A molybdenum-isotope perspective on Phanerozoic de-oxygenation events

Alexander J. Dickson

Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN
*alex.dickson@earth.ox.ac.uk

The expansion and contraction of sulphidic depositional conditions in the oceans can be tracked with the isotopic composition of molybdenum in marine sediments. However, molybdenum isotope data are often subject to multiple, conflicting interpretations. Here I present a compilation of molybdenum isotope data from three time intervals: the Toarcian Oceanic Anoxic Event about 183 million years ago, Oceanic Anoxic Event 2 about 94 million years ago, and two early Eocene hyperthermal events from 56 to 54 million years ago. A comparison of data from sites located in different hydrographic settings tightly constrains the molybdenum cycle for these intervals, allowing a direct comparison of the expanse of sulphidic conditions in each interval compared to today. Nonetheless, tracing rates of redox change over such rapid climatic events using molybdenum-isotopes remains challenging. Future efforts to achieve this goal might be accomplished by analysing specific mineral phases, using complementary redox-sensitive geochemical techniques, and by linking isotopic observations with Earth System modelling. Such improvements will make it possible to more fully assess the links between ocean deoxygenation, climatic and oceanographic changes, and biotic turnover.

Episodes of environmental change in Earth's history are often associated with the extinction, adaptation and turnover of marine fauna and flora, the widespread burial of organic matter and trace metals, and disruptions to biogeochemical cycling. These features have often been attributed to the expansion and intensification of deoxygenated water masses in the world's oceans. Deoxygenation occurs when the consumption of oxygen during microbial degradation of organic matter outstrips its supply by diffusion across the air-sea interface and subsequent advection into the ocean interior. Thus, changes in the composition of marine primary producers, alleviation of nutrient limitation, water mass stratification, and the flooding or desiccation of continental shelves and marginal marine basins during episodes of sea-level change, have all been invoked as key processes controlling marine deoxygenation, and in turn, on biogeochemical and biological perturbations that occurred episodically throughout geological time[1].

Assessing the magnitude of marine deoxygenation during geological episodes of environmental perturbation is an important task, because the importance of the different processes controlling oxygen distributions in the oceans may not have been constant through time. Furthermore, estimating rates of oxygen change is important because these can strongly impact the ability of organisms to adapt or respond to environmental stress[2]. Unfortunately, accurate reconstructions of oxygen concentrations in the past are difficult to achieve. This difficulty arises partly because of the lack of proxy approaches that are able to quantitatively constrain oxygen concentrations in seawater, and partly by the loss to subduction of the sedimentary record deposited on oceanic crust during some of the largest climatic and biotic extinction events in the Phanerozoic Aeon. Consequently, to assess the extent and magnitude of marine deoxygenation at these times, isotopic methods that can record global-scale redox processes need to be employed on fragments of the marine sedimentary record left preserved on the continental crust.

One such method, the molybdenum-isotope redox proxy, has been widely used to reconstruct the distribution of oxic and euxinic (anoxia with hydrogen sulphide in seawater) conditions in past oceans[3–10]. However, disentangling the isotopic effects of local Mo-speciation in sediments from global-scale changes in the Mo mass balance of the oceans can be difficult. This contribution highlights how data from multiple sedimentary successions deposited in demonstrably euxinic environments, but in contrasting hydrographic regimes, can be compared in order to arrive at precise estimates of the Mo-isotope composition of open-ocean seawater. The first compilation of Mo-isotope data for several rapid environmental change events of the Phanerozoic is presented, to highlight the progress that has been made using Mo isotopes to understand the magnitude of de-oxygenation during these events. The limitations of the Mo-isotope proxy are discussed, especially in view of understanding rates of redox change over geologically short time-intervals, and future research efforts are outlined that may be directed to circumvent these limitations.

