

Chapter 2

Molybdenum Availability in the Ecosystems (Geochemistry Aspects, When and How Did It Appear?)

Abstract The distribution of life on Earth is constrained by the distribution of 20 bio-essential nutrients. Particularly, the availability of those elements required as cofactor might have influenced the timing of origin and evolution of metabolic pathways. Since the amount of bio-available Mo strongly changed during evolution to form anoxic to oxygenic environments, it is interesting to speculate about the appearance of Mo containing enzymes in relation to other metals with similar chemical characteristics.

2.1 Elements and Evolution of Biological Systems

The current ecosystem is the result of the Earth 4.5 billion years of evolutionary history and has been modelled thanks to the combined effects of tectonic, photochemical and biological processes. The abundance of the elements in the universe and the way in which the planetary system was formed controlled the abundance of metals on the primitive Earth, which was (and still is) a metal rich planet (Prantzos et al. 1994). The fact that the metal elements and hydrogen were slightly in excess in respect to non-metals (such as oxygen) has very likely determined the initial reducing capacity of condensed matter.

Among the most important and relatively abundant non-metallic elements, oxygen appeared in liquid water and in solid (mainly in low-valent metal oxides or mixed oxides such as silicates); nitrogen in the atmosphere formed as N_2 or NH_3 ; carbon as CO, CO_2 (a large part of the carbon has always been oxidized to CO_2) and CH_4 , chlorine as HCl initially (if out of contact with metal oxides), and sulfur as metal sulfides and H_2S . Much of the carbon could not be reduced and remained as CO or CO_2 . Oxidation of sulphur and nitrogen was prevented by the overall lowered availability of molecular oxygen due to its high affinity for metals, hydrogen and carbon. Metals, which could not be reduced and were kept in their highest oxidation states occurred in large part as simple ions in oxide lattices or soluble salts. This is the case for Al^{3+} , Ca^{2+} , Mg^{2+} , Na^+ and K^+ . Some of them readily gave

insoluble mixed oxide based salts such as silicates and carbonates. The most soluble oxides then reacted with the limited amounts (by abundance) of HCl to give soluble chlorides (such as NaCl and KCl) in the sea once water condensed. Since oxygen was not in sufficient abundance those metals with a relatively low affinity for oxygen could not form oxides and they formed sulphides (e.g. of many transition metals) or metals and alloys (e.g. metals such as gold). Initially, there would have been no excess of oxygen or sulphur as elements though both were present as hydrides, H₂O and H₂S. All the associations in the exposed surface zones are firmly based on the restrictions of variables due to total composition (abundances) and certain equilibria at room temperature and pressure.

These concentrations of all important elements through time (shown in Fig. 2.1) along with their oxidation states represented extremely strong constraints upon the formation of an energized system. Thus, it was the combination of both of them that eventually led to the formation of organic systems which predated life or which grew simultaneously as encoded life.

2.1.1 Early Atmosphere and Early Sea Composition

Even though there is not a complete agreement on the composition of the **early atmosphere** it is likely that it was somewhat reducing since it contained H₂, CH₄, CO and H₂S in addition to CO₂ (Kasting 1993). On the basis of all the available data it is still not possible to state whether CO and CO₂ (oxidizing gases) were or were not in thermodynamic equilibrium with the reducing gases H₂ and CH₄ and with H₂O, given the uncertainty in their relative abundances. Also, the nitrogen content is uncertain since there could have been such gases as N₂, NH₃ and HCN. The exact partial pressure of these gases is unknown but it is possible that the most represented were N₂ and CO₂ with considerable amounts of CO. For clarity a table with the major constituents of early atmosphere is reported in Table 2.1.

Availability of different elements in the **early sea** is much more difficult to formulate since it depended on the solubility of the different compounds. The vast majority of abundant metal ions form rather insoluble salts with abundant anions such as silicate (Mg²⁺, Ca²⁺, Al³⁺) or sulphide (transition metal ions). The remaining few abundant metal ions are Na⁺ and K⁺, and one anion, Cl⁻, which do not easily give precipitates with abundant anions or cations respectively. As a consequence, especially Na⁺ and K⁺, and Cl⁻ were left in solution in the sea and were limited there by the lower abundance of chlorine relative to the combined abundances of Na and K. Almost all chlorine on Earth is still in the seas and oceans or it evaporates today as NaCl. A small quantity of bicarbonate/carbonate accompanied by the metal elements, Mg²⁺ and Ca²⁺, which form somewhat soluble salts, was also present. According to the idea of a reducing atmosphere it is very likely that no sulphate or nitrate were present since they were too oxidizing. Anyway, the transition metal elements, both silicates and sulphides are insoluble; nevertheless with increasing atomic number in the

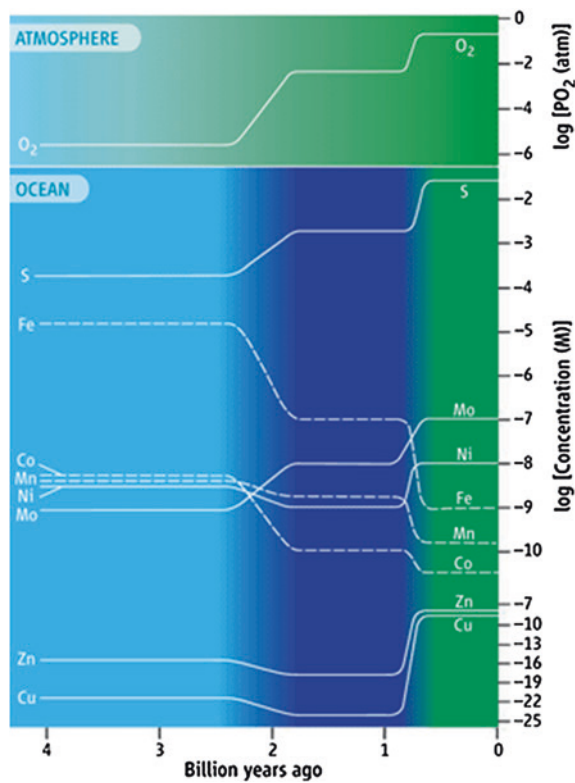


Fig. 2.1 Changes in element abundances through time. These histories are approximate, based on simple geochemical models and inferences from ancient sediments. An expansion in H₂S-rich ocean regions after 2.4 billion years ago is assumed. Color gradations indicate a transition from anoxic, S-poor oceans before 2.4 billion years ago (*light blue*) to H₂S-rich oceans between 1.8 billion and 800 million years ago (*dark blue*), subsequently giving way to complete ocean oxygenation (*green*). Different line styles are for clarity only; *dashed lines* are for elements with falling concentrations. Reproduced from Anbar (2008). With kind permission of © Science. CREDIT: Susan Selkirk/Arizona State University

