



Research paper

Analysis of marine environmental conditions based on molybdenum–uranium covariation—Applications to Mesozoic paleoceanography

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ABSTRACT

Patterns of uranium–molybdenum covariation in marine sediments have the potential to provide insights regarding depositional conditions and processes in paleoceanographic systems. Specifically, such patterns can be used to assess bottom water redox conditions, the operation of metal–oxyhydroxide particulate shuttles in the water column, and the degree of water mass restriction. The utility of this paleoenvironmental proxy is due to the differential geochemical behavior of U and Mo: (1) uptake of authigenic U by marine sediments begins at the Fe(II)–Fe(III) redox boundary (i.e., suboxic conditions), whereas authigenic Mo enrichment requires the presence of H₂S (i.e., euxinic conditions), and (2) transfer of aqueous Mo to the sediment may be enhanced through particulate shuttles, whereas aqueous U is unaffected by this process. In the present study, we examine U–Mo covariation in organic-rich sediments deposited mostly in the western Tethyan region during oceanic anoxic events (OAEs) of Early Jurassic to Late Cretaceous age. Our analysis generally confirms existing interpretations of redox conditions in these formations but provides significant new insights regarding water mass restriction and the operation of particulate shuttles in depositional systems. These insights will help to address contentious issues pertaining to the character and origin of Mesozoic OAEs, such as the degree to which regional paleoceanographic factors controlled the development of the OAEs.

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1. Introduction

Trace metals are commonly used for paleoenvironmental reconstruction, especially redox-sensitive and/or sulfide-forming elements that may become strongly enriched under low-oxygen and/or sulfidic water mass conditions. Among such elements, uranium (U) and molybdenum (Mo) have been extensively studied (Emerson and Husted, 1991; Klinkhammer and Palmer, 1991; Wignall, 1994; Crusius et al., 1996; Helz et al., 1996; Dean et al., 1999; Morford and Emerson, 1999; Erickson and Helz, 2000; Zheng et al., 2000, 2002a, 2002b; Chaillou et al., 2002; Bostick et al., 2003; Lyons et al., 2003; Algeo and Maynard, 2004; Tribovillard et al., 2004; Vorlicek et al., 2004; McManus et al., 2005; Morford et al., 2005; Brumsack, 2006; McManus et al., 2006; Tribovillard et al., 2006, 2008a, 2008b; Lyons et al., 2009; Morford et al., 2009; Piper and Calvert, 2009; Poulson Brucker et al., 2009). These two trace metals are especially useful for paleoenvironmental reconstructions owing to their geochemical properties and behavior: (1) both are present in low concentrations in the

upper continental crust (U ~2.7 ppm, Mo ~3.7 ppm; McLennan, 2001) and transferred to the ocean mainly by fluvial input; (2) both are present in low concentrations in marine plankton; (3) both have long residence times in seawater (U ~450 kyr, Mo ~780 kyr) and, hence, nearly uniform aqueous concentrations throughout the global ocean; and (4) both exhibit conservative behavior under oxic conditions but enhanced uptake by the sediment where the water mass is anoxic. As a consequence of these characteristics, enrichments of U and Mo in sediments or sedimentary rocks may generally be imputed to authigenic uptake of these elements from seawater.

The mechanisms of authigenic enrichment are somewhat different for U and Mo (for a detailed discussion, see Algeo and Maynard (2004), Tribovillard et al. (2006), Algeo and Tribovillard (2009), and references therein). The main mechanism by which aqueous U is removed from seawater is uptake across the sediment–water interface in reducing facies. Under conditions close to those required for conversion of Fe³⁺ to Fe²⁺, soluble U(VI) is reduced, possibly through microbial mediation, to insoluble U(IV). In this state, U removal to the sediment may be accelerated by the formation of organometallic ligands and by enhancing the influence of organic substrates on U uptake. The accumulation is (at least partly) mediated by bacterial sulfate reduction reactions, because without bacterial activity, the reduction

