-II)) (*e.g.,* Adelson et al., 2001), and understand early ocean productivity during the proliferation of multicellular life (*e.g.,* Anbar & Knoll, 2002). Additionally, the study of natural Mo reservoirs has significantly advanced the fields of biogeochemistry and astrobiology, in part because Mo is essential for life. Nitrogen fixation and biological nitrate reduction rely on Mo as a co-factor in nitrogenase and nitrate reductase enzymes. Both enzymes are critical to the nitrogen cycle and some research suggests could be responsible for the first stages life’s diversity around 2.1 Ga (Glass et al., 2009, Boyd et al., 2011). Interestingly, Reinhard et al. (2013) suggest that Mo enrichment in rocks from sulfidic depositional environments across stable and long timescales (e.g., mid-Proterozoic), reflect Mo–N colimitation in the surface ocean. Their model implies a strong control on carbon and oxygen cycling *via* “bioinorganic feedbacks” related to redox sensitive metals (i.e., Mo) and therefore highly influential but small seafloor regions could control biological cycling (Reinhard et al., 2013).

Until recently the roles of organic matter (OM) associations and microbiological interactions as controls on Mo behaviour have been difficult to quantify, compared to Mo-mineral associations (Wichard et al., 2009, Dahl et al., 2017, Wagner et al., 2017, King et al., 2018; Dickson et al., 2019). However, in highly productive systems OM associations appear to have potential as a significant contributor to Mo enrichment. Molybdenum-mineral associations, however, have long been recognized as clear indicator of redox setting when investigating Mo both isotopic signature and chemical composition (Helz et al., 1996, Tribovillard et al., 2006; Arnold et al., 2004; Chappaz et al., 2014; Scholz et al., 2017). For example, Scott et al., (2008) demonstrated the inorganic enrichment of Σ[Mo] recorded ancient oceanic and atmospheric redox history in shales and indicated an increase in oxidative weathering driving Mo to the oceans where a reducing redox gradient forced burial. This and other seminal works (e.g., Siebert et al., 2005; Anbar et al., 2007; Wille et al., 2007, Wille et al., 2008) helped improve our understanding concerning such important Earth events like the age of the first ‘whiffs’ of oxygen in the atmosphere, the rise of photosynthetic life, Archean paleoredox conditions, and hydrogen sulfide induced mass extinction events ().

Isotopic signatures of Mo (δ98Mo) considerably improved the utility of the paleoproxy by adding the capability of fingerprinting mineral pathways to Mo deposition, and the ability to trace variations in the redox-sensitive burial fluxes of Mo at a global scale (Barling et al 2001; Siebert et.al 2003). Further applications have included insights to oceanic circulation, extinction events, and indirectly to large scale glaciation (*e.g.*, Pearce et al., 2008; Proemse et al., 2013; Chen et al., 2015; Kendall et al., 2015; Zhou et al., 2015; Dickson et al., 2017). Combined with concentrations, isotopic signatures have also resulted in the development of conceptual models of Mo cycling and speciation in water and sediments (e.g. Neubert et al., 2008; Helz et al., 2011; Scholz et al., 2017). Yet, many models are derived from thermodynamic predictions with few empirical validations and/or limited observations of *in situ* Mo speciation (Erickson & Helz, 2000). This has led to a disparity between model predictions and empirical results (e.g., Dahl & Wirth, 2017). To overcome this discrepancy, Mo models require empirical measurements of *in situ* speciation and associated isotopic signature to validate parameters and/or proposed reactive pathways.

Herein, we present a synthesis of the new insights into the Mo paleoproxy offered by molecular geochemistry. We explore: the environmental controls on Mo-redox coupling, the details of Mo cycling in aquatic systems, Mo enrichments in sediments, and new models for Mo cycling in natural systems. We highlight the potential strengths and limitations of molecular geochemistry, while providing an update to the latest research, methods, and techniques. Finally, we conclude with suggestions on geochemical terminology, defined molecular geochemical processes, and future research directions.

