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-phase 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 (Chappaz et al., 2008; Rahaman et al., 2010; Miller et al., 2011; Reimann & de Caritat, 2012; Glass et al., 2013). 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 cofactor in nitrogenase and nitrate reductase enzymes. Both enzymes are critical to the nitrogen cycle, and some research suggests they could be responsible for the first stages of 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) reflects 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 behavior have been difficult to quantify,
compared to Mo–mineral associations (Wichard et al., 2009; Dahl et al., 2017; Wagner et al., 2017; Ardakani et al., 2018; 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 indicators of redox setting when investigating Mo in both isotopic signature and chemical composition (Helz et al., 1996; Arnold et al., 2004; Tribovillard et al., 2006; Chappaz et al., 2014; Scholz et al., 2017). For example, Scott et al. (2008) demonstrated the inorganic enrichment of \( \Sigma[Mo] \) 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 as 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 \((^{98}Mo)\) 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 into oceanic circulation, extinction events, anthropogenic sources, and, indirectly, large-scale glaciation (e.g., Pearce et al., 2008; Chappaz et al., 2012; 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; Näge
er 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 it 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 (NO$_3$–/NO), manganese (Mn(IV)/Mn(II)), and iron (Fe(III)/Fe(II)) redox couples respectively dominate, and neither O$_2$ nor ΣS(–II) can be measured. Finally, the “sulfidic” zone is...
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defined as the region where measurable \( \Sigma S(-II) \) exists, after iron reduction has occurred and sulfate (SO\(_4^{2-}\)) reduction dominates. In the geochemical literature, “anoxic” and “euxinic” are often used to describe the presence of \( \Sigma S(-II) \) in either the pore water or the 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 \( \Sigma S(-II) \) 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)O\(_4^{2-}\), Mo(VI)O\(_3\)), as cations adsorbed to mineral surfaces (e.g., Mo-FeOOH, Mo-MnOH\(_2\)), as solid amorphous minerals (e.g., Fe\(_x\)Mo\(_y\)OH, Mn\(_x\)Mo\(_y\)OH), and associated with organic matter (e.g., Mo-OM) (Fig. 3; Helz et al., 1996; Wasylentki 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 (\( \Sigma \{Mo\}_{(aq)} \)) 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)O\(_4^{2-}\)\(_{(aq)}\) has been demonstrated to contribute to Mo shuttling, sequestration, and overall availability of \( \Sigma \{Mo\}_{(aq)} \) 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)O\(_2\) surfaces (Wasylentki et al., 2011). This process facilitates particulate Mn-Mo shuttling to the SWI, causing a positive correlation of Mn(IV)O\(_2\) to \( \Sigma \{Mo\}_{(aq)} \) in suspended particles, while negatively correlating dissolved Mn and \( \Sigma \{Mo\}_{(aq)} \) (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