The molybdenum-isotope redox proxy

At a global scale, the Mo-isotope composition of seawater (expressed as $\delta^{98/95}Mo = (((98/95_{sample} – 98/95_{NIST\ 3134})/\ 98/95_{NIST\ 3134}) * 1000) + 0.25)$[11] is controlled by the amount and isotopic composition of input fluxes of Mo to the oceans from the weathering of upper continental crust rocks[12–14] and low-temperature hydrothermal fluids[14, 15]; and by the amount and isotopic composition of output fluxes of Mo into oxide-rich and sulphide-rich sedimentary deposits (Fig. 1). The input fluxes of Mo to the oceans may be altered by catchment-scale processes such as interaction with oxyhydroxides and organic matter in soils, rivers and estuaries[13, 14, 16, 17], and by incongruent weathering of rocks with varying concentrations and isotopic compositions of Mo in different mineral phases[13]. The output fluxes of Mo from the ocean are governed by the adsorption of Mo onto manganese and iron oxyhydroxide minerals, which are fractionated from seawater by -0.8 to -3‰[12, 18–21]; and by the formation of Mo-sulphides in the water column and below the sediment-water interface, which are -0.9‰ to -0.5‰ lighter than seawater[22, 23]. The exact magnitude of the difference between Mo-sulphides and seawater depends on the concentration of aqueous H_2S and the sulphur-speciation of dissolved Mo[24–27], with low aqueous H_2S concentrations yielding very light sedimentary isotope compositions[26–28]. Today, the balance between the input and output fluxes of Mo to the oceans results in a seawater residence time of ~440 ka[29] and a homogenous isotopic composition of 2.34 ‰[11, 30]. This composition reflects approximately equal removal fluxes of Mo into sulphide-rich and oxide-rich sediments, due to the higher efficiency of Mo removal into sulphidic environments, which cover <0.5 % of the present-day global seafloor[23, 31]. If the balance of the input and redox-dependent output fluxes change, the Mo-isotope composition of global seawater will change, with a decrease to lighter values signifying a proportional increase in the removal flux of Mo into sedimentary sulphides.

The seawater Mo-isotope composition of past oceans can be traced in marine basins where deep-water renewal rates are low, where a stable chemocline is located within the water column, where the remineralisation of organic matter enables aqueous H_2S concentrations to increase, and where there is a supply of reactive iron[32]. In these circumstances, the removal flux of Mo into sediments can be efficient due to the conversion of molybdate to tetrathiomolybdate[24].

Tetrathiomolybdate (or polysulphide molybdenum species[33]) can be rapidly scavenged by organic matter[34], pyrite[34], or Mo-Fe-S colloids[32]. The removal of >90 % of dissolved Mo into accumulating sediments (e.g. in the Black Sea[27, 35]) can cause the basin seawater to evolve to a heavier isotopic composition. Sediments accumulating from the seawater in these settings can ultimately evolve to isotope compositions that are close to that of dissolved Mo in the global ocean (Fig. 1). This behaviour is referred to as 'quantitative drawdown'.

Identifying quantitative drawdown of Mo in the palaeo-record is difficult. Verifying the presence of palaeo-euxinia is an important first step[36], using methods including iron-speciation[8, 9, 31, 36], biomarkers for H_2S in the water column[6, 37] and trace-metal distributions[3–8]. Euxinia limits the potential for the mixing of isotopically light Mo into sediments, and increases the likelihood that H_2S_{aq} concentrations were high enough to allow the conversion of Mo into tetrathiomolybdate. However, quantitative removal of Mo may be inhibited in euxinic basins due to extremely high or extremely low concentrations of aqueous H_2S, very high seawater pH, or where Mo renewal rates through exchange with open-ocean seawater are high[32, 35]. In these settings, sedimentary Mo-isotope compositions are typically ~0.7 ‰ lower than that of global seawater[3, 4, 22, 31], with much lower values in situations with very low H_2S concentrations[26] (Fig. 1). The Mo-isotope composition of sediments deposited in euxinic conditions is therefore often considered as a minimum constraint on the composition of coeval seawater[9, 31, 37, 38]. Over ~$10^{7–9}$ year intervals of Earth history, this problem does not inhibit the use of Mo isotopes to discern first-order shifts in global ocean redox[3, 9, 38]. However, for the shorter, potentially smaller magnitude shifts in redox hypothesized for Phanerozoic events[1], such imprecision in detecting the seawater Mo-isotope composition complicates interpretations of redox change.