**2. Refining redox conditions**

In the following sections, Mo reactions and processes are divided into distinct redox zones within an aquatic system (i.e., water column and sediments). Thus, before continuing it is vital to provide clear definitions of terminology used to characterize these redox conditions (Fig. 2). Building upon the redox scheme proposed by Canfield and Thamdrup (2009), the term ‘oxic’ hereafter is defined as a zone where aerobic respiration is dominant, and oxygen is the major electron acceptor (Fig. 2). The term ‘suboxic’ is commonly used in geochemical literature, yet, has no definitive consensus with varied meanings across the field (Canfield and Thamdrup, 2009). Therefore, the term ‘suboxic’ will only be used as an analogy when unavoidable to indicate nitrogenous, manganous, and ferruginous zones (Fig. 2). The intermediate redox zones (i.e., nitrogenous, manganous, ferruginous) exist when nitrate (NO3-/NO), manganese (Mn(IV)/Mn(II)), and iron (Fe(III)/Fe(II)) redox couples respectively dominate, and neither O2 nor ΣS(-II) can be measured. Finally, the ‘sulfidic’ zone is defined as the region where measurable ΣS(-II) exists, after iron reduction has occurred and sulfate (SO42-) reduction dominates. In the geochemical literature, ‘anoxic’ and ‘euxinic’ are often used to describe the presence of ΣS(-II) either in the porewater or water column, respectively. Unfortunately, the term ‘anoxia’ is imprecise for the evaluation of molecular geochemistry since it can span multiple redox zones, and potentially a large range of Mo isotopic signatures. Therefore, the term ‘anoxic’ is avoided since it does not adequately describe the dominant redox chemistry at work. Similarly, ‘euxinic’ is commonly used as an aquatic condition where abundant free ΣS(-II) is present in the water column (e.g., Lyons et al., 2009) and hereafter is considered equivalent to the ‘sulfidic’ zone.

**3. Molybdenum speciation**

**3.1 The Oxic redox zone**

In the oxic environment several Mo species can be simultaneously present: as a soluble anion (*e.g.,* Mo(VI)O42-, Mo(VI)O3), as cations adsorbed to mineral surfaces (*e.g.*, Mo-FeOOH, Mo-MnOH2), as solid amorphous minerals (*e.g.*, FexMoyOH, MnxMoyOH), and associated with organic matter (*e.g.*, Mo-OM) (Fig. 3; Helz et al., 1996, Wasylenki et al., 2008, Chappaz et al., 2014, Dahl et al., 2017). Each of these species in the natural environment plays an important role in the cycling and (bio)availability of Mo to both solid and dissolved reservoirs. Dissolved Mo (Σ{Mo}(aq)) in oxic waters is often considered less reactive and conceptually only becomes a particle reactive element under strongly reducing conditions (*e.g*., Helz et al., 1996). However, Mo(VI)O42-(aq) has been demonstrated to contribute to Mo shuttling, sequestration, and overall availability of Σ{Mo}(aq) in some systems (Siebert et al., 2003, Glass et al., 2013, Smedley & Kinniburgh, 2017). For example, oxic zone adsorption to manganese (Mn) and iron (Fe) oxyhydroxides, and associations to OM can actively shuttle Mo to the sediment-water interface (SWI) where enrichment occurs often in the presence of sulfidic pore water (Scott & Lyons, 2012).