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process seems to be very slow (McManus et al., 2005, and references therein). Mo is also likely to be taken up across the sediment–water interface under reducing conditions (Zheng et al., 2000). However, removal of Mo to the sediment requires formation of particle-reactive thiomolybdates ($\text{MoO}_x\text{S}_{4-x}^{2-x}$, where $x=0$ to 3), which are then scavenged by sulfidized (S-rich) organic material or Fe–S phases (Tribovillard et al., 2004). Thiomolybdate formation occurs only in the presence of free hydrogen sulfide (H_2S) (Helz et al., 1996, 2011) and, thus, at a lower redox potential than that for sedimentary uptake of U, creating the potential for enhanced uptake of U relative to Mo where suboxic conditions prevail (Algeo and Tribovillard, 2009). A second difference between the behavior of U and Mo is that the latter element is vigorously scavenged by metal oxyhydroxides (especially MnOOH but including FeOOH), probably in relation to a speciation change from the dissolved MoO_4^{2-} to the particle reactive MoO_3 (Tossell, 2005). Particulate Mn-oxides adsorb molybdate oxyanions during transit through the water column, playing the role of a shuttle (Algeo and Tribovillard, 2009; Dellwig et al., 2010). Usually, upon reaching the sediment/water interface, these particles are reductively dissolved, releasing molybdate ions that then either diffuse back into the water column or are scavenged by other phases within the sediment.

In a recent paper, Algeo and Tribovillard (2009) used these differences in the geochemical behavior of U and Mo to demonstrate how patterns of authigenic U–Mo co-variation may be related to specific redox conditions and processes in marine depositional systems. These authors, using enrichment factors (EFs; see definition in Section 2.2), identified three patterns of U–Mo covariation, each associated with a different modern marine setting. First, sediments of the eastern tropical Pacific exhibit a pattern of greater relative U_{auth} enrichment (Mo:U ratios of ~ 0.1 to $0.3 \times \text{SW}$) at low EFs, indicative of suboxic conditions, and progressively greater relative Mo_{auth} enrichment (Mo:U ratios $> 1 \times \text{SW}$) at high EFs, indicative of a shift toward more intense and/or sustained anoxia in the water column (Fig. 1A). This trend is characteristic of “unrestricted marine” settings (Fig. 1B). Second, sediments of the Cariaco Basin exhibit strong enrichment of Mo relative to U at all EFs, reflecting the operation of a metal-oxyhydroxide particulate shuttle that enhances the export of aqueous Mo to the sediment (with little effect on aqueous U; Fig. 1A). Mo:U ratios are generally much greater (3 to $10 \times \text{SW}$) than the seawater ratio, defining a “particulate shuttle” trend that is distinct from the unrestricted marine trend (Fig. 1B). Finally, Algeo and Tribovillard (2009) identified a third pattern, characterized by decreasing Mo:U ratios with increasing EFs. This pattern is characteristic of sediments of the modern Black Sea and is inferred to represent the influence of changes in water mass chemistry with water depth (n.b., the deepwater mass of the Black Sea contains $\sim 70\%$ of the seawater concentration of U but only $\sim 3\%$ of the Mo concentration; Algeo and Maynard, 2008). This pattern, development that requires an extended interval of deepwater isolation to allow chemical evolution of the water mass, was tentatively identified in some Devonian black shales by Algeo and Tribovillard (2009).

In the present paper, we extend the ideas developed in Algeo and Tribovillard (2009) to an analysis of depositional conditions and processes in organic-rich units of Mesozoic age (Fig. 2). The Mesozoic experienced multiple episodes of oceanic anoxia commonly extending across broad portions of the Tethys Ocean and sometimes developed concurrently in the Panthalassic/Paleo-Pacific Ocean and in epicratonic seas. These episodes, termed Oceanic Anoxic Events (OAEs), were more or less protracted, ranging from a few thousand years to several million years in duration. They were commonly limited to oceanic deepwaters but sometimes impinged on the platform domain, depending on the paleogeographical configuration and other paleoceanographic factors (see the recent review by Jenkyns (2010)). The OAEs and other episodes of extensive organic matter storage studied here are the Toarcian OAE-T (Early Jurassic), the Kimmeridgian and early Tithonian (Late Jurassic), the Hauterivian (Early Cretaceous), and the Cenomanian–Turonian OAE-2 and Coniacian–Santonian OAE-3 (Middle to Late Cretaceous;