Constraining seawater Mo-isotope compositions with multi-site data compilations

The problem of identifying quantitative Mo drawdown in the geological past can be tackled empirically. In the absence of oxyhydroxide-associated molybdenum phases, time-equivalent successions of marine sediments deposited in euxinic conditions should exhibit Mo-isotope compositions approximately spanning the ~0.7 ‰ range that exists between modern euxinic settings experiencing quantitative and non-quantitative removal of Mo from seawater (Fig. 2). If this isotopic range can be identified in time-equivalent black-shale deposits that accumulated underneath euxinic water columns, the global seawater isotope composition can be estimated from the upper end of the measured range of values. This assumption would hold regardless of the removal mechanism invoked to explain the high proportion of Mo removal from the water column in restricted marine basins[24, 25, 32–34].

This approach can be demonstrated for three time intervals from the early Cenozoic and Mesozoic eras: the early Eocene, encompassing the Paleocene–Eocene Thermal Maximum (PETM, ~55.9 Ma) and Eocene Thermal Maximum 2 (ETM-2, ~54 Ma); the mid-Cretaceous, encompassing Oceanic Anoxic Event 2 (OAE-2, ~94 Ma); and the early Jurassic, encompassing the Toarcian Oceanic Anoxic Event (T-OAE, ~183 Ma). Each of these intervals is associated with perturbations to the global carbon cycle, climatic disruption, and enhanced organic matter burial[1]. Organic-rich mudrock successions have been identified for each interval where depositional euxinia has been independently demonstrated, and where molybdenum isotopes have been measured[5–8, 31, 40–43]. The datasets can be categorized for their hydrographic situation using elemental co-variation plots such as Mo/total organic carbon and Mo_{EF}/U_{EF} (where 'EF' denotes the elemental enrichment above typical upper continental crust concentrations), which reflect the Mo inventory and the degree of hydrographic restriction in euxinic ocean basins[35, 44]. The modern Black Sea, where quantitative drawdown occurs, is characterized by low Mo/TOC ratios and a shallow gradient of Mo_{EF}/U_{EF}[35, 44]. Additionally, a host of additional observations, such as sedimentary structures and the occurrence of sea-floor dwelling fauna, can provide evidence for the hydrographic situation of a marine basin[6–8, 37].

When categorized by hydrographic state, the comparison of Mo-isotope data for euxinic settings in each episode of geological time in Fig. 2 clearly exhibits the same ~0.7 ‰ range between 'restricted' and 'unrestricted' settings as seen for the modern data. This range can also be observed as oscillations in $\delta^{98/95}$Mo over short stratigraphic intervals at the same site, where associated elemental indices demonstrate repeated shifts between 'quantitative drawdown' and 'non-quantitative' drawdown of Mo, along with the sustained presence of euxinic depositional conditions[5, 7, 42]. The heaviest value for each event can be taken to approximate the Mo-isotope composition of global seawater, especially when the lower range of the oscillations is independently pinned with data from a separate euxinic location experiencing non-quantitative drawdown.

Estimating the magnitude of past marine euxinia

The compilations in Fig. 2 show that the seawater Mo-isotope compositions during the early Eocene, mid-Cretaceous, and the Early Jurassic were unambiguously lower than at the present day. Furthermore, the range of values for demonstrably euxinic sedimentary successions highlights the danger of taking evidence for palaeo-euxinia as *de-facto* reasoning to infer quantitative drawdown of Mo in the sedimentary record, especially in the absence of additional constraints on basin configuration and palaeogeography[9, 31, 37, 38].

