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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.

Keywords: Geochemistry; Trace metals; Paleoredox conditions; Paleoproductivity; Paleoenvironments; Organic matter; Molybdenum; Uranium; Vanadium; Copper; Nickel

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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 oxyhydroxides. 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.

for their metabolism (i.e., OM degradation). As dissolved oxygen becomes depleted, OM decomposition continues via organisms using secondary oxidant sources (in order of consumption dictated by the relative free energy gain stemming from each microbial process; Froelich et al., 1979): nitrate, manganese oxides and iron oxides and oxyhydroxides, and sulfate. Ultimately, when all free oxidants are exhausted, methanogenic bacteria begin to break down organic matter via an oxidative–reductive disproportionation of carbon. This classical early diagenesis sequence can be illustrated by the sequence of equations illustrated in Table 2 and using organic matter with a Redfield stoichiometry (e.g., Shimmield and Pedersen, 1990; Chester, 2000 and references therein).

At the sediment–water interface or within sediments, oxygen-limited conditions and ultimately anoxia may develop when the oxygen demand exceeds the supply. In the water column, anoxia may develop in stagnant or confined water masses where insufficient circulation prevent O_2 renewal, or in places where intense OM degradation consumes O_2 faster than it is replenished, even in open-marine conditions. The same is true of sediment, with the additional feature that O_2 replenishment is also linked to their composition (clay vs. sands), texture (fine- vs. coarse-grained) and the intensity of bioturbation.

Table 2
The classical sequence of equations illustrating how heterotrophic bacterial activity consumes organic matter, using various electron acceptors

In the presence of free O_2:
Aerobic respiration
$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \rightarrow H_3PO_4 + 16HNO_3 + 106CO_2 + 122H_2O$

In the absence of free O_2:
Denitrification
$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 94.4HNO_3 \rightarrow H_3PO_4 + 55.2N_2 + 106CO_2 + 177.2H_2O$
Manganese reduction
$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 236MnO_2 + 472H^+ \rightarrow H_3PO_4 + 236Mn^{2+} + 16NH_3 + 106CO_2 + 366H_2O$
Iron reduction
$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 212Fe_2O_3 + 848H^+ \rightarrow H_3PO_4 + 424Fe^{2+} + 16NH_3 + 106CO_2 + 530H_2O$
Sulfate reduction
$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53SO_4^{2-} \rightarrow H_3PO_4 + 53S^{2-} + 16NH_3 + 106CO_2 + 106H_2O$

Absence of free and linked oxygen:
Disproportionation
$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 \rightarrow H_3PO_4 + 16NH_3 + 53CO_2 + 53CH_4$

The Redfield stoichiometry is used here.

3. Mode of presentation of trace elements—normalization

To use trace-element concentrations to reconstruct paleoenvironmental conditions, one must assess whether they are relatively enriched or depleted. Commonly, the degree of enrichment or depletion of a trace element in a sample is evaluated relative to its concentration in a reference that is commonly the average crustal rocks or average shale (Wedepohl, 1971, 1991; McLennan, 2001). Most of the times, trace elements are used for paleoenvironmental work emphasizing fine-grained siliciclastic sediments and sedimentary rocks relatively rich in OM, such as gray and black shales. The classic standard of comparison is average shale (Wedepohl, 1971; Taylor and McLennan, 1985; Wedepohl, 1991; McLennan, 2001; Table 3).

Sediments and sedimentary rocks may have variable proportions of mineral phases, often of biogenic origin, that dilute the trace-element abundance of a sample. The most common biogenic diluents are calcium carbonate and opal. Thus, to be able to compare trace-element proportions in samples with variable carbonate and opal contents, it is customary to normalize trace-element concentrations to aluminum content (e.g., Calvert and Pedersen, 1993). For most sedimentary deposits, aluminum can be considered as an indicator of the aluminosilicate fraction of the sediments, with very little ability to move during diagenesis (Brumsack, 1989; Calvert and Pedersen, 1993; Morford and Emerson, 1999; Piper and Perkins, 2004). To make results of the normalization procedure easier to interpret, it is common to use enrichment factors (EF): $EF_{\text{element X}} = X/Al_{\text{sample}} / X/Al_{\text{average shale}}$. If EF_X is greater than 1, then element X is enriched relative to average shales and, if EF_X is less than 1, it is depleted. Table 3 gives values for average shales from various sources—see also Hild and Brumsack (1998) and Lipinski et al. (2003) for trace-element contents of various geological formations of broad geological interest.

Although Al normalization is an attractively quick and easy way to normalize geochemical data for comparisons among different units, this method also has some drawbacks (or even pitfalls under certain circumstances). Van der Weijden (2002) demonstrated that uncorrelated variables (e.g., trace-metal concentrations) may acquire spurious correlations when normalized, and that normalization can also increase, decrease, change the sign of or even blur the correlations between unmodified variables. This is most likely to occur when the coefficient of variation (i.e., the standard deviation divided by the mean) of the Al concentration is large

