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## Editorial

Reprint of: New Applications of Trace Metals as Proxies in Marine Paleoenvironments<sup>☆</sup>

## 1. Introduction

Trace metals that can provide insight into the long-term evolution of Earth-surface conditions are proving to be increasingly important for paleoceanographic studies (Anbar et al., 2007; Lyons et al., 2009). They play an essential role in many biogeochemical cycles, such as Mo and V in nitrogenase, an enzyme used by nitrogen-fixing bacteria, and Cu and Zn in many other enzymes and proteins (Kieffer, 1991; Glass et al., 2009). Because of such roles, the relative availability of trace metals in ancient seawater may have been an important factor that regulated the development of microbial communities and, hence, chemical changes in the ocean and atmosphere through time (Canfield, 1998; Anbar and Knoll, 2002; Saito et al., 2003; Konhauser et al., 2009). The extant evidence suggests that large changes in the trace-metal inventory of seawater have occurred during both the Precambrian and Phanerozoic (Algeo, 2004; Scott et al., 2008). Our ability to track such changes in seawater composition and to determine their relationship to the evolution of biogeochemical systems through time depends on a thorough understanding of the processes that influence trace-metal uptake by the sediment and on the development of suitable trace-metal proxies for paleoceanographic research.

The present issue of *Chemical Geology* consists of 11 papers on the theme of “New applications of trace metals as proxies in marine paleoenvironments.” The volume is an outgrowth of a theme session organized for the 20th Annual V.M. Goldschmidt International Geochemistry Conference held in Knoxville, Tennessee, in June 2010. The contributions to this issue include one review paper, eight case studies (two on modern sediments, six on Ordovician to Cretaceous paleomarine units), and two methods papers (Table 1). All of the contributions consider applications of trace-metal concentration data—primarily molybdenum (Mo) and uranium (U), although one study has a focus on rhenium (Re) and a few papers consider other metals. In addition, three studies investigate the utility of Mo isotopes for paleoceanographic research.

## 2. Applications of trace-metal concentration data

The utility of redox-sensitive trace metals as proxies in paleoceanographic research has been extensively investigated (see Tribouillard et al., 2006, for a review). Because of specific attributes,

Mo and U are among the most useful metals in this regard. In oxic seawater, both elements exhibit conservative behavior and have long residence times (~800 kyr for Mo, ~450 kyr for U). Consequently, both elements exhibit nearly uniform concentrations in the global ocean (~105 nM for Mo, ~13 nM for U; Morris, 1975; Chen et al., 1986; Millero, 1996) and low concentrations in oxic marine facies (Zheng et al., 2000; Morford et al., 2009a, 2009b). Under anoxic conditions, both metals exhibit strong authigenic enrichment. One hypothesis is that Mo becomes “activated” at a critical activity of hydrogen sulfide, facilitating conversion of molybdate ( $\text{MoO}_4^{2-}$ ) to more particle-reactive thiomolybdates ( $\text{MoO}_x\text{S}_{(4-x)}^{2-x}$ ,  $x = 0$  to 3) (Helz et al., 1996; Zheng et al., 2000) that are readily adsorbed onto humic substances or Mn- and Fe-oxyhydroxides (Berrang and Grill, 1974; Magyar et al., 1993). An alternative hypothesis calls for precipitation of a nanoscale Fe(II)–Mo(VI) sulfide mineral (Helz et al., 2011). Under anoxic conditions, U(VI) is reduced to the less soluble U(IV) within the sediment (Anderson et al., 1989; McManus et al., 2005), possibly catalyzed by enzymes produced by iron- and sulfate-reducing bacteria (Zheng et al., 2002a; Sani et al., 2004). Authigenic U enrichment commences at the Fe(II)–Fe(III) redox boundary, hence at shallower depths within the sediment than for authigenic Mo enrichment, which requires free  $\text{H}_2\text{S}$  (Helz et al., 1996; Zheng et al., 2000, 2002b; Morford et al., 2005, 2007). Mn–Fe redox cycling within the water column represents an important additional vector on authigenic Mo enrichment, but U is not known to be influenced by this process (Berrang and Grill, 1974; Algeo and Tribouillard, 2009). Authigenic Mo and U uptake and remobilization are also influenced by bio-irrigation of the sediment (Zheng et al., 2002a; Morford et al., 2009a) and the development of oxidation fronts (Colley and Thomson, 1985; Thomson et al., 1995; McManus et al., 2005).