Assuming minimal change in the input flux of Mo to the oceans over long (10^7 year) timescales (Fig. 3), the estimates of the seawater Mo-isotope composition for the events in Fig. 2 require the removal flux of molybdenum into sulphidic sediments to have been higher at these times compared to the present. Quantifying the extent of seafloor euxinia from these data can be achieved by scaling the present day Mo-sulphide removal flux to the equivalent area of seafloor receiving this flux (~0.1–0.5 %), and applying this scaling factor to the Mo-sulphide removal fluxes estimated from the isotopic data[45, 46]. This exercise is subject to considerable uncertainties. Complexities include the incorporation of Mo sulphides into sediments accumulating in zones of sulphate reduction within the sedimentary column, but where aqueous H_2S is not present in the overlying water column; and the fact that the scaling function exhibits non-linearity both due to the progressive depletion of the oceanic dissolved Mo inventory during periods of expanded marine euxinia, and due to the development of low-oxygen conditions mainly on oceanic shelves and marginal basins[46]. Nonetheless, such calculations provide crude limits on the extent of seafloor euxinia during the two Mesozoic intervals of ~2–10 %, a range that is in agreement with estimates from sulphur-isotope data[47]. The extent of euxinia estimated from the Mo-isotope data imply that substantial areas of the ocean remained non-euxinic during the two Mesozoic intervals. Non-euxinic areas may have been fully oxygenated; or characterized by low-oxygen, but non-euxinic conditions. The latter situation may have prevailed over large parts of the global seafloor during OAE-2[48].

The compilation (Fig. 2) also shows that the Mo-isotope composition of euxinic rocks deposited in restricted and non-restricted settings during the Jurassic and Cretaceous intervals were strikingly similar. This similarity may point to near-identical redox conditions in the global oceans. Alternatively, the input flux of Mo to the oceans may have been different during each event. At the present day, the flux-weighted average Mo-isotope composition of rivers is higher than that of upper continental crust rocks (~0.7 ‰ versus ~0.3 ‰[3, 16]), a difference which is likely to be due to trapping of the lighter Mo isotopes during their transit through river catchments. If the gross weathering regime was more congruent during either the early Jurassic or the mid-Cretaceous, it might have been possible for the flux-weighted riverine input of Mo to have had an isotopic composition that was somewhat closer to that of upper continental crust rocks. Such a difference would allow the inferred seawater Mo-isotope composition to reflect ~15% less burial of Mo in sulphidic sediments globally than for a situation where the riverine input was isotopically closer the present-day average of ~0.7 ‰[16] (Fig. 3).

Estimating rates of change of past marine euxinia

Despite the ability of multi-site Mo-isotope compilations to advance our understanding of the magnitude of marine deoxygenation, it is still difficult to use Mo isotopes to estimate rates of redox change at a resolution $<10^{6-7}$ years. This difficulty mainly arises because organic-rich sedimentary archives are discontinuous in the geological record, making it difficult to splice together data from multiple deposits (and also ideally from temporally equivalent successions).

Limitation on the temporal resolution of redox reconstructions obtainable from Mo isotopes is a particular problem for investigating episodes of rapid environmental change where redox conditions in the ocean may evolve over short timescales of $<10^{3-4}$ years. For OAE-2, the global seawater Mo inventory is likely to have experienced a ≤10 fold decrease[49]. This decrease is likely to have impacted the global seawater Mo-isotope composition, but current reconstructions only allow for a snapshot of global redox from organic-rich sediments deposited at the peak of the event[7, 8, 40].

Finding new ways for Mo isotopes to estimate rates of ocean de-oxygenation is an important challenge. One approach is to investigate the use of alternative sedimentary phases as carriers of the seawater Mo-isotope composition. Early investigations of carbonates are promising[10], but the fractionation of Mo from seawater into carbonates needs to be determined experimentally, and the possible roles of biology and diagenesis in altering this signal need to be better understood[10, 50]. Furthermore, since Mo abundances are extremely low in carbonates, but comparatively high in detrital phases, effective leaching techniques need to be established to extract isotopic signals from the bulk carbonates that typify the ancient geological record. The Mo-isotope composition of Fe-Mn crusts may also provide a route towards reconstructing secular shifts in the global seawater composition[12]. However, this approach is hindered by the difficulty of generating accurate age-models for such sedimentary deposits. Additionally, there are a range of fractionation factors for Mo adsorption onto different Mn and Fe minerals[18–21]. Unless the precise mineralogy of the measured crust can be established, correcting their Mo-isotope compositions to the coeval seawater value is inherently uncertain. Fe-Mn crusts also typically accumulate very slowly, limiting their ability to record rapid environmental change events.

