



Continental margin molybdenum isotope signatures from the early Eocene



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ABSTRACT

Molybdenum (Mo) isotope compositions of marine sedimentary deposits that span the Paleocene–Eocene Thermal Maximum (PETM, approximately 56 Ma) are presented from two Tethys Ocean sites (Guru Fatima, Tajikistan and Kheu River, Georgia). Local redox indicators suggest that both locations experienced anoxia and intervals of euxinia (with hydrogen sulphide present in seawater) during the early part of the PETM. However, the Mo-isotope compositions (expressed as $\delta^{98/95}\text{Mo}$) for each site differ significantly. Local redox conditions were very stable at Guru Fatima, where $\delta^{98/95}\text{Mo}$ reached a maximum of 0.96‰, which is $\sim 0.7\text{‰}$ lower than for early Eocene seawater as recently inferred from euxinic Arctic Ocean deposits. This observation supports the argument that a $\sim 0.7\text{‰}$ difference between seawater and anoxic continental margin marine sediments documented at the present day might also be found in the paleo-record. In contrast, local redox conditions at Kheu River were not stable over the study interval, and $\delta^{98/95}\text{Mo}$ were much lower than at Guru Fatima. The low $\delta^{98/95}\text{Mo}$ values at Kheu River are attributed to the influence of post-depositional remobilization of Mo by repeated adsorption and dissolution of Fe–Mn oxides during brief intervals of bottom water oxidation. The data highlight the importance of obtaining multi-proxy constraints on both local redox and paleoceanographic setting before the Mo-isotope compositions of sedimentary deposits can be interpreted accurately.

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1. Introduction

Over recent years there has been significant interest in understanding the role of seawater oxygen concentrations in driving and responding to ecological and environmental change, both past and present. This interest has led to the development of several geochemical proxies to constrain the oxygenation state of seawater using marine sedimentary deposits. These techniques include redox sensitive trace element enrichments (Emerson and Husteded, 1991; Crusius et al., 1996; Tribouillard et al., 2006), proportions of reactive and unreactive iron species (e.g. Raiswell et al., 1988; Canfield, 1989), organic biomarkers (Summons and Powell, 1987; Pancost et al., 2004) and variations in the stable isotope compositions of redox sensitive elements such as molybdenum, uranium and chromium (e.g. Siebert et al., 2003; Stirling et al., 2007; Pearce et al., 2008; Weyer et al., 2008; Montoya-Pino et al., 2010; Brennecke et al., 2011). In particular, trace metal abundances have proven to be useful indicators of marine redox conditions. Vari-

ations in sedimentary trace metal abundances can result from the changing solubility of elements as their oxidation states alter, and/or variable speciation under differing levels of dissolved oxygen in seawater and in sediment pore waters (Tribouillard et al., 2006; Piper and Calvert, 2009). Enrichments of trace elements alone, however, can be strongly overprinted by changes in the dissolved trace metal inventory in seawater either due to expansion/contractions in the extent of marine anoxia globally, or within hydrographically restricted basins (Algeo and Lyons, 2006). For these reasons, the redox dependency of the isotope compositions of transition metal elements (including molybdenum, uranium, chromium) has recently been explored as redox proxies to circumvent ‘reservoir’ effects on trace metal inventories and to obtain better estimates of marine redox conditions over a range of spatial scales.

The molybdenum (Mo) isotope composition of marine sedimentary deposits (expressed as $\delta^{98/95}\text{Mo} = ((^{98/95}\text{Mo}_{\text{sample}} - ^{98/95}\text{Mo}_{\text{standard}}) / ^{98/95}\text{Mo}_{\text{standard}}) * 1000$) has been particularly useful as a seawater redox proxy, because Mo removal from seawater carries distinct isotope fractionations that depend upon the local redox environment (Fig. 1). The global balance of the redox-dependent Mo fluxes determines the isotopic composition of seawater (e.g. Siebert et al., 2003; Poulson-Brucker et al., 2009).