Table 2.1 Principal constituents of early atmosphere

Constituents	Percent by volume
CO ₂	91
N ₂	6.4
H ₂ S	2.0
HCl	0.2
H ₂ O	0.2
NH ₃	0.01
CH ₄	0.02
Cl ₂	0.01

Data are taken from Rubey (1955)

transition metal series from Mn to Cu the sulphides become the dominant species. The insolubility of precipitated sulphides was responsible for the absence of copper and initially of molybdenum and the very low content of zinc, on the contrary iron as Fe^{2+} , Mn^{2+} and even tungsten (W) remained in soluble forms in the primitive sea. The approximate probable concentrations of all of the major ions in the primitive sea under either anaerobic or aerobic conditions is shown in Table 2.2.

However, the composition of both the early sea and atmosphere might have changed since the different compounds were not in temperature equilibrium with the hot core and the very high temperature on Earth's surface. As a consequence, the environment was liable to thermal and photochemical kinetic changes even before the appearance of the first living forms.

The gases H_2 and O_2 are more prone to react with other chemicals than with themselves, so that the reverse reaction did not appear before the changing in the oxidation state of the earth. The kinetic and sustained traps for hydrogen were mainly light non-metals such as carbon and nitrogen while the traps for oxygen were heavier non-metals such as sulphur and then various metal sulphides such as V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Mo slowly producing more soluble oxides. A feature of the states of these metals is that over a reasonable period of time they equilibrate with oxygen and amongst themselves but not with C/H compounds so that we can believe that the sea and atmosphere changed continuously through an increase in redox potential equilibrated with the slowly increasing O_2 partial pressure. At the same time more reducing equivalents were trapped (stored) in organic molecules and the carbon and nitrogen compounds in the atmosphere were also oxidised so that the atmosphere became increasingly composed by CO_2 and N_2 . Later still surface sulphides were oxidized to sulphate and N_2 to some nitrate in the sea.

Table 2.2 Approximate probable concentrations of the major ions in aerobic and anaerobic conditions in the primitive seas

Metal ion	Anaerobic conditions (M)	Aerobic conditions (M)
Na^+	$>10^{-1}$	$>10^{-1}$
K^+	10^{-2}	10^{-2}
Mg^{2+}	10^{-2}	10^{-2}
Ca^{2+}	10^{-3}	10^{-3}
Mn^{2+}	10^{-6}	10^{-6}
Fe	10^{-7} (Fe^{II})	10^{-19} (Fe^{III})
Co^{2+}	$<10^{-9}$	10-set
Ni^{2+}	$<10^{-9}$	$<10^{-9}$
Cu	$<10^{-20}$, Cu^{I}	$<10^{-10}$, Cu^{II}
Zn^{2+}	$<10^{-12}$	$<10^{-8}$
Mo	$<10^{-10}$ (MoS_4^{2-})	10^{-8} (MoO_4^{2-})
W	$<10^{-9}$ (WS_4^{2-})	10^{-9} (WO_4^{2-})
H_2S	10^{-2}	$<10^{-10}$
HPO_4^{2-}	$<10^{-3}$	$<10^{-3}$

Moreover, the distribution of bio-essential elements in early sea, is not easy to be studied, but inferences can be drawn from the characteristics of rocks formed from seafloor sediments. The best example is the abundance of iron in the geologic record (Isley and Abbott 1999), massive deposits of iron sedimentary ore older than 1.8 billion years. Such deposits almost disappear from the more recent record. The analysis of Banded Iron Formations (BIFS) suggests that the iron-rich oceans in the first half of Earth's history gave way to later iron scarcity (Poulton et al. 2004; Holland 2006). The changes in the availability of other bio-essential elements are subtler and must be inferred by sophisticated methods of analysis.

Due to recent instrumental analytical advances it was possible to identify new paleoredox state markers (e.g. molybdenum isotopes, Re, Os), and to improve existing ones (e.g. Mo-TOC, Re/Mo). In this sense, the sedimentary molybdenum is commonly used as a paleoredox conditions marker. An enrichment of this element in sediments and sedimentary rocks, is interpreted as reflecting low potentials redox in the environment (Sageman and Lyons 2003; Tribovillard et al. 2006; Pearce et al. 2008; Böning et al. 2008). Thus, anoxic facies are generally enriched in molybdenum with respect to oxic and suboxic ones and the mechanics of this enrichment process have been analysed extensively (e.g. Emerson and Huested 1991; Crusius et al. 1996; Helz et al. 1996; Zheng et al. 2000). The mobilization of molybdenum enrichment in the marine sedimentary environment also produces an isotope fractionation of mercury (Siebert et al. 2003; Arnold et al. 2004; Poulson et al. 2006; Pearce et al. 2008; Neubert et al. 2008; Archer and Vance 2008). Thus, changes in redox conditions in the marine depositional environment can be determined by the isotopic composition of molybdenum.