Another key limitation with using the Mo-isotope proxy to track rates of change of marine de-oxygenation is the insensitivity of Mo to subtle (but biologically important) changes in oxygenation that may occur prior to sulphate reduction, or in oxygen minimum zones located within the water column with limited geochemical interaction with the seafloor. At the other extreme, in situations where the rapid removal of Mo from seawater is facilitated by the spread of marine euxinia, the seawater Mo inventory can be depleted until its isotope composition effectively equals that of the flux-weighed inputs[12, 16]. Since the removal rate of Mo into sulphidic deposits can be very fast, this behaviour places an upper limit on the ability of Mo-isotopes to record expansions of marine euxinia greater than a few percent of the total seafloor[46]. One approach for circumventing these problems is to use the isotopic composition of redox-sensitive elements such as zinc, vanadium, thallium and chromium. These elements have shorter oceanic residence times than Mo, and may respond faster to abrupt perturbations to their elemental cycles. Furthermore, their isotopic behaviour is governed by reactions that take place at differing redox potentials, thereby allowing a richer insight into the progression of marine de-oxygenation at a global scale during past climatic events[9, 28].

Data-model comparisons and outlook

Earth-system modelling might further advance our understanding of molybdenum cycling in two key respects. Firstly, the complexity of the Mo-isotope cycle, with multiple input and output fluxes to the oceans, can yield non-unique interpretations of palaeo-data. In this situation, biogeochemical models that are able to simulate realistic changes in the Mo cycle will be extremely helpful in generating more accurate reconstructions of past ocean chemistry. Secondly, Earth System models constrained by isotopic data could allow an improved process-based understanding of how multiple drivers (temperature, ventilation rates, etc) might have interacted to produce significant de-oxygenation in the past. Such exercises require realistic model parameterization, not least of the biogeochemically important redox transformations that take place on shallow continental shelves and in marine embayments, which may not be well represented in simplified model palaeogeographies. The coupling of isotope geochemistry and Earth System modelling, while non-trivial to achieve, may improve our understanding of the palaeo Mo cycle; the rate, magnitude and spatial extent of past ocean redox changes; and our understanding of how temperature, organic-matter productivity, and ocean circulation interacted to control oxygen distributions in the past.

For all its complexities, the Mo-isotope composition of organic-rich marine sediments is one of only a few proxies available to reconstruct the extent of marine euxinia in ancient oceans. It thus holds a critical role in testing hypotheses linking biotic change, climate and ocean chemistry. The multi-site compilations presented here demonstrate how precise reconstructions of the Mo cycle can be obtained for past intervals of Phanerozoic environmental change. These reconstructions of expanded euxinia show that ocean de-oxygenation is linked with warmer climate conditions, and also with extinction events in the marine realm. These events signpost the likely trajectory of ocean de-oxygenation under a rapidly warming climate system.

References

1. Jenkyns, H.C., Geochemistry of Oceanic Anoxic Events. *Geochem., Geophys., Geosyst.* **11**, Q03004, doi:10.1029/2009GC002788 (2010).

2. Ridgwell, A. &d Schmidt, D.N., Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release. *Nat. Geosci.* **3**, 196–200 (2010).

3. Kendall, B., Dahl, T.W. & Anbar, A.D., Good golly, why moly? The stable isotope geochemistry of molybdenum. *Reviews in Mineralogy and Geochemistry* **82**, 683–732 (2017).

4. Arnold, G.L., Anbar, A.D., Barling, J. & Lyons, T.W.,, Molybdenum isotope evidence for widespread anoxia in Mid-Proterozoic Oceans. *Science* **304**, 87–90 (2004).

5. Pearce, C.R., Cohen, A.S. Coe, A.L. & Burton, K.W., Molybdenum isotope evidence for global ocean anoxia coupled with perturbations to the carbon cycle during the Early Jurassic, *Geology* **36**, 231–234 (2008).

