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Trace metals as paleoredox and paleoproductivity proxies: An update

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Abstract

This paper is a synthesis of the use of selected trace elements as proxies for reconstruction of paleoproductivity and paleoredox conditions. Many of the trace elements considered here show variations in oxidation state and solubility as a function of the redox status of the depositional environment. Redox-sensitive trace metals tend to be more soluble under oxidizing conditions and less soluble under reducing conditions, resulting in authigenic enrichments in oxygen-depleted sedimentary facies. This behavior makes U, V and Mo, and to a lesser extent certain other trace metals such as Cr and Co, useful as paleoredox proxies. Some redox-sensitive elements are delivered to the sediment mainly in association with organic matter (Ni, Cu, Zn, Cd) and they may be retained within the sediment in association with pyrite, after organic matter decay in reducing sediment. This particularity confers to Ni and Cu a good value as proxies for organic C sinking flux (frequently referred to as productivity). Elements with only one oxidation state such as Ba and P are classically used to assess paleoproductivity levels but they suffer from the fact that they are solubilized under reducing conditions and may be lost from oxygen-deprived sediments. The combined used of U, V and Mo enrichments may allow suboxic environments to be distinguished from anoxic–euxinic ones. Specifically, these elements tend to be much more strongly enriched in anoxic–euxinic environments and to exhibit weaker covariation with TOC than in suboxic environments.

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1. Introduction

Many trace elements are present in seawater either in soluble form or adsorbed onto particles. Removal of dissolved trace elements from the water column to the sediments results from either biotic or abiotic processes. Biotic processes comprise the uptake of trace elements that serve as minor or micronutrients for plankton (mainly phytoplankton). Abiotic processes are relatively limited in oxic environments, but in suboxic environments, some enrichment may occur through diffusion of dissolved trace elements from the water column across the sediment–water interface or through remobilization and repartitioning along redox gradients within the sediments. Trace elements may also be efficiently concentrated through the redox cycling of manganese and iron. Abiotic processes are particularly efficient under reducing conditions, including adsorption of metallic ions or ionic species onto organic or mineral substrates, formation of organometallic complexes, and

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precipitation of (iron-) sulfides and/or insoluble oxy-hydroxides. In theory, this variety of processes results in trace-element enrichments that mirror the specific conditions prevailing by the time of deposition and early diagenesis. Consequently, trace-element abundances in sediments and sedimentary rocks allow us to reconstruct paleodepositional conditions (e.g., among recent papers, Werne et al., 2003; Lyons et al., 2003; Riboulleau et al., 2003; Sageman et al., 2003; Rimmer, 2004; Rimmer et al., 2004; Algeo and Maynard, 2004; Algeo, 2004; Nameroff et al., 2004; Tribovillard et al., 2004a, 2005; Riquier et al., 2005). The wealth of papers devoted to trace-element geochemistry is such that we see the value of a synthesis emphasizing the most recent work in the field. In the present paper, we explore the environmental parameters that control trace-element distributions in modern and ancient sediments. In doing this, we emphasize selected trace elements and their mechanisms of enrichment and highlight the associated strengths and limitations. Finally, we explain how an integrated perspective of trace-element enrichments/depletions can facilitate reconstruction of paleodepositional conditions, most notably paleoproductivity and paleoredox.

2. The paleoenvironmental parameters concerned with trace-element geochemistry

2.1. Productivity

Concentrations of organic matter (OM) in sediments and sedimentary rocks record only a fraction of the total biological productivity in surface waters of the ocean. Export productivity is the part of the phytoplankton biomass that “escapes” from the generally efficient recycling operating in the upper portion of the water column (organic C sinking flux). This material is delivered to the sediment–water interface following additional degradation during passage through the water column. Under normal marine conditions, only about 10% of total productivity leaves the euphotic zone (e.g., Seibold and Berger, 1993; Chester, 2000). In upwelling areas, export productivity may reach higher values (occasionally 30%). However, the part of the productivity that actually reaches the sediment–water interface and that is stored within sediments is much lower (a few percent only; e.g., Canfield, 1994), in part reflecting additional remineralization within the sediment.

Despite the complications attributable to highly efficient organic recycling, export productivity, delivery to the sediment–water interface and the final burial flux are generally proportional to surface-water productivity. Many authors have proposed transfer equations and related models that estimate surface-water productivity from the (often small) fraction that is stored in sediments and sedimentary rocks (e.g., Henderson, 2002 and references therein). Such models are not the focus of the present study. Instead, we focus on geochemical proxies that illuminate levels of primary production through trace-element distributions.

2.2. Redox conditions

In the simplest sense, studies of redox conditions in marine settings track the relative distributions of oxidizing agents across depositional and diagenetic gradients and biogeochemical processes that control these distributions. Discerning paleoredox conditions typically means determining whether conditions were oxidizing or reducing; in this paper we shall refer to the following redox gradation: oxic–suboxic–anoxic (Table 1; Tyson and Pearson, 1991). Anoxic conditions may be nonsulfidic or sulfidic; in the latter case, they are also called euxinic when hydrogen sulfide occurs within the water column. Euxinic conditions are usually restricted to semi-enclosed basins like the Black Sea or Cariaco Trench. H_2S is a catabolic by-product of sulfate-reducing bacteria (see below). In some cases, as in the Black Sea, euxinic conditions may reach the photic zone, where photosynthetic sulfide-oxidizing bacteria may develop (Chlorobiaceae; e.g., Repeta, 1993). Suboxic settings are characterized by extremely low but generally nonzero oxygen concentrations in the water column, where H_2S is limited to pore waters below the sediment–water interface. Transitional settings can occur wherein the first appearance of H_2S coincides with the sediment–water interface.

Under oxic conditions, aerobic organisms can use dissolved O_2 from the overlying and interstitial waters

Table 1
Redox classification of the depositional environments, after Tyson and Pearson (1991)

Redox classes	Oxic	Suboxic	Anoxic	Euxinic
			No free H_2S in the water column	Free H_2S present in the water column
O_2 concentration in bottom waters (ml O_2/l H_2O)	$[O_2]>2$	$2>[O_2]>0.2$	$[O_2]<0.2$	$[O_2]=0$

The values for O_2 concentrations in bottom waters are valid for present-day ocean.

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