2.1.2 Elements Availability and Emergence of Life

Since the onset of primordial living systems, which most likely occurred around 3.8–3.5 billion years ago (Lazcano and Miller 1996), nearly all elements have been used by microbial metabolic activities. From a geochemical perspective the cycles of energy and minerals (especially H, C, N, O and S) required by vital processes and the biogeochemistry processes can be considered thermodynamically constrained redox reactions catalyzed by microbial metabolic pathways (Falkowski et al. 2008). Thus, the biogeochemical cycles might be interpreted as the interconnection between abiotic driven acid-base reactions (acting on the geological time scale to supply the system with elements through volcanism and rock weathering) and biotic redox reactions. Such metabolic reactions transformed the redox state of the planet into an oxidative environment once oxygenic photosynthesis appeared in cyanobacteria about 3–2.7 billion years ago (Canfield 2005). The appearance of this crucial metabolic ability led to a progressively strong increase of the O₂ concentration in the atmosphere in a relatively short timescale between 2.4 and 2.2 billion years ago, as shown in Fig. 2.2 (Bekker et al. 2004). Depending on the composition and original redox state of the prebiotic atmosphere

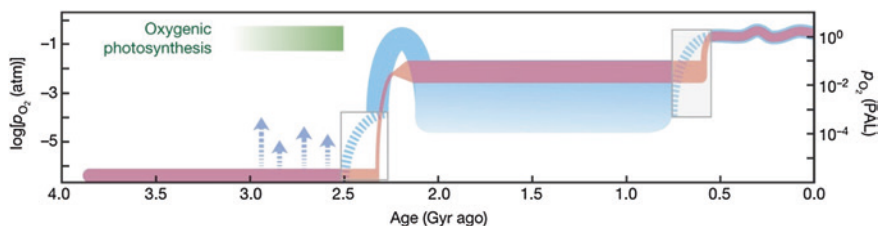


Fig. 2.2 Evolution of Earth's atmospheric oxygen content through time. The faded red curve shows a 'classical, two-step' view of atmospheric evolution, while the *blue curve* shows the emerging model (PO_2 , atmospheric partial pressure of O_2). *Right axis* PO_2 relative to the present atmospheric level (PAL); *left axis* $\log PO_2$. Arrows denote possible 'whiffs' of O_2 late in the Archaean; their duration and magnitude are poorly understood. An additional frontier lies in reconstructing the detailed fabric of 'state changes' in atmospheric PO_2 , such as occurred at the transitions from the late part of the Archaean to the early Proterozoic and from the late Proterozoic to the early Phanerozoic (*blue boxes*) Reproduced from Lyons et al. (2014). With kind permission of © Nature

(Kasting and Siefert 2002), various models can be proposed for the evolution of abiotic and biotic factors cycles and the microbial lineages (metabolic pathways) capable of driving them (Zerkle et al. 2006; Capone et al. 2006; Navarro-González et al. 2001; Wächtershäuser 2007), but it is clear that oxygenation led to drastic changes in the availability of mineral factors required for metabolic reactions.

The distribution of life on earth is constrained also by the distribution of 20 bio-essential nutrients such as Calcium (Ca), Chloride (Cl^-), Chromium (Cr), Cobalt (Co), Copper (Cu), Magnesium (Mg), Manganese (Mn), Nickel (Ni), Iodine (I), Iron (Fe), **Molybdenum (Mo)**, Phosphorus (P), Potassium (K), Selenium (Se), Sodium (Na), Sulfur (S), Tungsten (W), Vanadium (V), and Zinc (Zn), which are relatively rare, but that are key components of DNA, RNA, enzymes, and other biomolecules. Therefore, the availability of these bio-essential elements must have shaped the evolution of life (Williams and Fraústo da Silva 2003). Particularly, the availability of those elements required as cofactor might have influenced the timing of origin and evolution of metabolic pathways (and hence of phenotypic characteristics). This idea relies on fossil evidences that suggest that the diversification of eukaryotes substantially coincided with the increase in redox potential of the deep oceans about 800 million years ago (Knoll et al. 2006), with a subsequent increase in zinc's, molybdenum's and other elements' availability and the parallel decrease of iron, manganese, and cobalt concentrations. Bioinformatic analyses of protein-metal binding motifs have shown that eukaryotes require more zinc and less iron, manganese and cobalt in respect to prokaryotes (Dupont et al. 2006). Eukaryotes also require molybdenum for nitrate assimilation (Anbar and Knoll 2002) and can use zinc instead of cobalt for assimilation of carbon through the enzyme carbonic anhydrase. It is therefore possible that eukaryotes emerged from ecological niches such as oceanic chemical mass shifted to favor the needs for the elements (Anbar and Knoll 2002; Knoll 2006). A similar pathway could explain the arisal of red eukaryotic phytoplankton after 250 million years ago (Falkowski et al. 2004).

Moreover, for example, the availability of trace metals of importance to the N cycle (Fe, Mo, and Cu) was influenced by increasing concentration of oxygen since they are redox sensitive and display different availability depending on redox state of the environment. Indeed, they exhibit sharp changes in the geochemical behaviour with changes in environmental oxygenation; Fe and Mo, for example, are a complementary pair because they are geochemical opposites. In Earth's crust (Taylor and McLennan 1982), Fe is the fourth most abundant element ($\sim 5\%$), whereas Mo is a trace element (~ 1 ppm). This situation is reversed in the oceans where Fe concentrations rarely exceed ~ 2 nM (Bruland et al. 1979; Wu et al. 2001), whereas the concentration of Mo is a uniform ~ 105 nM (Collier 1985). In oxygenated waters, Fe (III) oxidizes and hydrolyzes forming an insoluble oxyhydroxide whereas Fe (II) is mobile, but is sequestered into sulfides. Molybdenum (VI) forms a soluble oxyanion (MoO_4^{2-}) in oxic water, and is readily transferred to the oceans in which its residence time is $\sim 800,000$ years (Morford and Emerson 1999). On the contrary, $\text{MoO}_{4-x}\text{S}_x^{2-}$ is formed in reduced conditions.

2.2 The History of Molybdenum Availability and Utilisation

Molybdenum (Mo) is an elemental metal of the second transition series, which is adjacent to chromium (Cr) and tungsten (W); Mo occurs in nature with a + 6 oxidation state, its Pauling electro negativity of 2.16 allows it to form covalent bonds. A summary of molybdenum physical and atomic properties is shown in Table 2.3. Molybdenum has a diagonal relationship with vanadium (V) and rhenium (Re) in the periodic table; an example of this is that in their highest oxidation states, these elements form tetrahedral oxyanions VO_4^{3-} , MoO_4^{2-} and ReO_4^- , rhenium minerals may be associated with molybdenum disulfide (molybdenite, MoS_2).