Molybdenum’s affinity to Mn occurs most commonly in fully oxic ocean basins where nodules can form. Manganese oxides occur in the water column *via* precipitation, hydrolysis, and oxidation of Mn(II)(aq) to Mn(IV)(s) (Barling & Anbar, 2004, Kendall et al., 2017), leading to Mo adsorption on Mn(IV)O2 surfaces (Wasylenki et al., 2011). This process facilitates particulate Mn-Mo shuttling to the SWI, causing a positive Mn(IV)O2 to Σ[Mo](s) correlation in suspended particles, while negatively correlating dissolved Mn and Σ{Mo}(aq) (Berrang & Grill, 1974). Manganese shuttling is most prevalent in zones of oceanic upwelling (e.g., west coast of South America) where lower oxygen content waters reach the surface, oxidizing Mn(II) species and facilitating Mn(IV)O2 precipitation and promoting Mo adsorption (Bertine & Turekian, 1973, Calvert & Price, 1983, Seralathan and Hartmann, 1986). Molybdenum can adsorb in significant amounts to Fe oxides and hydroxides such as goethite (FeO(OH)) at lower pH (*e.g.*, ≤ 6). However, this effect is more common in surficial sediments, soils, and pore waters than oceanic systems (Goldberg et al., 1996). Clay minerals (e.g., illite, smectite) can also adsorb Mo most effectively at pH 5–6 but kinetically slows to a stop at pH ≥ 8 (Goldberg et al., 1996, Goldberg & Forster, 1998).

Molybdenum mineral adsorption shuttling is well documented in low oxygen concentration ([O2](aq) < 5 µM) systems (e.g., Santa Monica Basin) where significant amounts of Mo, Fe, and Mn coexist (Shaw et al., 1990). In seasonally oxic ocean basins (e.g., Saanich Inlet) where [O2](aq)can reach 0 µM during occasional manganous to ferruginous reducing events, mineral adsorption and shuttling has been found to be a primary Mo enrichment mechanism (Crusius et al., 1996). These pathways, however, do not appear to cause a reduction of Mo (i.e., Mo(VI) → Mo(IV)) within the water column, but can initiate Mo(VI) → Mo(IV) tranisitonsin reducing pore waters and/or sediments. Isotopically, Mo mineral oxide adsorption does cause a well-documented isotopic fractionation to lower δ98Mo values, observed in both laboratory experiments and natural samples (Barling & Anbar, 2004; Reitz et al., 2007 Wasylenki et al., 2008, 2011; Goldberg et al., 2009, Kashiwabara, et al., 2011). Molybdenum and OM concentrations have been commonly observed to covary linearly together in the geologic record and are a potentially an important primary sink for sedimentary rocks (i.e., shales) and ocean sediments (Brumsack & Gieskes, 1983; Holland, 1984; Brumsack, 1986; Algeo & Lyons, 2006;). The mechanism explaining the variation of slopes related to the positive Mo-OM correlation are still poorly understood and actively debated with a variety of proposed interactions between Mo and OM or basin configurations during deposition. For example, Helz *et al.*, (2019) calculated the hypothetical influence of OM on Mo, concluding that correlations found in the geologic record are due to simultaneous OM and Mo sequestration pathway(s). These pathways act independently from each other concentrating both Mo and OM which by happenstance linearly correlate. However, laboratory-based results refute these predictions showing that Mo readily associates with organic acids (e.g., Wagner et al., 2017) and particulate OM (e.g., Dahl et al., 2017). In natural samples, Mo has been observed to associate with dissolved organic carbon (DOC) and/or low molecular weight OM (Brumsak & Gieskes, 1983; Scholz et al., 2018; Tessin et al., 2018; Greaney et al., 2020). For instance, in organic rich sections of diatomaceous sediments from Namibia, Mo is associated with fulvic and humic acids (Calvert & Morris,1977). Various explanations have been put forth to explain these Mo-OM data, ranging from Mo sorption on particulate organic matter (POM), complexation of Mo to unknown organic molecules, bonding to humic acids (e.g., Szilagyi, 1967, Nissenbaum & Swaine, 1976), or high biological productivity causing Mo(VI) reduction to Mo(V) *via* an OM electron donor (e.g., Brumsak & Gieskes, 1983). However, there is still not a consensus on the dominant mechanism(s) relating Mo to OM in sediments (Algeo & Lyons, 2006). Indeed, the sheer complexity of OM and the observed associations with Mo point to a likely multi-pathway shuttle dependent on OM type and dominant redox conditions. Isotopically, few direct measurements of natural δ98Mo from organic associations are published to date, however, results from Dickson et al., (2019) suggest a lack of fractionation from the bulk δ98Mo signal. Yet, hypothetically a Mo-OM association should lead to lower isotopic fractionation when Mo transitions to solid phase(s), similar to biological mediated fractionation (e.g., Zerkle et al., 2011; Wasylenki et al. 2007). This complicates the already intricate isotope system with possible unknown Mo-organic contributions in geologic samples (Kendall et al., 2017)