6. Dickson, A.J., Cohen, A.S. & Coe, A.L., Seawater oxygenation during the Paleocene-Eocene Thermal Maximum. *Geology* **40**, 639–642 (2012).

7. Dickson, A.J., Jenkyns, H.C., Porcelli, D., van den Boorn, S. & Idiz, E., Basin-scale controls on the molybdenum isotope composition of seawater during Oceanic Anoxic Event 2 (Late Cretaceous). *Geochim. Cosmochim. Acta* 178, 291–306 (2016).

8. Westermann, S., Vance, D., Cameron, V., Archer, C. & Robinson, S.A., Heterogeneous oxygenation states in the Atlantic and Tethys oceans during Oceanic Anoxic Event 2. *Earth Planet. Sci. Lett.* 4**04**, 178–189 (2014).

9. Kendall, B. et al., Uranium and molybdenum isotope evidence for an episode of widespread ocean oxygenation during the late Ediacaran Period. *Geochim Cosmochim Acta* **156**, 173–193 (2015).

10. Voegelin, A.R., Nägler, T.F., Samankassou, E. & Villa, I.M., Molybdenum isotopic composition of modern and Carboniferous carbonates*. Chem. Geol.* **265**, 488–498 (2009).

11. Nägler, T.F. et al., Proposal for an international molybdenum isotope measurement standard and data representation. *Geostand. Geoanal. Res.* 38, 149–151 (2014).

12. Siebert, C., Nägler, T.F., von Blanckenburg, F., & Kramers, J.D.,, Molybdenum isotope records as a potential new proxy for paleoceanography: *Earth Planet. Sci. Lett.* **211**, 159–171 (2003).

13. Neubert, N. et al., The molybdenum isotopic composition in river water: constraints from small catchments. *Earth Planet. Sci. Lett.* **304**, 180–190 (2011).

14. Pearce, C.R., Burton, K.W., Pogge van Strandmann, P.A.E., James, R.H. & Gíslason, S.R., Molybdenum isotope behaviour accompanying weathering and riverine transport in a basaltic terrain. *Earth Planet. Sci. Lett.* **295**, 104–114 (2010).

15. McManus, J., Nägler, T, Siebert, C., Wheat, C.G. & Hammond, D.E., Oceanic molybdenum isotope fractionation: diagenesis and hydrothermal ridge-flank alteration. *Geochem., Geophys., Geosyst.* **3**, 1078, doi:10.1029/2002GC000356 (2002).

16. Archer, C. & Vance, D., The isotopic signature of the global riverine molybdenum flux and anoxia in the ancient oceans. *Nat. Geosci.* **1**, 597–600 (2008).

17. Siebert, C. et al., Molybdenum isotope fractionation in soils: influence of redox conditions, organic matter and atmospheric inputs. *Geochim. Cosmochim. Acta* **62**, 1–24 (2015).

18. Barling, J., Arnold, G.L. & Anbar, A.D., Natural mass-dependent variations in the isotopic composition of molybdenum. *Earth Planet. Sci. Lett.* **193**, 447–457 (2001).

19. Barling, J. & Anbar, A.D., Molybdenum isotope fractionation during adsorption by manganese oxides, *Earth Planet. Sci. Lett.* **217**, 315–329 (2004).

20. Wasylenki, L.E., Rolfe, B.A., Weeks, C.L., Spiro, T.G. & Anbar, A.D., Experimental investigation of the effects of temperature and ionic strength on Mo isotope fractionation during adsorption to manganese oxides. *Geochim. Cosmochim. Acta* **72**, 5997–6005 (2008).

21. Goldberg, T., Archer, C., Vance, D. & Poulton, S.W., Mo isotope fractionation during adsorption to Fe (oxyhydr)oxides, *Geochim. Cosmochim. Acta* **73**, 6502–6516 (2009).

22. Poulson, R.L., Siebert, C., McManus, J. & Berelson, W.M., Authigenic molybdenum isotope signatures in marine sediments, *Geology* **34**, 617–620 (2006).