The concentrations of Mo, U, and other redox-sensitive trace metals in marine sediments and sedimentary rocks have been widely used to infer paleoredox conditions (Dean et al., 1997; Algeo and Maynard, 2004; Cruse and Lyons, 2004; Brumsack, 2006; Tribouillard et al., 2008). Although some open-marine environments exhibit positive covariation between the concentrations of these metals and the intensity of reducing conditions (e.g., Zheng et al., 2000; McManus et al., 2005, 2006), this is not the case for restricted marine environments such as the modern Black Sea and Cariaco Basin (Algeo and Lyons, 2006) and many ancient marine deposits in epicontinental settings (e.g., Algeo et al., 2007; McArthur et al., 2008; Rowe et al., 2008; Hetzel et al., 2009). In such settings, trace-metal concentrations generally decrease as facies become more euxinic because the first-order control is aqueous metal concentration (which declines in restricted marine settings with limited deepwater renewal) rather than benthic redox conditions (Algeo and Lyons, 2006). Patterns of trace-metal enrichment can thus be used in paleoceanographic studies to evaluate deepwater restriction, deepwater residence time, and changes in deepwater chemical composition (Algeo

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**Table 1**  
Contributions to present special issue on trace metal proxies.

No.	Authors	Paper type	Age	Elemental				Isotopic	
				Mo	U	Re	Other	Mo	Re-Os
1	Algeo & Rowe	review	modern & ancient	✓	✓	✓	✓		
2	Scott & Lyons	case study	modern	✓				✓	
3	Morford et al.	case study	modern			✓			
4	Dale et al.	case study	Cretaceous	✓					
5	Tribovillard et al.	case study	Triassic-Cretaceous	✓	✓				
6	Georgiev et al.	case study	Permian-Triassic			✓			✓
7	Williams et al.	case study	Permian-Triassic	✓	✓		✓		
8	Xu et al.	methods	Permian-Triassic	✓	✓	✓	✓		
9	Zhou et al.	case study	Permian-Triassic & Ordovician-Silurian	✓	✓		✓		✓
10	Hermann et al.	case study	Pennsylvanian	✓					✓
11	Rowe et al.	methods	Devonian-Cretaceous	✓	✓	✓	✓		

and Lyons, 2006; Algeo and Maynard, 2008; Algeo and Tribovillard, 2009). The paper by Algeo and Rowe (this volume) provides a review of these new applications of trace-metal concentration data.

Euxinic organic-rich shales are typically strongly enriched in trace metals, but not all ancient black shales accumulated in euxinic environments. The paper by Scott and Lyons (this volume) examines Mo uptake by non-euxinic facies, demonstrating systematic differences in sediment Mo concentrations relative to euxinic facies that may assist in analysis of redox conditions in paleomarine systems. They develop a theoretical model for relationships between the concentration profiles of Mo, Mn, Fe, and H<sub>2</sub>S relative to sediment redox zones in non-euxinic facies. This work may help in refining the oceanic Mo budget because non-euxinic facies represent a large but imprecisely quantified sink for seawater Mo (Siebert et al., 2006). Finally, they report systematic changes in sediment  $\delta^{98}\text{Mo}$  as a function of redox conditions (cf. Poulson et al., 2006; Neubert et al., 2008) but note that  $\delta^{98}\text{Mo}$  may also have potential as a proxy to identify MnOOH cycling in paleomarine systems (cf. Algeo and Tribovillard, 2009; Dahl et al., 2010).