In general, burial and enrichment of Mo in oxic redox regimes is a function of both mineral and organic pathways shuttling dissolved and solid (particulate) phase Mo to the SWI. However, most literature has focused on mineral phases (*e.g.*, Mo-FeO(OH), Mo-MnO2) and not OM leading to a significant research gap. This is partly due to practical and logistic impediments to direct measurements of Mo below the SWI while preserving speciation and depositional redox state. Merely sampling pore waters can alter Mo speciation and oxidation state even under the best field circumstances by introducing atmospheric O2. Additionally, in an ideal oxic system, the top centimeters of the SWI is likely dominated by diffusive fluxes of Σ{Mo}(aq), while Mo solid phase transitions occur deeper in the sediment (Crusius et al., 1996). Attempting to capture this redox profile and original depositional conditions is problematic, since Mo below the first few centimeters of the SWI can have multiple transport or burial processes occurring at the same time.

**3.2 The nitrogenous, manganous, ferruginous redox zone(s*)***

Studies of these redox zones are limited in the literature since they are not well documented in natural samples, difficult to analyze *in situ*, and lack agreed upon methods to capture Mo speciation and oxidation state without influencing results. There is strong environmental evidence that very low, or zero bottom water oxygen ([O2](aq) < 1 µM) concentrations promote formation of measurable authigenic solid phase Mo minerals (Crusius et al., 1996). However, little data exists on water column redox zone transitions (from oxic to ferruginous) and the subsequent effect on Mo speciation (Scholz et al., 2017). In continental margin sediments with oxic water columns and small amounts of sulfide in pore waters—well below the SWI—Mo solid phase enrichments can range up one order of magnitude from crustal levels (Hardisty et al., 2018). These Mo enrichments demonstrate a reliable Mo shuttle to the SWI with sequestration enhanced by nitrogenous, manganous, ferruginous redox gradients until some sulfide is available (Scholz, et al., 2017). Furthermore, Scott & Lyons, (2012) imply that although these intermediate redox regimes are less common, they still contribute significantly to solid phase Mo concentrations. However, in a SWI profile under an oxic water column the transition across these redox regimes would account for only very thin layers (10–20 mm) of pore space where redox reactions could occur (Pederson et al., 1989, Zheng et al., 2000). In these layers, increased solubility of iron within the ferruginous zone promotes a downward flux due to Mo-mineral precipitation deeper in the sediment profile (Hardisty et al., 2018). These redox gradients might provide kinetically favorable conditions for mineral Mo co-precipitation of poorly crystalline to amorphous materials (Vorlicek et al., 2018). Furthermore, Mo-OM associations have been found in sediments deposited within these intermediate redox zones (Crusius et al., 1996). In some specialized systems organically bound Mo may be more effectively buried than mineral pathways, either through shuttling to a SWI with sulfidic pore water or becoming a OM bound sink before any sulfide mineral precipitation can occur (Dahl et al., 2017; Scott et al., 2017). In sediments the overall solubility of Σ{Mo}(aq) decreases rapidly in pore waters as oxygen is consumed and continues to decrease with depth as Σ[Mo](s) gradually increases, presumably from precipitation of authigenic solid phases. However, it is unclear if and when solid phase Mo(VI) undergoes reduction to Mo(IV) during burial or diagenesis in these systems. In several cases, Mo oxidation state has been reported as mixed between Mo(VI) and Mo(IV) with potentially intermediate redox zones during deposition (Dahl et al., 2017). It is likely that in intermediate redox zones Mo tends to remains in an oxidized state Mo(VI) and only undergoes a coordination change (e.g., tetrahedral to trigonal) promoting a solid phase precipitation as Mo solubility decreases. Once in a solid phase, Mo is more susceptible to reduction Mo(IV) especially in the presence of sulfide commonly found in pore waters below the SWI.