23. Poulson-Brucker, R.L., McManus, J., Severmann, S. & Berelson, W.M., Molybdenum behavior during early diagenesis: insights from Mo isotopes. *Geochem., Geophys., Geosyst.* **10**, Q06010, doi: 10.1029/2008GC002180 (2009).

24. Helz, G.R. et al., Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. *Geochimica et Cosmochimica Acta* **60**, 3631–3642 (1996).

25. Eriksson, B.E. a& Helz, G.R., Molybdenum (IV) speciation in sulphidic waters: stability and lability of thiomolybdates, *Geochim. Cosmochim. Acta* **64**, 1149–1158 (2000).

26. Neubert, N., Nägler T.F., & Böttcher, M.E., Sulphidity controls molybdenum isotope fractionation into euxinic sediments: evidence from the modern Black Sea, *Geology* **36**, 775–778 (2008).

27. Nägler, T.F., Neubert, N., Böttcher, M.E., Dellwig, O. & Schnetger, B. Molybdenum isotope fractionation in pelagic euxinia: evidence from the modern Black and Baltic Seas. *Chem. Geol.* **289**, 1–11 (2011).

28. Azrieli-Tal, I. et al., Evidence from molybdenum and iron isotopes and molybdenum–uranium covariation for sulphidic bottom waters during Eastern Mediterranean sapropel S1 formation. *Earth Planet. Sci. Lett.,* **393**, 231-242 (2014).

29. Miller, C.A., Peucker-Ehrenbrink, B., Walker, B.D. & Marcantonio, F., Re-assessing the surface cycling of molybdenum and rhenium. *Geochim. Cosmochim. Acta* **75**, 7146–7179 (2011).

30. Nakagawa, Y. The molybdenum isotopic composition of the modern ocean. *Geochemical Journal* **46**, 131–141 (2012).

31. Dickson, A.J., Cohen, A.S. & Coe, A.L., Continental margin molybdenum isotope signatures from the early Eocene*. Earth. Planet. Sci. Lett.* **405**, 389–395 (2014).

32. Helz, G.R., Bura-Nakić, E. Mikac, N. & Ciglenečki, I., New model for molybdenum behavior in euxinic waters. *Chem. Geol.* **284**, 323–332 (2011).

33. Dahl, T.W., Chappaz, A., Fitt, J.P. & Lyons, T.W., Molybdenum reduction in a sulphidic lake: evidence from X-ray adsorption fine-structure spectroscopy and implications for the Mo paleoproxy. *Geochim. Cosmochim. Acta* **103**, 213–231 (2013).

34. Chappaz, A. et al., Does pyrite act as an important host for molybdenum in modern and ancient euxinic sediments? *Geochim. Cosmochim. Acta* **126**, 112–122 (2014).

35. Algeo, T.J. & Lyons, T.W., Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrologic conditions. *Paleoceanography* **21**, PA1016, doi: 10.1029/PA001112 (2006).

36. Gordon, G.W. et al., When do black shales tell molybdenum isotope tales? *Geology* **37**, 535–538 (2009).

37. Ruebsam, W., Dickson, A.J., Hoyer, E-M. & Schwark, L., Multiproxy reconstruction of oceanographic conditions in the southern epeiric Kupferschiefer Sea (Late Permian) based on redox-sensitive trace elements, molybdenum isotopes and biomarkers. Gondwana Research **44**, 205–218 (2017).

38. Chen, X. et al., Rise to modern levels of ocean oxygenation coincided with the Cambrian radiation of animals. *Nat. Comms* **6**, doi:10.1038/ncomms8142 (2015).

39. Schlanger, S.O. & Jenkyns, H.C., Cretaceous oceanic anoxic events: causes and consequences. *Geol. Mijnbouw* **55**, 179–184 (1976).

40. Goldberg, T., Poulton, S.W., Wagner, T., Kolonic, S.F. and Rehkämper, M., Molybdenum drawdown during Cretaceous Oceanic Anoxic Event 2. *Earth Planet. Sci. Lett.,* **440**, 81–91 (2016).