Table 2.3 Atomic and physical properties of molybdenum and tungsten

	Molybdenum	Tungsten
Atomic number	42, transition metal	74, transition metal
Atomic mass	95.94 g amu	183.84 g amu
Electronic configuration	$[\text{Kr}]4d^55s^1$	$[\text{Xe}]4f^{14}5d^46s^2$
Oxidation states	2, 3, 4, 5, 6	3, 4, 5, 6
Density	$10,280 \text{ kg/m}^3$	$19,300 \text{ kg/m}^3$
Covalent radius	145 pm	137 pm
Cristal structure	Body centered cubic	Body centered cubic
Melting point	2896 K	3695 K
Boiling point	4912 K	6203 K
Electronegativity	2.16	2.36
Free energy of solvation	$-226.8 \text{ kcal mol}^{-1}$	$-230.1 \text{ kcal mol}^{-1}$
Covalent solution radii	2, 75 Å	2, 83 Å

From a geochemically viewpoint, Mo is mainly found in nature in the form of molybdate (MoO_4^{2-}). Mo is so unreactive in oxygenated aqueous solutions that is the most abundant transition metal in the modern oceans ($\sim 105 \text{ nmol kg}^{-1}$), with a residence time of $\sim 800 \text{ ka}$ (Morford and Emerson 1999), despite being a component whose concentration in the cortex is found only in parts per million (ppm). In contrast, Mo is easily removed from the water column in euxinic conditions, i.e. anoxic environments with high concentrations of H_2S , so that the enrichment of Mo in sediments is considered diagnostic of reducing deposition conditions (Calvert and Pedersen 1993; Anbar 2004; McManus et al. 2006; Tribouillard et al. 2006), in fact where sulfide is present in the water column or in pore fluids, Mo accumulates at a 100–1000 fold higher rate than when sulfide is absent. Thus, the aqueous Mo-cycle and Mo isotope mass balance are obviously affected by these different settings that may occur, i.e. euxinic and oxic conditions.

Molybdenum enters the oceans largely via rivers. In oxygenated waters, Mo speciation is mostly represented by the molybdate anion, MoO_4^{2-} . However, under euxinic conditions, such as in the modern Black Sea, where the concentration of H_2S is very high (about 100 M) several Mo species are readily removed from solution (Emerson 1991; Erickson and Helz 2000; Morford and Emerson 1999). As a result, ocean sediments accumulating today beneath euxinic waters account for 10 to 50 % of the annual removal flux of Mo from the oceans even though such waters cover an extremely small percentage of the modern seafloor (0.5 %) (Emerson 1991; Morford and Emerson 1999). The remaining marine Mo is primarily removed in association with sedimentary Mn in oxygenated environments (Morford and Emerson 1999). It is not known if sediments accumulating under bottom waters with low O_2 concentration and lacking sulfide (“suboxic” sediments) constitute a net source or sink of Mo from the oceans (Morford and Emerson 1999; McManus 2002), but they probably account for about 10% of Mo cycling today (Morford and Emerson 1999). The ocean Mo budget is therefore highly sensitive to the extent of euxinic bottom waters (Emerson 1991).

2.2.1 Isotope Fractionation in the Modern Ocean

Mo has seven naturally occurring stable isotopes: ^{92}Mo (14.84 %), ^{94}Mo (9.25 %), ^{95}Mo (15.92 %), ^{96}Mo (16.68 %), ^{97}Mo (9.55 %), ^{98}Mo (24.13 %), and ^{100}Mo (9.63 %). Natural mass-dependent Mo-isotope variations span a range of $\sim 1 \text{ ‰}$ (amu^{-1} Atomic Mass Unit) difference, usually reported as $\delta^{97/95}\text{Mo}$ or $\delta^{98/95}\text{Mo}$.

The largest known Mo-isotope effect occurs during adsorption of dissolved Mo to Mn-oxide particles and Fe(oxyhydr)oxides, (Siebert et al. 2003; Barling and Anbar 2004; Wasylenki et al. 2006; Goldberge al. 2009), concentrating isotopically-light Mo in ferromanganese sediments deposited in oxic settings (e.g., Barling et al. 2001). In contrast, in euxinic basins with free sulfide in the water column, Mo is nearly completely removed into the sediments such that no fractionation from the seawater value is expressed (Barling et al. 2001;

Arnold et al. 2004; Nägler et al. 2005). Light isotopes are preferentially removed from solution, so dissolved Mo is $\sim 1\text{‰}$ amu^{-1} heavier than particle-bound Mo.

First inferred from natural observations in oxic seawater and sediments (Barling et al. 2001), this fractionation has been reproduced in the laboratory (Barling and Anbar 2004; Wasylenko et al. 2006). The fractionation factor is relatively unaffected by pH or temperature. Ironically, despite the rich redox chemistry of Mo (Anbar 2004), this fractionation may not involve a change in Mo-oxidation state. It may result from the fractionation between MoO_4^{2-} , which dominates Mo speciation in seawater, and one or more scarce, dissolved Mo species, such as $\text{Mo}(\text{OH})_6$ or MoO_3 , that adsorbs more readily (Siebert et al. 2003; Tossell 2005). Alternatively, fractionation may result from isotope exchange between MoO_4^{2-} and a surface-bound Mo species (Barling and Anbar 2004).

Smaller but significant Mo-isotope effects are inferred to exist during the reduction of Mo in suboxic and euxinic environments based on observations in reducing sedimentary basins (McManus et al. 2002, 2006; Nägler et al. 2005; Poulson et al. 2006; Siebert et al. 2003). Mo is highly reactive in reduced settings, particularly when dissolved (H_2S) $> 11\text{ }\mu\text{mol kg}^{-1}$ and MoO_4^{2-} is transformed to particle-reactive oxythiomolybdates, $\text{MoO}_{4-x}\text{S}_x^{2-}$ (Erickson and Helz 2000; Helz et al. 1996; Zheng et al. 2000).