The difficultly of studying such redox zones stems from their sensitivity to oxygen or sulfide. To properly examine molecular geochemistry of these redox zones, collected samples need to be flash frozen at temperatures ≤ -80 °C and maintained in anoxic non-reactive (e.g., nitrogen) atmosphere to completely halt redox reactions. These methods need to be maintained consistently during sample collection, preparation and even analysis to avoid any introduced bias. Additionally, in the natural environment there are few regions that are consistently stable within these redox zones, with most localities being seasonal or existing as end members of oxic to sulfidic (Berrang & Grill, 1974). Thus, the best picture of molecular geochemistry in nitrogenous, manganous, and ferruginous redox zones is inferred from sediment core profiles when both pore water Mo and solid phase Mo can be collected, preserved, and analyzed.

**3.3 The sulfidic zone(s)**

In sulfidic redox zones Mo enrichments follow a predictable pattern depending on ΣS(-II) free in the water column and/or pore waters below the SWI (Scott and Lyons, 2012). This is generally related to an increased affinity for solid phases as solubility decreases because of Mo thiolation. Contrary to other Mo shuttles, natural sulfidic waters (pH 6–8) thermodynamically favour thiolation of dissolved Mo(VI)O42- and promote solid phase sequestration in sediments (Helz et al., 1996, Erickson & Helz, 2000, Chappaz et al., 2014). Thiomolybdates are known to easily concentrate in solid phases orders of magnitude higher than average crustal backgrounds (e.g., 10–100 ppm) via reactive pathways involving OM and sulfide mineral phases (Dahl & Wirth, 2017, Wagner et al., 2017, Chappaz et al., 2014,). Since many interpretations of Mo redox sensitivity exist within the sulfidic redox regime (e.g., Helz et al., 1996, Dahl et al., 2010, Chappaz et al., 2014), hereafter it is defined as Mo thiolation when ΣS(-II) ≥ 100 µM often coinciding with formation of sulfide mineral phases. Additionally, the Mo sulfide sensitivity is detailed in numerous studies quantifying the specifics of Mo cycling, partitioning, burial, reaction kinetics, and isotopic signature during times where water column ΣS(-II) ≥ 100 µM (Helz et al., 1996, Tribovillard et al., 2006, Scott & Lyons, 2012, Chappaz et al., 2014). This large body of research exists likely due to the ease of measuring significant (e.g., 2–10 orders of magnitude greater than crustal values) Mo enrichments in sediments and rocks, which consistently occur when ΣS(-II) ≥ 100 µM.

A common misconception of Mo(VI)O42- thiolation, is that it is accompanied by an immediate reduction of Mo(VI) to Mo(IV). Thiolation, however, only describes substitution and not a reduction reaction. Molybdenum reduction is likely promoted as solubility decreases causing solid phase formation of Mo species (Erickson & Helz, 2000). However, several studies show that Mo oxidation state is not as simplistic as previously thought (Dahl et al., 2013). Research measuring oxidation state using X-ray Absorption Fine Structure (XAFS) has demonstrated that solid phase Mo can exist in multiple oxidation states associated with different mineral phases, OM, or amorphous solids (Ardakani et al., 2016; Tessin et al., 2018; Vorlicek et al., 2018). In systems with mixed Mo oxidation states, the ratio of Mo(VI) to Mo(IV) might represent a gradient related to ΣS(-II) availability, total iron (ΣFe) availability, Mo species, and total organic carbon (TOC) content. In rare cases, Mo(V) has been reported, however, there is little evidence to suggest that Mo(V) is a stable long-lived and thermodynamically favorable state to consistently be preserved in sediments (Wang et al., 2011). In seasonally sulfidic depositional basins such as the Saanich Inlet or the Namibian Shelf, solid phase Mo enrichments and water column thiolation are well documented, however the dominant sequestration mechanism likely varies depending on the redox seasonality (Brongersma-Sanders et al., 1980). This also occurs in so called ‘weakly euxinic’ zones (20 µM ≤ ΣS(-II) ≤ 100 µM) where intermediate thiolated species can dominate and Mo is enriched in solid phases (Berrang & Grill, 1974).