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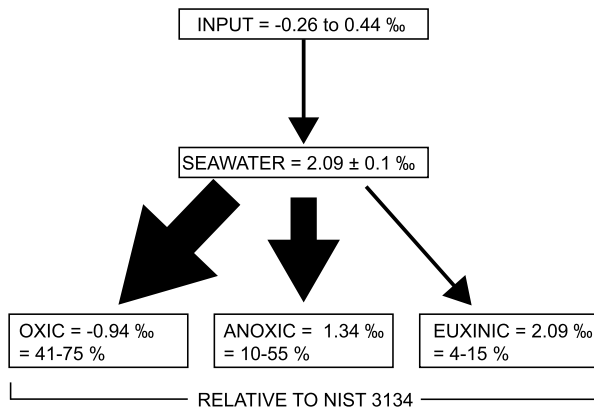


Fig. 1. Global Mo fluxes calculated using $\delta^{98/95}\text{Mo}$ data from different laboratories (Siebert et al., 2003; Poulson et al., 2006; Poulson-Brucker et al., 2009; Archer and Vance, 2008; Neubert et al., 2008; Greber et al., 2012; Goldberg et al., 2013) renormalised to NIST 3134 (Goldberg et al., 2013). The range of the euxinic, anoxic and oxic Mo fluxes are determined by the choice of $\delta^{98/95}\text{Mo}$ for riverine input (igneous rocks = -0.26‰ , Siebert et al., 2003 or mean river water = 0.44‰ , Archer and Vance, 2008), and by varying the size of the euxinic flux according to divergent past estimates ($<5\%$, Neubert et al., 2008 versus $\sim 15\%$, Scott et al., 2008). Estimates are largely within the uncertainties of previous mass balances for Mo (Morford and Emerson, 1991; Poulson-Brucker et al., 2009).

Mo-isotope compositions of past seawater have been inferred from measurements of sedimentary deposits from euxinic environments (e.g. Arnold et al., 2004; Lehmann et al., 2007; Pearce et al., 2008; Wille et al., 2008; Gordon et al., 2009; Wen et al., 2009; Duan et al., 2010; Kendall et al., 2011; Dickson et al., 2012; Dickson and Cohen, 2012; Zhou et al., 2012) under the assumption that in highly sulphidic conditions ('euxinic,' with $>11\ \mu\text{mol/l}$ H_2S , Eriksson and Helz, 2000; Neubert et al., 2008), Mo is removed quantitatively from seawater into seafloor sediments. In these instances, the possible confounding influence of variable isotope fractionations imparted by non-quantitative Mo scavenging by sedimentary phases such as Fe and Mn-oxides (Goldberg et al., 2009; Barling and Anbar, 2004; Siebert et al., 2003), and by conversion of Mo to thiomolybdates ($\text{MoO}_x\text{S}_{4-x}^{2-}$) under low-sulphide concentrations (e.g. Tossell, 2005; Eriksson and Helz, 2000; Nägler et al., 2011) are, theoretically, avoided.

A key question regarding the interpretation of Mo-isotope systematics at the present day is the origin of a $\sim 0.7\text{‰}$ offset observed between sediments deposited in anoxic open-ocean (continental margin) settings and coeval seawater ($\Delta\text{Mo} = \delta^{98/95}\text{Mo}_{\text{seawater}} - \delta^{98/95}\text{Mo}_{\text{anoxic sediments}}$) (Poulson et al., 2006; Poulson-Brucker et al., 2009). This fractionation, which has been used to calculate the present-day fluxes of Mo into different marine redox environments (Poulson-Brucker et al., 2009, recalculated in Fig. 1), may either reflect a mechanism of Mo incorporation into anoxic sediments by conversion to sulphide (e.g. Poulson et al., 2006; Siebert et al., 2006; Poulson-Brucker et al., 2012) or a fortuitous mixing of Mo-isotope fractionations imparted by conversion to $\text{MoO}_x\text{S}_{4-x}^{2-}$, and by adsorption to organic matter/pyrite and Fe/Mn-oxides (Barling and Anbar, 2004; Goldberg et al., 2009; Poulson-Brucker et al., 2012). Reproduction of the $\Delta 0.7\text{‰}$ offset in the paleo-record would support the former mechanism, but this has not previously been demonstrated.