Mo isotope variations magnitudes are also seen in continental molybdenites (Barling et al. 2001; Malinovsky et al. 2005; Pietruszka et al. 2006; Wieser and de Laeter 2003). Biological isotope effects appear to be minor, although there are reports of preferential uptake of light isotopes (by $\sim 0.25\text{‰}$ amu^{-1}) by nitrogen-fixing bacteria (Liermann et al. 2005; Nägler et al. 2004).

It follows from the long residence time of Mo in oxic seawater that, in contrast to Fe, Mo-isotope composition of bulk oxic sediments is controlled by fractionation during Mo removal to such sediments, if such fractionation occurs, as well as by the isotopic composition of Mo sources to the oceans. Similar considerations can be applied to suboxic sediments, which are turning out to be important to the Mo ocean budget (McManus et al. 2006). Hence, Mo-isotope oceanographic research has focused at least as much on understanding isotope effects during Mo removal to sediments as on Mo sources to the oceans. Changes in Mo removal fluxes under steady-state conditions are shown in Fig. 2.3.

Early data pointed to a first-order model in which Mo entering the oceans primarily from continental sources with average $\delta^{97/95}\text{Mo} \sim 0\text{‰}$ undergoes fractionation during removal to Mn oxides, resulting in an isotopically heavy reservoir of Mo dissolved in seawater. The removal of Mo to euxinic sediments imparts little isotope effect. From a paleoceanographic perspective, this model implies that $\delta^{97/95}\text{Mo}$ seawater should vary with the extent of oxic deposition; if there were no Mn-oxide deposition, $\delta^{97/95}\text{Mo}$ seawater $\sim 0\text{‰}$ (Barling et al. 2001; Siebert et al. 2003). This schematic concept underlies the use of Mo isotopes as paleoredox proxy, but has three major uncertainties. First, continental rocks being weathered may not be isotopically uniform, so changes in weathering regimes could lead to changes in $\delta^{97/95}\text{Mo}$ seawater independent of ocean redox. Second, the extent of Mo-isotope fractionation during weathering and transport to the oceans

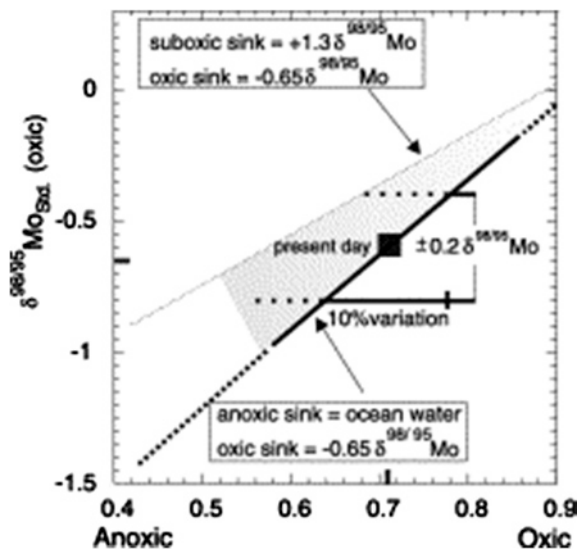


Fig. 2.3 Changing anoxic to oxic removal flux in the oceans under steady-state conditions. The oxic fraction of total Mo removal in the modern oceans must be around 0.7 to maintain steady-state conditions. Variations in the relative amount of oxic and reducing Mo removal flux greater than 10 % should result in a shift in ocean water $\delta^{98/95}\text{Mo}$, detectable in the Fe–Mn crust time series. *Shaded area* various mixtures of anoxic (ocean water Mo) to suboxic (lighter isotope compositions) fractionation result in a variety of slopes. A lighter suboxic sink results in less resolution for the detection of variations in the ratio of oxic to anoxic Mo fluxes. Reproduced from Siebert et al. (2003). With kind permission of © Earth and Planetary Science Letters

is not known. Leaching experiments with igneous rocks suggest that weathering effects are minimal (Siebert et al. 2003), but isotopic research in rivers and estuaries is needed. Third, and most important, suboxic sedimentary environments, once thought to be of negligible importance to the Mo elemental and isotope budgets (Barling et al. 2001; Morford and Emerson 1999), may account for as much as 60 % of Mo removal (McManus et al. 2006). If so, an effect on the ocean isotope budget is likely because Mo isotopes are significantly fractionated in pore waters and sediments from such settings (McManus et al. 2002; Poulson et al. 2006). Relative to seawater Mo, the direction of this effect is the same as fractionation by removal to Mn-oxide sediments, so in paleoceanographic reconstructions changes in $\delta^{97/95}\text{Mo}$ seawater owing to the contraction of oxic deposition could be partially countered by the expansion of suboxic deposition, and *vice versa*.

Researchers are exploring three types of Mo-isotope paleorecords. Temporal variations of $\delta^{97/95}\text{Mo}$ seawater could be mirrored in Fe–Mn crusts, providing a paleorecord through the Cenozoic (Siebert et al. 2003). An alternative record extending much further in time may exist in black shales (Barling et al. 2001). Finally, Mo isotopes may also be useful in probing local, rather than global, redox conditions.

Siebert et al. (2003) examined Mo isotopes in well-dated Fe-Mn crusts from the Pacific, Atlantic, and Indian Oceans. These sediments span ~ 60 million years and were sampled at a resolution of $\sim 1\text{--}3$ million years. The Mo- isotope composition of all these samples is remarkably uniform. Overall, Mo in these sediments varies within a range of $<\pm 0.25\text{‰}$. The data overlap with measurements of Atlantic and Pacific Fe-Mn nodules (Barling et al. 2001), despite greatly different accumulation rates of these sediment types. The only significant $\delta^{97/95}\text{Mo}$ variation in these samples is a small offset of $\sim 0.15\text{‰}$ seen between Pacific and Atlantic crusts, just outside the $\pm 2\sigma$ uncertainties of Siebert et al. (2003). The isotopic uniformity of this record is taken to reflect the invariance of $\delta^{97/95}\text{Mo}$ seawater at the sampled resolution through the Cenozoic and may indicate that ocean oxygenation has varied less than 10 % from modern values over this time (Siebert et al. 2003). Although larger ocean redox perturbations are possible during this time in association with glacial pCO_2 drawdown, their duration does not approach the $\sim 10^6$ year timescale of crust sampling and the mean ocean residence time of Mo.