Uptake of authigenic Mo by the sediment is generally considered to be directly related to the intensity of reducing conditions in open-marine environments (e.g., Zheng et al., 2000). However, the paper by Dale et al. (this volume) concludes that other factors, such as reactive Fe availability, were more important than benthic redox conditions in determining authigenic Mo enrichment of OAE-2 sediments (i.e., the ocean anoxic event at the Cenomanian-Turonian boundary, Late Cretaceous) in the North American Western Interior Seaway. During OAE-2, an increased availability of reactive Fe prevented Mo sequestration as thiomolybdate ( $\text{MoS}_4^{2-}$ ) both by inhibiting sulfate reduction and by buffering any free sulfide that formed, whereas following OAE-2, Mo accumulation was favored by a large reduction in Fe flux. Their modeling results further suggest that Mo and organic carbon accumulation was not tightly coupled to benthic redox conditions, and that neither Mo nor organic carbon burial fluxes are unequivocal indicators of anoxia.

Although most redox-sensitive elements are enriched in marine sediments under reducing conditions, relative rates of enrichment may vary as a consequence of interelemental differences in reactivity, water-column cycling, availability of host substrates, and other factors. Investigation of the controls on covariation is a relatively new area of investigation, with studies by Algeo and Maynard (2008) and Algeo and Tribovillard (2009) examining covariation in modern marine settings

and applying these findings to analysis of Devonian and Pennsylvanian paleomarine systems. The paper by Tribovillard et al. (this volume) examines patterns of covariation between Mo and U in Jurassic and Cretaceous anoxic marine facies. Mo-U covariation is a particularly promising proxy owing to the differential geochemical behavior of these elements: (1) authigenic Mo enrichment requires euxinic conditions (presence of H<sub>2</sub>S), whereas authigenic U enrichment begins under suboxic conditions (at the Fe(II)-Fe(III) redox boundary), and (2) transfer of Mo (but not U) to the sediment is enhanced through redox cycling of MnOOH in the water column. This study confirms prevailing interpretations of redox conditions during Mesozoic OAEs but provides new insights regarding watermass restriction and the operation of Mn-particulate shuttles in various depositional basins, which helps in addressing issues such as the degree to which regional versus global factors controlled OAE development.

Fine-grained siliciclastic rocks (shales) are commonly altered by burial diagenesis or near-surface weathering, but methods to recognize such geochemical changes have received only limited attention to date (e.g., Petsch et al., 2000; Hannigan and Sholkovitz, 2001; Lev and Filer, 2004). The paper by Williams et al. (this volume) develops chemometric techniques based on principal components analysis and cluster analysis to recognize diagenetic and weathering overprints on shale composition and applies them to an analysis of a Permian-Triassic boundary section at Attargoo (Kashmir, India). After accounting for weathering effects, they were able to recognize a series of geochemical event beds associated with transient development of euxinia in an otherwise dysoxic depositional environment.

Rhenium (Re) in marine systems has received relatively less attention in the past (Anbar et al., 1992; Colodner et al., 1993, 1995; Crusius et al., 1996) but is the focus of the paper by Morford et al. (this volume). They measured Re concentrations at three sites on the Mid-Atlantic Bight (eastern margin of United States) representing shallow (75 m; mixed surface layer), intermediate (647 m; intra-thermocline), and deep (2648 m) sites. They show that rates of Re removal to the sediment correlate positively with organic carbon oxidation rates and 'reducing intensity', which are greatest at the intermediate site and least at the deep site, and negatively with depth to the O<sub>2</sub>-H<sub>2</sub>S interface. Bio-irrigation of the sediment, which is most important in coastal (shallow) settings, augments the diffusive flux of Re across the sediment-water interface and enhances net removal of Re to the sediment. Seasonal fluctuations in oxygen penetration depths at each site result in remobilization of Re within the upper ~1 cm of the sediment column. These findings provide new insights into controls on Re accumulation in marine sediments and the potential application of Re as a proxy for both paleoredox conditions and organic carbon oxidation rates.