A second key question is the extent to which Mo-isotope compositions in organic-rich sediments record the Mo-isotope composition of coeval seawater. Independent evidence is required to verify the presence of highly sulphidic depositional conditions (with $\text{H}_2\text{S} > 11\ \mu\text{mol/l}$, Neubert et al., 2008) that are required for sedimentary Mo-isotope compositions to approach the seawater value (e.g. Poulson et al., 2006; Gordon et al., 2009). To date, however, there is no proxy that can be used to quantitatively reconstruct the concentration of H_2S in past seawater, despite

some preliminary efforts (e.g. Arnold et al., 2012). Furthermore, there is evidence that Mo can be remobilised if redox conditions in the sediment change after deposition (e.g. Reitz et al., 2007; Scheiderich et al., 2010), thus altering the primary Mo-isotope composition and limiting the use of Mo-isotopes to reconstruct primary depositional processes (e.g. Siebert et al., 2006; Poulson et al., 2006).

In this paper, Mo-isotope compositions of sedimentary deposits are presented from two stratigraphic successions from the Tethys Ocean continental margin that span the Paleocene–Eocene Thermal Maximum (PETM, 56 Myr ago). The main aim of the study is to test whether the 0.7‰ Mo-isotopic difference observed between anoxic continental margin sediments and seawater at the present day (Poulson et al., 2006; Poulson-Brucker et al., 2009) occurred during earlier intervals in Earth's history. Key to testing this hypothesis is the recent characterisation of the Mo-isotope composition of early Eocene seawater from Arctic Ocean sediments (Dickson et al., 2012; Dickson and Cohen, 2012). A secondary aim was to investigate whether slight differences in depositional conditions during the study interval (Dickson et al., 2014) caused different Mo-isotope compositions in contemporaneous sedimentary records.

2. Methods

Samples were obtained from two sections spanning the PETM at Guru Fatima, Tajikistan and Kheuv River, Georgia. The geological setting of these sites has been discussed by Gavrilov et al. (1992, 1997, 2009).

$\delta^{98/95}\text{Mo}$ compositions were determined under trace-metal clean laboratory conditions. Sample powders were accurately weighed and digested using inverse aqua-regia following addition of a ^{97}Mo and ^{100}Mo enriched isotope spike. Mo was purified from matrix elements and potential interferences using a single anion-exchange column pass procedure (Pearce et al., 2009) that has been shown to produce $\delta^{98/95}\text{Mo}$ compositions for standard reference materials that are indistinguishable, within the ascribed uncertainties, to results from other laboratories currently producing Mo-isotope data (Goldberg et al., 2013). Analyses were made on a Thermo-Finnegan Neptune MC-ICP-MS, using solutions containing ~ 50 ppb natural Mo, monitoring within runs for possible interferences from Ru (^{99}Ru) and Zr (^{91}Zr). Data reduction was carried out off-line using a spreadsheet-based deconvolution routine (Pearce et al., 2009). Procedural blanks for Mo were less than ~ 2 ng, contributing an insignificant amount to the measured Mo. All $\delta^{98/95}\text{Mo}$ data have been calculated relative to an in-house Mo solution standard (Fisher Chemicals, ICP Mo standard solution, lot 9920914-150) and have been re-normalised to NIST 3134 following Greber et al. (2012) and Goldberg et al. (2013). Data are quoted in the text relative to NIST 3134. External reproducibility for $\delta^{98/95}\text{Mo}$ was $\pm 0.10\text{‰}$ (2 S.D., $n = 9$), as determined by repeated processing an in-house mudrock standard (Monterey Formation sample 00N118) through the full chemical procedure. Two powder aliquots of three samples each from Guru Fatima and Kheuv River were also passed through the full chemical procedure and gave indistinguishable $\delta^{98/95}\text{Mo}$ values (within analytical uncertainty). Mo abundances were calculated using isotope dilution from the $^{100}\text{Mo}/^{95}\text{Mo}$ ratio obtained during Mo-isotope analyses. All data are listed in Tables 1 and 2.

3. Results

The new $\delta^{98/95}\text{Mo}$ data are presented in Fig. 2, together with previously published geochemical data for Guru Fatima and Kheuv River (Dickson et al., 2014). $\delta^{98/95}\text{Mo}$ for samples from Guru Fatima exhibit a clear stratigraphic trend across the carbon isotope

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