Since the amount of bio-available Mo strongly changed during evolution to form anoxic to oxic environments, it is interesting to speculate about the appearance of Mo containing enzymes in relation to other metals with similar chemical characteristics.

2.3 Molybdenum Versus Tungsten

It is interesting and intriguing to speculate on the reason why evolution selected Mo and W as the metal component of enzymes cofactor. It is known that in oxic aqueous systems, these metals exist in the form of their tetrahedral MoO_4^{2-} or WO_4^{2-} oxyanions; therefore, they are easily mobilizable into enzyme systems with the important caveat that they must be distinguished during enzyme maturation to ensure proper redox function and therefore catalysis.

But how did these two systems arise? And why have both of them been selected?

It is plausible that, at the beginning, W might have been preferred by the early biological systems since tungsten–sulphur bonds, such as those found in tungsten-containing enzymes, are more stable than their molybdenum counterparts. Moreover, if we agree with the idea of an anaerobic and (highly) reducing environment, low-valent tungsten sulfides are also more soluble in aqueous solutions and, as a result, W would have been more bioavailable than Mo in the primordial Earth's biosphere (Andreesen and Makdessi 2008). Lastly, the reduction potentials of tungsten-containing complexes are lower than those containing molybdenum and therefore more useful to early life forms, which probably had a low intracellular redox poise. To date the most reliable explanation for the existence of both Mo and W containing enzymes is based on the evolution of life on Earth along with the subsequent biogeochemistry impact of (micro)organisms on the biosphere (Hille 2002; Dietrich et al. 2006). In fact,

as organisms performing oxygenic photosynthesis rendered the atmosphere progressively aerobic, the O₂ sensitivity of tungsten compounds became a liability and the water-solubility of high-valent molybdenum oxides an asset; the elevated intracellular redox poise of aerobic organisms would have also made molybdenum more suitable. Following the evolution of biological water oxidation, oxygenic photosynthetic organisms caused a dramatic increase in ambient redox potential that paralleled the increase in atmospheric oxygen, and this resulted in the appearance and bioavailability of Mo in the form of MoO₄²⁻. As a consequence, the bioavailability of the two elements was reversed, with Mo being present at a concentration in seawater at 100 times that of W (Anbar 2008). Quite interestingly, the processes that rendered Mo bioavailable had an opposite effect on iron bioavailability; indeed the increasing oxygen concentrations allowed to oxidize iron(II) to iron(III) oxyhydroxides, which are (essentially) insoluble and hence less bioavailable (Anbar and Knoll 2002; Fike et al. 2006). Since tungsten and molybdenum have similar chemistry, it is possible that, initially, as the transition to an oxygen-rich environment occurred, the latter progressively substituted for the former in enzyme active sites. Indeed, molybdenum and tungsten containing enzymes often catalyze the same kind of reactions, such as the oxidation of aldehydes to carboxylic acids. This idea is supported by the biological distribution of these elements today: molybdenum containing enzymes are found in all aerobic organisms, whereas tungsten occurs only in obligate, typically thermophilic, anaerobes. Accordingly, some mesophilic anaerobes are more “plastic” than their aerobic counterparts, in the sense that they can utilize either molybdenum or tungsten depending on their availability and growth conditions. However, both Mo and W are able to assemble into mononuclear molybdoenzymes in an almost identical manner causing a biological problem since redox reactions catalyzed by W typically occur at much lower potentials than those catalyzed by Mo, and the active sites of the enzymes have evolved to modulate the redox properties of their cognate metal ion. Therefore, the replacement of Mo by W in a *bona fide* molybdoenzyme would elicit dramatic changes in catalytic efficacy. This has been demonstrated using W substituted dimethyl sulfoxide reductase from *Rhodobacter capsulatus* in which the (V/VI) and (IV/V) redox potentials were decreased by −220 and −334 mV, respectively (Hagedoorn et al. 2003). The W substituted enzyme is able to catalyze dimethyl sulfoxide reduction (the forward reaction), but cannot catalyze dimethylsulfide oxidation (the backward reaction) (Hagedoorn et al. 2003). In the *Escherichia coli* trimethylamine-N-oxide reductase, substitution of Mo with W also results in retention of catalysis in the forward direction while considerably perturbing its substrate specificity (Buc et al. 1999). In the case of sulfite oxidase, W substitution results in completely inactive enzyme (Johnson and Rajagopalan 1977). In the aldehyde: ferredoxin oxidoreductase of the Archaeon *Pyrococcus furiosus*, substitution of Mo for W results in enzyme unable to catalyze aldehyde oxidation (Sevcenco et al. 2010). Toxicity of the antagonist oxyanion *via* incorrect metal insertion occurs in both W toward molybdoenzymes and Mo toward tungstoenzymes.