41. Dickson, A.J. & Cohen, A.S., A molybdenum isotope record of Eocene Thermal Maximum 2: Implications for global ocean redox during the early Eocene. *Paleoceanography* **27**, PA3230, doi:10.1029/2012PA002346 (2012).

42. Dickson, A.J. et al., Molybdenum isotope chemostratigraphy and paleoceanography of the Toarcian Oceanic Anoxic Event (Early Jurassic). *Paleoceanography* **32,** doi:10.1002/2016PA003048 (2017).

43. Dickson, A.J. et al., A Southern Hemisphere record of global trace-metal drawdown and orbital modulation of organic-matter burial across the Cenomanian–Turonian boundary (ODP Site 1138, Kerguelen Plateau). *Sedimentology* **64**, 186–203 (2017).

44. Algeo, T.J. & Tribovillard, N., Environmental analysis of paleoceanographic systems based on molybdenum-uranium covariation. *Chem. Geol.* **268**, 211–225 (2009).

45. Ling, H-F., Gao, J-F., Zhao, K-D., Jiang, S-Y. & Ma, D-S., Comment on "Molybdenum isotope evidence for widespread anoxia in Mid-Proterozoic oceans." *Science* **309**, 1017 (2005).

46, Reinhard, C.T. et al. Proterozoic ocean redox and biogeochemical stasis. *Proc. Natl. Acad. Sci USA* **110**, 5357–5362 (2013).

47. Owens, J.D. et al., Sulfur isotopes track the global extent and dynamics of euxinia during Cretaceous Oceanic Anoxic Event 2. *Proc. Natl. Acad. Sci USA* **110**, 18407–18412 (2013).

48. Monterio, F.M., Pancost, R.D., Ridgwell, A. & Donnadieu, Y., Nutrients as the dominant control on the spread of anoxia and euxinia across the Cenomanian-Turonian oceanic anoxic event [OAE2]: model-data comparison. *Paleoceanography* **27**, PA4209, doi: 10.1029/2012PA002351 (2012).

49. Hetzel, A., Böttcher, M.E., Wortmann, U.G. & Brumsack, H-J., Paleo-redox conditions during OAE 2 reflected in Demerara Rise sediment geochemistry (ODP Leg 207). *Palaeogeogr., Palaeoclimatol., Palaeoecol.* **273**, 302–328 (2009).

50. Romaniello, S.J., Herrmann, A.D. & Anbar, A.D., Syndepositional diagenetic control of molybdenum isotope variations in carbonate sediments from the Bahamas. *Chem. Geol.* **438**, 84–90 (2016).

Corresponding author

Correspondence and requests for materials and data should be addressed to the author (alex.dickson@earth.ox.ac.uk).

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Figure captions

Figure 1: Molybdenum-isotope fluxes in the modern marine environment. Mo-isotope compositions of sediments and waters are from refs 4,12–18, 22, 23, 26, 27, and 30. Mo_{aq} and H_2S_{aq} concentrations are schematic. All Mo-isotope values are relative to NIST 3134 + 0.25 ‰[11].

Figure 2: Compilation of sediment Mo-isotope data. Modern data are from refs 4, 12, 18, 22, 23 and 26. Early Eocene data are from refs 6, 31 and 41. OAE-2 data are from refs 7, 8, 40 and 43. T-OAE data are from refs 5 and 42. The present-day riverine input is from ref. 16. Data for each interval were selected only from stratigraphically coeval intervals, as detailed in the supplementary information. A lower Mo-isotope composition of global seawater reflects more extensive removal of Mo into sulphidic sediments. All Mo-isotope values are relative to NIST 3134 + 0.25 ‰[11].

Figure 3: Simplified mass-balance model of the fractional removal of molybdenum into sulphidic and oxic marine sediments as a function of the isotopic composition of seawater and riverine inputs. The model assumes that the amount and composition of input and output fluxes of Mo are balanced (‘steady state’). The modern flux-weighed average riverine composition of 0.7 ‰[16] is highlighted in bold. The estimated Mo-isotope compositions of seawater for the modern ocean, PETM, OAE-2 and T-OAE are highlighted by dashed lines, with coloured shaded denoting a ±0.1 ‰ uncertainty.