**4. Molybdenum isotopes**

Molybdenum isotopes can characterize the end-member compositions of Mo adsorbed or bound to oxic minerals (e.g. birnessite or haematite), with values ~2.2–3 ‰ lower than seawater (Barling and Anbar, 2004; Wasylenki et al., 2007; Goldberg et al., 2009). In sulfidic redox regimes when ΣS(-II) ≥ 100 µM, heavy Mo isotopic signatures in sediments are interpreted to represent the thiolation of dissolved Mo towards an estimated equilibrium fractionation for tetrathiomolybdate (MoS42-) approaching ~0.5 ‰ lower than coeval basin seawater (Nägler et al., 2011). In practice, the rapid sequestration of dissolved Mo into sediments after thiolation leads to near quantitative removal in some settings and a sedimentary isotope composition approaching that of open-ocean seawater (today ~ 2.3 ‰).

Open-ocean sulfidic sediments have compositions approaching seawater but are usually offset by ~0.5–0.9 ‰ due to non-quantitative removal (Poulson-Brucker et al., 2009; Hutchings et al., 2020; Sweere et al., 2021), or mixing with isotopically lighter ferruginous or manganiferous sedimentary phases (e.g. Siebert et al., 2006; Scholz et al., 2017).

However, the interpretation of Mo isotope signatures is complicated in intermediate redox zones (nitrogenous, manganous, ferruginous, weakly sulfidic) when oxygen ([O2](aq) ≤ 5 µM) and free sulfide (ΣS(-II) ≤ 100 µM) are low. In these settings, equilibrium fractionation signatures of intermediate thiomolybdates (MoOxS4-x2-) are several per mil lower than seawater when preserved (Tossell, 2005; Azrieli-Tal et al., 2014). Sedimentary Mo isotopes in ferruginous or nitrogenous conditions are further complicated by mixing of sulfide, ferruginous and manganiferous phases which lead to highly variable isotopic signatures (e.g., -1‰ to 2.3‰) (Poulson-Brucker et al., 2009; Hutchings et al., 2020; Sweere et al., 2021). However, the lack of speciation data for Mo buried in intermediate redox-state conditions makes the interpretation of isotopic signatures difficult. Depending on the dominant thiolated species, isotopic signature of dissolved Mo could be vastly different from typical seawater values especially in systems with ΣS(-II) ≤ 100 µM as specific species are preferentially sequestered to solid phases over others. Additionally, the already difficult δ98Mo system has an unknown isotopic contribution from Mo-OM associations (Kendall et al., 2017), and might be affected by mixing with allochthanous organic rich fluids following geological burial (e.g., Ardakani et al., 2020). Within the oxic setting the well-known Mn–Fe-oxyhydroxide shuttle can accelerate enrichment of Mo into seafloor sediments (Algeo & Tribovillard, 2009). However, as Mo is supplied to the sediments if the redox setting at or below the sediment water interface is sufficiently sulfidic (e.g., beyond the switch-point Helz et al., 1996) Mo is removed from the aqueous phase into the solid phase and generally not recycled in the water column altering its isotopic profile. Transition between dissolved and solid phases of Mo indeed contribute to isotope fractionation as observed in the shallow Black Sea (Nägler et al., 2005, 2011). Additionally, understanding these modern systems (e.g., Cariaco Basin) can stand as potential exemplars of ancient ocean basins and thus help to deconvolute the Mo geologic isotope record as a whole (e.g. Brueske et al., 2019; Noordman et al., 2015).