Bibliography

- Anbar, A. D. (2004). Molybdenum stable isotopes: Observations, interpretations and directions. *Reviews in Mineralogy and Geochemistry*, 55(1), 429–454.
- Anbar, A. D. (2008). Elements and evolution. *Science*, 322, 1481–1483.
- Anbar, A. D., & Knoll, A. H. (2002). Proterozoic ocean chemistry and evolution: A bioinorganic bridge? *Science*, 297(5584), 1137–1142.
- Andreesen, J. R., & Makdessi, K. (2008). Tungsten, the surprisingly positively acting heavy metal element for prokaryotes. *Annals of the New York Academy of Sciences*, 1125(1), 215–229.
- Archer, C., & Vance, D. (2008). The isotopic signature of the global riverine molybdenum flux and anoxia in the ancient oceans. *Nature Geoscience*, 1(9), 597–600.
- Arnold, G. L., Anbar, A. D., Barling, J., & Lyons, T. W. (2004). Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science*, 304(5667), 87–90.
- Barling, J., & Anbar, A. D. (2004). Molybdenum isotope fractionation during adsorption by manganese oxides. *Earth and Planetary Science Letters*, 217(3), 315–329.
- Barling, J., Arnold, G. L., & Anbar, A. D. (2001). Natural mass-dependent variations in the isotopic composition of molybdenum. *Earth and Planetary Science Letters*, 193(3), 447–457.
- Bekker, A., Holland, H. D., Wang, P. L., Rumble, D. I. I., Stein, H. J., Hannah, J. L., & Beukes, N. J. (2004). Dating the rise of atmospheric oxygen. *Nature*, 427(6970), 117–120.
- Böning, C. W., Dispert, A., Visbeck, M., Rintoul, S. R., & Schwarzkopf, F. U. (2008). The response of the Antarctic circumpolar current to recent climate change. *Nature Geoscience*, 1(12), 864–869.
- Bruland, K. W., Franks, R. P., Knauer, G. A., & Martin, J. H. (1979). Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in sea water. *Analytica Chimica Acta*, 105, 233–245.
- Buc, J., Santini, C. L., Giordani, R., Czjzek, M., Wu, L. F., & Giordano, G. (1999). Enzymatic and physiological properties of the tungsten-substituted molybdenum TMAO reductase from *Escherichia coli*. *Molecular Microbiology*, 32(1), 159–168.
- Calvert, S. E., & Pedersen, T. F. (1993). Geochemistry of recent oxic and anoxic marine sediments: Implications for the geological record. *Marine Geology*, 113(1), 67–88.
- Canfield, D. E. (2005). The early history of atmospheric oxygen: Homage to Robert M. Garrels. *Annual Review of Earth and Planetary Sciences*, 33, 1–36.
- Capone, D. G., Popa, R., Flood, B., & Nealson, K. H. (2006). Geochemistry. Follow the nitrogen. *Science*, 312(5774), 708–709.
- Collier, R. W. (1985). Molybdenum in the northeast Pacific Ocean. *Limnology and Oceanography*, 30(6), 1351–1354.
- Crusius, J., Calvert, S. E., Pedersen, T. F., & Sage, D. (1996). Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and anoxic conditions of deposition. *Earth and Planetary Science Letters*, 145, 65–79.
- Dietrich, H. M., Törnroos, K. W., & Anwander, R. (2006). “Ionic carbenes”: Synthesis, structural characterization, and reactivity of rare-earth metal methyldiene complexes. *Journal of the American Chemical Society*, 128(29), 9298–9299.
- Dupont, C. L., Yang, S., Palenik, B., & Bourne, P. E. (2006). Modern proteomes contain putative imprints of ancient shifts in trace metal geochemistry. *Proceedings of the National Academy of Sciences*, 103(47), 17822–17827.
- Emerson, S. R., & Huested, S. S. (1991). Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. *Marine Chemistry*, 34(3), 177–196.
- 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.
- Falkowski, P. G., Fenchel, T., & DeLong, E. F. (2008). The microbial engines that drive Earth’s biogeochemical cycles. *Science*, 320(5879), 1034–1039.

- Falkowski, P. G., Katz, M. E., Knoll, A. H., Quigg, A., Raven, J. A., Schofield, O., & Taylor, F. J. R. (2004). The evolution of modern eukaryotic phytoplankton. *Science*, 305(5682), 354–360.
- Fike, D. A., Grotzinger, J. P., Pratt, L. M., & Summons, R. E. (2006). Oxidation of the Ediacaran ocean. *Nature*, 444(7120), 744–747.
- Goldberg, T., Archer, C., Vance, D., & Poulton, S. W. (2009). Mo isotope fractionation during adsorption to Fe (oxyhydr) oxides. *Geochimica et Cosmochimica Acta*, 73(21), 6502–6516.
- Hagedoorn, P. L., Hagen, W. R., Stewart, L. J., Docrat, A., Bailey, S., & Garner, C. D. (2003). Redox characteristics of the tungsten DMSO reductase of *Rhodobacter capsulatus*. *FEBS Letters*, 555(3), 606–610.
- Helz, G. R., Miller, C. V., Charnock, J. M., Mosselmans, J. F. W., Patrick, 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.
- Hille, R. (2002). Molybdenum and tungsten in biology. *Trends in Biochemical Sciences*, 27(7), 360–367.
- Holland, H. D. (2006). The oxygenation of the atmosphere and oceans. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 361(1470), 903–915.
- Isley, A. E., & Abbott, D. H. (1999). Plume-related mafic volcanism and the deposition of banded iron formation. *Journal of Geophysical Research: Solid Earth (1978–2012)*, 104(B7), 15461–15477.
- Johnson, J. L., & Rajagopalan, K. V. (1977). Tryptic cleavage of rat liver sulfite oxidase. Isolation and characterization of molybdenum and heme domains. *Journal of Biological Chemistry*, 252(6), 2017–2025.
- Kasting, J. F. (1993). Earth's early atmosphere. *Science*, 259(5097), 920–926.
- Kasting, J. F., & Siefert, J. L. (2002). Life and the evolution of Earth's atmosphere. *Science*, 296(5570), 1066–1068.
- Knoll, A. H., Javaux, E. J., Hewitt, D., & Cohen, P. (2006). Eukaryotic organisms in Proterozoic oceans. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 361(1470), 1023–1038.
- Lazcano, A., & Miller, S. L. (1996). The origin and early evolution of life: Prebiotic chemistry, the pre-RNA world, and time. *Cell*, 85(6), 793–798.
- Liermann, L. J., Guynn, R. L., Anbar, A., & Brantley, S. L. (2005). Production of a molybdophore during metal-targeted dissolution of silicates by soil bacteria. *Chemical Geology*, 220(3), 285–302.
- Lyons, T. W., Reinhard, C. T., & Planavsky, N. J. (2014). The rise of oxygen in Earth's early ocean and atmosphere. *Nature*, 506, 307–315.
- Malinovsky, D., Rodushkin, I., Baxter, D. C., Ingri, J., & Öhlander, B. (2005). Molybdenum isotope ratio measurements on geological samples by MC-ICPMS. *International Journal of Mass Spectrometry*, 245(1), 94–107.
- McManus, J., Berelson, W. M., Severmann, S., Poulson, R. L., Hammond, D. E., Klinkhammer, G. P., & Holm, C. (2006). Molybdenum and uranium geochemistry in continental margin sediments: Paleoproxy potential. *Geochimica et Cosmochimica Acta*, 70(18), 4643–4662.
- McManus, J., Nägler, T. F., Siebert, C., Wheat, C. G., & Hammond, D. E. (2002). Oceanic molybdenum isotope fractionation: Diagenesis and hydrothermal ridge-flank alteration. *Geochemistry, Geophysics, Geosystems*, 3(12), 1–9.
- Morford, J. L., & Emerson, S. (1999). The geochemistry of redox sensitive trace metals in sediments. *Geochimica et Cosmochimica Acta*, 63(11), 1735–1750.
- Nägler, T. F., Mills, M. M., & Siebert, C. (2004). Biological fractionation of Mo isotopes during N₂ fixation by *Trichodesmium* sp. IMS 101. *Geochimica et Cosmochimica Acta*, 68, A364.
- Nägler, T. F., Siebert, C., Lüschen, H., & Böttcher, M. E. (2005). Sedimentary Mo isotope record across the Holocene fresh-brackish water transition of the Black Sea. *Chemical Geology*, 219(1), 283–295.
- Navarro-González, R., McKay, C. P., & Mvondo, D. N. (2001). A possible nitrogen crisis for Archaean life due to reduced nitrogen fixation by lightning. *Nature*, 412(6842), 61–64.