### 3. Applications of trace-metal isotope data

Recent work has provided a foundation for paleoceanographic applications of the isotopes of Mo (Barling et al., 2001; Siebert et al., 2003; Anbar, 2004; Barling and Anbar, 2004; Nägler et al., 2005; Anbar and Rouxel, 2007; Wasylenski et al., 2008; Gordon et al., 2009) and U (Stirling et al., 2007; Weyer et al., 2008; Brennecke et al., 2010, 2011a). These relatively new but incompletely understood isotopic systems have generated considerable interest owing to their potential as global paleoredox proxies. This potential exists because the residence times of both elements in seawater (Mo ~800 kyr; U ~450 kyr) are far longer than the ocean mixing time (~1-2 kyr; Wright and Colling, 1995), resulting in globally uniform seawater  $\delta^{98}\text{Mo}$  and  $\delta^{238}\text{U}$  values. A number of such investigations have now been carried out for Mo (Arnold et al., 2004; Siebert et al., 2005; Pearce et al., 2008) and U (Montoya-Pino et al., 2010; Brennecke et al., 2011b), and two studies in the present volume provide additional insights into the application of Mo isotopes as a global paleoredox proxy.

The paper by Herrmann et al. (this volume) assesses the use of the Mo-isotope system as a global redox proxy during the Pennsylvanian. In this study of the Hushpuckney Shale, strongly euxinic facies (representing maximum interglacial highstands) yield low  $\delta^{98}\text{Mo}$  values ( $\sim +0.6\%$ ) whereas weakly euxinic to suboxic facies (representing lower eustatic levels) yield higher  $\delta^{98}\text{Mo}$  values ( $+1.1$  to  $+1.8\%$ ). These results are inconsistent with a simple redox control on Mo isotopes (cf. Poulson et al., 2006). Two alternative interpretations are that interglacial stages of the Late Paleozoic Ice Age were characterized by (1) expanded oceanic anoxia and a larger anoxic:oxic Mo burial sink ratio, resulting in a  $\sim 1.2\%$  decrease in the  $\delta^{98}\text{Mo}$  of Late Pennsylvanian seawater, and (2) intensified Mn redox cycling locally within the water column of the North American Midcontinent Sea, during which isotopically light Mo was adsorbed onto sinking particles and rapidly transferred to the sediment. Each scenario has important implications for the application of Mo isotopes in paleoceanographic research. The oceanic-anoxia hypothesis is consistent with the use of Mo isotopes as a global redox proxy, but it requires a large decrease in the residence time of Mo in seawater (to  $<100$  kyr) in order to allow variation in seawater  $\delta^{98}\text{Mo}$  of  $\sim 1.2\%$  at sub-cyclothermic timescales. On the other hand, the Mn-cycling hypothesis challenges the assumption of quantitative removal of seawater Mo to euxinic facies, which is a key assumption of the application of Mo isotopes as a global redox proxy. Further work will be needed to test these hypotheses.