**5. Research gaps**

**5.1 Limitations of current approaches**

The current arsenal of methods available to geochemists is vast, however, most rely on the combination of two methods; inductively coupled plasma mass spectrometry (ICP-MS) for concentration and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) for isotope measurements. Rapid simultaneous measurements of multiple trace metal concentrations (~µg/L) only become feasible with wide-spread availability, reduced cost, and user-friendliness of ICP-MS. This technology allows measurements of additional redox sensitive trace metals such as; iron (Fe), manganese (Mn), vanadium (V), chromium (Cr), and uranium (U) in rocks and sediments at concentrations orders of magnitude (*e.g.*, ≤ 1 µg/kg) lower than conventional sequential extraction methods (Tribovillard et al., 2006). So called “non-traditional” (i.e*.*, Fe, Mn, Mo, V, Cr, U) isotopic measurements *via* MC-ICP-MS better constrain redox chemistry of aquatic systems. When combined these tools impart a considerable amount of information for the user, however they are not without limitations.

Historically, geochemical measurements of redox sensitive trace metals were confined to bulk geochemistry of rocks, water, or sediments often using sequential extraction, ultraviolet visible light absorption, or flame atomic absorption analysis (Goldschmidt 1954, Kuroda & Sandell, 1954, Wedepohl, 1971). Although these techniques have helped interpret the redox setting within ancient oceans (e.g., Anbar & Knoll, 2002), they often do not uniquely quantify the specific mechanisms enriching trace metals. With ICP-MS and MC-ICP-MS, geochemical interpretations have improved drastically allowing major discoveries on the paleoredox history of Earth to be made (e.g., Anbar et al., 2007). However, the shortfall of these bulk geochemical methods resides in the inability to resolve specific mechanistic trace metal pathways, due to sample size requirements and the need to homogenize materials before analysis. Bulk measurement requirements cause ambiguity in trace metal sequestration and loss of information when measuring geologic materials. Despite this, these methods are rapid and offer a low cost and as a ‘first pass’ to identity key intervals in a geologic record or sediment archive.

**5.2 Molecular geochemistry**

Molecular geochemistry (*i.e.,* combining analyses of concentration, isotope ratio, elemental mapping, and speciation) of trace metals has gained momentum amongst geochemists by providing a more nuanced geologic interpretations identifying specific species, reactions, and sequestration pathways (e.g., Ardakani et al., 2020). Specifically, it can be used to directly measure oxidation state, dominant species, bonding distance, coordination, and adsorptive affinity of trace metals. However, until recently these methods have been underused by geochemists due to lack of general awareness, access to advanced training, and misunderstanding of costs. The lack of use of molecular geochemistry is unfortunate since foundational works such as; Siebert et al. (2003) demonstrate the importance of recognizing that fractionation of isotopic values could be tied to coordination change of tetrahedral to octahedral, outweighing a simple model of kinetic fractionation of an initial isotope pool. Still, these practices are continuing to spur a geochemical renaissance by improving and refining depositional settings, defining precise water column redox conditions, and by identifying paleo pH.

Molecular geochemistry is a rapidly evolving sub-field; however, the primary obstacle to its continued advancement is the need for rigorous laboratory-based experimental data combined with innovation of existing methods coupled to ‘cutting-edge’ analytical instrumentation (e.g., Vorlicek at al., 2018 and references therein). For example, high energy X-rays (*i.e.*, X-ray Absorption Fine Structure (XAFS)) can measure oxidation state and coordination number; nuclear scattering (*i.e.*, neutron diffraction (ND)) can measure crystal structure and light isotopes; and nanometer scale ionization (*e.g.*, secondary ion mass spectrometry (SIMS)) can measure isotopic fractionation associated within single mineral matrices or OM complexes (Liang et al., 2008, Reich et al., 2013). However, before using these technologies the geologic materials in question need to have a complete and comprehensive geochemical evaluation to gain the most value from the output molecular geochemical data. Thus, the best practice to study of Mo systematics uses a multi-prong approach of bulk concentrations and isotopic signatures coupled with molecular geochemistry to paint a complete paleoredox picture.