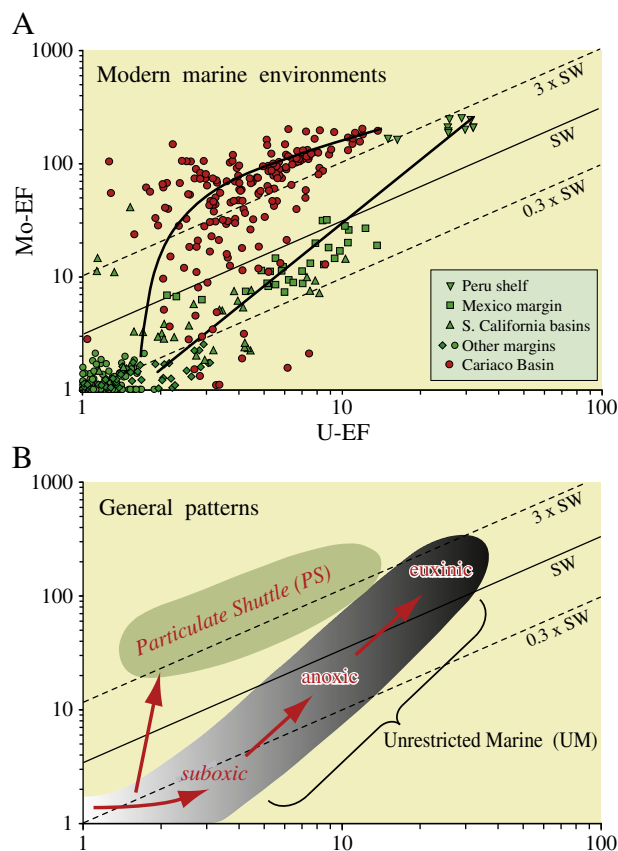


Fig. 1. (A) U–EF vs. Mo–EF for modern marine environments. Samples are from unrestricted marine facies of the eastern tropical Pacific (green symbols) and the restricted Cariaco Basin (modified from Algeo and Tribovillard (2009)). The heavy solid lines highlight the pattern of U–Mo covariation in each environment. The eastern tropical Pacific is subject to a wide range of bottom water redox conditions, including fully oxic along the Chilean margin, suboxic to episodically anoxic along the California and Mexican margins, and perennially anoxic within depressions of the Peru margin. Redox variation among these settings shows a strong relationship to the degree of authigenic U–Mo enrichment. Data from McManus et al. (2006). EF = enrichment factor (see Eq. (1) in the text). The diagonal lines represent multiples (0.3, 1, and 3) of the Mo:U ratio of present-day seawater: molar ratios of ~ 7.5 for the Pacific and ~ 7.9 for the Atlantic have been converted to an average weight ratio of 3.1 for the purpose of comparison with sediment Mo:U weight ratios. (B) General patterns of U–EF vs. Mo–EF covariation in modern marine environments. The gray field represents the “unrestricted marine” (UM) trend, characteristic of the eastern tropical Pacific, whereas the green field represents the “particulate shuttle” (PS) trend, characteristic of depositional systems such as the Cariaco Basin in which intense redox cycling of metal (especially Mn–) oxyhydroxides occurs within the water column.

Fig. 2). We chose to examine geological formations that have already been well studied because we intend to (1) test the robustness of U–EF vs. Mo–EF covariation as a proxy for paleoredox conditions and processes that were previously interpreted using independent parameters, and (2) determine whether U–EF vs. Mo–EF covariation provides new insights regarding the paleoceanography of these organic-rich depositional systems.

2. Material and methods

2.1. Study units

Here we study the respective EF of U and Mo of well-known geological formations ranging in age from the Early Jurassic to the Late Cretaceous and mostly from the western Tethyan region. Only their main features are summarized here, but we provide references where more

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