- Neubert, N., Nögler, 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.
- Pearce, C. R., Cohen, A. S., Coe, A. L., & Burton, K. W. (2008). Molybdenum isotope evidence for global ocean anoxia coupled with perturbations to the carbon cycle during the early Jurassic. *Geology*, 36(3), 231–234.
- Pietruszka, A. J., Walker, R. J., & Candela, P. A. (2006). Determination of mass-dependent molybdenum isotopic variations by MC-ICP-MS: An evaluation of matrix effects. *Chemical Geology*, 225(1), 121–136.
- Poulson, R. L., Siebert, C., McManus, J., & Berelson, W. M. (2006). Authigenic molybdenum isotope signatures in marine sediments. *Geology*, 34(8), 617–620.
- Poulton, S. W., Fralick, P. W., & Canfield, D. E. (2004). The transition to a sulphidic ocean ~1.84 billion years ago. *Nature*, 431(7005), 173–177.
- Prantzos, N., Vangioni-Flam, E., & Chauveau, S. (1994). Evolution of carbon and oxygen in the galaxy: The effect of metallicity dependent yields. *Astronomy and Astrophysics*, 285, 132–139.
- Rubey, W. W. (1955). Development of the hydrosphere and atmosphere, with special reference to probable composition of the early atmosphere. *Geological Society of America Special Papers*, 62, 631–650.
- Sageman, B. B., & Lyons, T. W. (2003). Geochemistry of fine-grained sediments and sedimentary rocks. *Treatise on Geochemistry*, 7, 115–158.
- Sevcenco, A. M., Bevers, L. E., Pinkse, M. W., Krijger, G. C., Wolterbeek, H. T., Verhaert, P. D., et al. (2010). Molybdenum incorporation in tungsten aldehyde oxidoreductase enzymes from *Pyrococcus furiosus*. *Journal of Bacteriology*, 192(16), 4143–4152.
- Siebert, C., Nögler, T. F., von Blanckenburg, F., & Kramers, J. D. (2003). Molybdenum isotope records as a potential new proxy for paleoceanography. *Earth and Planetary Science Letters*, 211(1), 159–171.
- Taylor, S. R., & McLennan, S. M. (1982). Geochemical constraints on the growth of the continental crust. *The Journal of Geology*, 90, 347–361.
- Tossell, J. A. (2005). Calculating the partitioning of the isotopes of Mo between oxidic and sulfidic species in aqueous solution. *Geochimica et Cosmochimica Acta*, 69(12), 2981–2993.
- Tribouillard, N., Algeo, T. J., Lyons, T., & Riboulleau, A. (2006). Trace metals as paleoredox and paleoproductivity proxies: An update. *Chemical Geology*, 232(1), 12–32.
- Wächtershäuser, G. (2007). On the chemistry and evolution of the pioneer organism. *Chemistry and Biodiversity*, 4(4), 584–602.
- Wasylenki, L. E., Anbar, A. D., & Gordon, G. W. (2006). Temperature dependence of Mo isotope fractionation during adsorption to δ -MnO₂: Implications for the paleoredox proxy. *Geochimica et Cosmochimica Acta*, 70(18), A691.
- Wieser, M. E., & de Laeter, J. R. (2003). A preliminary study of isotope fractionation in molybdenites. *International Journal of Mass Spectrometry*, 225(2), 177–183.
- Williams, R. P., & Fraústo da Silva, J. J. R. (2003). Evolution was chemically constrained. *Journal of Theoretical Biology*, 220(3), 323–343.
- Wu, J., Boyle, E., Sunda, W., & Wen, L. S. (2001). Soluble and colloidal iron in the oligotrophic North Atlantic and North Pacific. *Science*, 293(5531), 847–849.
- Zerkle, A. L., House, C. H., Cox, R. P., & Canfield, D. E. (2006). Metal limitation of cyanobacterial N₂ fixation and implications for the precambrian nitrogen cycle. *Geobiology*, 4(4), 285–297.
- Zheng, Y., Anderson, R. F., van Geen, A., & Kuwabara, J. (2000). Authigenic molybdenum formation in marine sediments: A link to pore water sulfide in the Santa Barbara Basin. *Geochimica et Cosmochimica Acta*, 64(24), 4165–4178.

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