**6. Future research directions**

Molybdenum is a powerful geochemical tool which has evolved significantly in use during the past fifty years. Although many important scientific questions were answered using Mo systematics (i.e., total concentrations and isotopic signatures), these alone are not enough to answer many current geochemical research questions. Most notably the Mo paleoproxy falls short in intermediate redox conditions (nitrogenous, manganous, ferruginous) where multiple dissolved and solid phase sequestration pathways appear to be acting together on the bulk geochemical signal of Mo. These redox zones remain a problem for the geochemical community due to the potential for misinterpretations or oversimplification in the geologic record. To improve the geochemist’s ability to understand the dynamics of Mo cycling across all redox systems, training in and use of molecular geochemistry to measure species, oxidation state, coordination, bonding, and phase association is needed. By combining these state-of-the-art analytical techniques with traditional approaches, the possibility of fully understanding Mo geochemistry is within the reach of scientists. Additionally, molecular geochemistry is not only limited to the Mo paleoredox proxy, the usefulness of these methods applies to any redox sensitive trace metal and through continued research endeavors will expand the ability of anyone to precisely describe depositional redox settings. The future geochemical frontier, therefore, lies in the ability to analyze trace metal molecular geochemistry *in situ* and across a wide variety of environmental conditions to build a robust geochemical knowledge base of different proxies.

**7. Recommended reading:**

1. Smedley, P. L., & Kinniburgh, D. G. (2017). Molybdenum in natural waters: A review of occurrence, distributions and controls. Applied Geochemistry, 84, 387-432

Smedley & Kinniburgh (2017) provide the most extensive review of molybdenum in the natural world from solid to dissolved phases as it cycles in the environment.

1. Kendall, B., Dahl, T. W., & Anbar, A. D. (2017). The stable isotope geochemistry of molybdenum. Reviews in Mineralogy and Geochemistry, 82(1), 683-732.

Kendall et al., (2017) summarizes the major concepts in the use of molybdenum isotopes as a paleoproxy and provides an excellent summary of the current research gaps concerning isotope interpretation.

1. Dickson, A. J. (2017). A molybdenum-isotope perspective on Phanerozoic deoxygenation events. Nature Geoscience, 10(10), 721-726.

Dickson (2017) covers the important and recent advances in isotope interpretations from the Phanerozoic and provides as useful synopsis complementing Kendall et al., (2017).

1. 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.

Helz et al., (1996) is likely the most seminal and important paper concerning the use of molybdenum as a paleoproxy. In this manuscript Helz et al., (1996) stage for studying the speciation of molybdenum in ancient systems.

1. Scott, C., Lyons, T. W., Bekker, A., Shen, Y. A., Poulton, S. W., Chu, X. L., & Anbar, A. D. (2008). Tracing the stepwise oxygenation of the Proterozoic ocean. Nature, 452(7186), 456-459.

Scott et al., (2008) is a seminal paper illustrating the use of the molybdenum paleoproxy to understand Earth’s oxygenation and documents the power of molybdenum as a redox sensitive tracer of past conditions.

1. 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.

Erickson & Helz (2000) outline the chemistry of molybdenum speciation under sulfidic redox conditions, and describe the kinetics of molybdenum thiolation to help interpret both modern and ancient sedimentary systems.

1. Scott, C., & Lyons, T. W. (2012). Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies. Chemical Geology, 324, 19-27.

Scott & Lyons (2012) identify the behavior of molybdenum across a range of redox conditions in both sediments and rocks. This paper illustrates the mechanics of molybdenum sequestration under reducing conditions and how geochemical signals can be interpreted for paleoredx reconstruction.

1. 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 & Lyons (2006) address the long-standing question of the role of organic matter in association with molybdenum commonly found in ancient rocks. This paper sets the stage for future research into organic matter dynamics relating to molybdenum.

1. Chappaz, A., Lyons, T. W., Gregory, D. D., Reinhard, C. T., Gill, B. C., Li, C., & Large, R. R. (2014). Does pyrite act as an important host for molybdenum in modern and ancient euxinic sediments?. Geochimica et Cosmochimica Acta, 126, 112-122.

Chappaz et al., (2014) outlines the burial pathways for molybdenum sequestration in sediments, commonly thought to be dominated by pyrite precipitation. They highlight current hypothesis for possible molybdenum pathways and postulate on the potential of additional sequestration pathways.

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