The paper by Zhou et al. (this volume) investigates variation in  $\delta^{98}\text{Mo}$  (and other trace-metal proxies) in conjunction with the Ordovician-Silurian and Permian-Triassic boundary mass extinctions. Euxinic facies of Ordovician-Silurian age exhibit a gradual trend toward higher  $\delta^{98}\text{Mo}$  values (from  $+0.4$  to  $+1.2\%$ ), suggesting a shift toward lower anoxic:oxic Mo burial sink ratios as a consequence of long-term improvements in deep-ocean ventilation. In addition,  $\delta^{98}\text{Mo}$  values exhibit an abrupt, short-term excursion to  $+2.1\%$  during the latest Ordovician Hirnantian glaciation that they interpret as evidence of a sharp rise in ocean ventilation as a result of glacially invigorated ocean circulation. In the Late Permian Dalong Formation, oxic-suboxic facies exhibit generally low  $\delta^{98}\text{Mo}$  values ( $-1.0$  to  $+1.2\%$ ), but a 7-m interval of euxinic sedimentation around the latest Permian mass extinction horizon is characterized by  $\delta^{98}\text{Mo}$  values of  $+0.3$  to  $+2.2\%$ . Differences in  $\delta^{98}\text{Mo}$  between euxinic facies of Ordovician-Silurian ( $+0.4$  to  $+1.2\%$ ), Permian-Triassic ( $+0.3$  to  $+2.2\%$ ), and Recent age ( $+2.3\%$ ) reflect a general decline in the importance of euxinic marine sedimentation since the Early Paleozoic.

The paper by Georgiev et al. (this volume) investigates the effects of weathering on Re-Os isotope, elemental, and organic matter proxies in shales by comparing signals in correlative units from outcrops and drillcore in East Greenland. They report systematic differences in major- and trace-element content and kerogen quality between weathered and fresh samples that can be used to characterize and quantify the effect of weathering on shale chemistry. The Re-Os isochronicity of shale sections was also affected by weathering and can be used to distinguish chemically unaltered shale from macroscopically fresh but chemically altered shale. They develop a protocol for assessment of alteration in shale samples based on a combination of Rock-Eval indices and sulfur content (proxies for oxidation of OM and pyrite) that will assist in more accurate and precise Re-Os geochronology. They also note the seemingly global occurrence of high Re/Os and high  $^{187}\text{Os}/^{188}\text{Os}$  ratios in shales of Late Permian-Early Triassic age, possibly indicative of a major disturbance to the exogenic cycles of Re and Os in conjunction with the largest mass extinction in Earth history (cf. Georgiev et al., 2011).

#### 4. Methodological advances

While the interpretation of trace-metal data in the context of paleoceanographic studies has made tremendous strides, as discussed above, there have also been improvements related to the development of new instrumental or analytical approaches to the analysis

of trace metals in marine sediments. The paper by Rowe et al. (this volume) investigates the application of a portable energy-dispersive XRF instrument to the analysis of the geochemical composition of mudrocks. They report on the development of a large suite of mudrock reference materials that can be used for calibration of the ED-XRF instrument. Their protocol will be useful for researchers wishing to rapidly develop a quantitative chemostratigraphic framework that can be integrated with lithostratigraphic and biostratigraphic data. Furthermore, geochemical analysis using a portable ED-XRF instrument is a non-destructive analytical procedure that should find wide application wherever conservation of geological samples is necessary. The examples given in their study are from the Devonian Ohio Shale of eastern Kentucky, and the Devonian Woodford Formation, the Mississippian Barnett Shale, the Pennsylvanian Smithwick Formation, and the Cretaceous Eagle Ford Shale of eastern Texas.

The authigenic fraction of a trace metal is commonly assessed by subtracting an Al-based estimate of the detrital fraction from the total trace-metal concentration in a sediment (e.g., Brumsack, 2006; Perkins et al., 2008). The paper by Xu et al. (this volume) investigates an alternative approach to determining authigenic trace-metal concentrations based on chemical digestion procedures. They tested three different procedures: (1–2) *aqua regia* and inverse *aqua regia*, which dissolve the organic matter, sulfide, and carbonate phases that host trace metals of hydrogenous (seawater) origin, and (3) multi-acid total digestion, which yields multiple trace-metal fractions. These chemical digestion procedures yield relatively consistent results, suggesting that they are able to isolate the authigenic fraction of trace metals with  $\sim \pm 10\%$  analytical uncertainty, although their efficacy relative to the Al-based procedure remains to be tested.

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