Table 3
Geochemical data about the trace elements studied

Elements	Main species in oxic seawater and oxidation state	Average concentration in seawater (nmol/kg)	Residence time in seawater (kyr)	Speciation in reducing conditions	Average upper crust abundance (μg/g)[a]	Post-Archean average Australian shale (μg/g)[b]	Average shale (μg/g)[c]
Mn	MnO_2 and Mn^{2+}/Mn(IV) and Mn(II)	0.36	0.06	See text	600	1400	850
Ba	Ba^{2+}	109	10	See text	550	650	650
Cd	$CdCl^+$/Cd(II)	0.62	50	CdS/Cd(II)	0.1	0.1	0.3
Co	Co^{2+}/Co(II)	0.02	0.34	CoS/Co(II)	17	20	19
Cr	Dominantly CrO_4^{2-}/Co (VI) + $Cr(OH)_2^+$ and Cr $(OH)_3^0$/Cr(III)	4.04	8	$Cr(OH)_2^+$, $Cr(OH)_3$, $(Cr,Fe)(OH)_3$/Cr(III)	83	100	90
Cu	$CuCl^+$/Cu(II)	2.36	5	CuS CuS_2/Cu(I)	25	75	45
Mo	MoO_4^{2-}/Mo(VI)	105	800	Thiomolybdates	1.5	1	1.3
Ni	$NiCl^+$, $NiCO_3$, Ni^{2+}/Ni(II)	8.18	6	NiS/Ni(II)	44	60	68
U	$UO_2(CO_3)_3^{4-}$/U(VI)	13.4	400	UO_2, U_3O_7 or U_3O_8	2.8	0.91	3
V	HVO_4^{2-} and $H_2VO_4^-$/V(V)	39.3	50	VO^{2-}, $VO(OH)_3^-$, $VO(OH)_2$/V(IV) V_2O_3, $V(OH)_3$/V(III)	107	140	130
Zn	$Zn^{2+}ZnCl^+$/Zn(II)	5.35	50	ZnS, (Zn,Fe)S	71	80	95
Al					80,400	84,000	88,900

[a] McLennan (2001).
[b] Taylor and McLennan (1985).
[c] Wedepohl (1971, 1991).

compared to the coefficients of variation of the other variables (e.g., trace elements) (Van der Weijden, 2002). In addition, there are also distinct instances when Al should not be used for normalization (Murray and Leinen, 1996). This is the case for marine sediments with a detrital fraction lower than 3–5% and a relative excess of aluminum compared to other detrital elemental proxies such as titanium (Kryc et al., 2003a). The excess Al may have been scavenged as hydroxides coating biogenic particles (Murray and Leinen, 1996; Dymond et al., 1997; Yarincik et al., 2000; Kryc et al., 2003a). A part of the excess Al could also result from authigenic clay-mineral formation (Timothy and Calvert, 1998). Nevertheless, such instances are fairly uncommon.

Van der Weijden (2002) also showed that the comparison to average shale values may raise some complications. Firstly, the composition of the commonly used standard shale and, consequently, the reference values of normalized elements are not necessarily representative of the local/regional sediments in the study area. This fact may complicate the comparison of the chemical composition of geological formations that are geographically and/or stratigraphically somewhat atypical. Secondly, reference shales may also include a diagenetic component, leading to systematic underestimation of EFs for certain trace elements. More thorough analysis of the provenance of reference shales is needed. One approach to minimizing normalization biases is to focus on stratigraphic variation in EFs or Al-normalized elemental concentrations rather than on absolute values provided that the coefficient of variation of Al is not too large, which is generally the case with studies involving high-resolution sampling of stratigraphically limited sequences. To summarize, Al normalization of elemental concentrations is a useful procedure for examining the degree of enrichment of an element in sediments and sedimentary rocks but it cannot be relied on alone to identify and quantify contributions by sediment components other than the detrital fraction (Van der Weijden, 2002).

4. Non-hydrogenous sources of trace metals

4.1. Detrital sources

A portion of the trace-metal content of most sediments is of detrital provenance. An easy means to check whether the content of a given element is dominantly controlled by the detrital flux is to crossplot the trace element versus aluminum or titanium, which are commonly overwhelmingly of detrital origin and which are usually immobile during diagenesis (see e.g., Calvert and Pedersen, 1993; Tribovillard et al., 1994; Hild and Brumsack, 1998; Böning et al., 2004). If a good correlation is observed and if the trace element exhibits concentrations that do not deviate too greatly from average shale concentrations, it can be inferred that the trace element is mainly of detrital provenance and cannot be used for paleoenvironmental analysis. This is often the case for chromium, for example, but only occasionally so for U and Ba and rarely for V and Mo (Jones and Manning, 1994; Caplan and Bustin, 1999).

More generally, if some trace elements are suspected to be of mixed origin, that is, detrital and authigenic, the authigenic fraction can be estimated as the part in excess of the average shale abundance. The clastic fraction of element X in a sample can be estimated as: detrital X = $(X/Al)_{\text{average shale}} \times Al_{\text{sample}}$. Consequently, the authigenic fraction of element X is calculated as total X − detrital X.

Beyond these simple procedures for determining the detrital fraction of a given trace element, more sophisticated statistical or chemical procedures are available, e.g., multivariate factor analysis, or sequential chemical extraction (e.g., Jacot des Combes et al., 1999; Wijsman et al., 2001; Kryc et al., 2003b and references therein).

4.2. Hydrothermal sources

Hydrothermal fluxes also represent a potentially important source of trace elements, especially if cold seeps are considered in this category. High-temperature hydrothermal fluxes commonly can be inferred on the basis of characteristic tectonic and mineralogical associations, but the influence of cold seeps may be more difficult to recognize. The trace elements that are commonly enriched in these environments include Ba, Sr, Pb, Zn and Mn, commonly hosted by a suite of minerals such as barite, celestite, galena, blende and rhodochrosite (Pujol et al., in correction and references therein). Hydrothermal activity can be important also owing to release large quantities of manganese and iron, which can influence the sedimentary accumulation of other trace elements through their redox cycling in oxygen-deficient environments (see below) (Morford et al., 2005).

5. Manganese: a special minor element influencing the behavior of trace metals

Manganese has only limited utility as a redox proxy (e.g. Calvert and Pedersen, 1993), but its peculiar geochemical behavior makes it play a prominent role in the transfer of trace metals from the water column to the sediment and their subsequent uptake by authigenic phases. The dominant manganese species in seawater are Mn^{2+} and $MnCl^+$, but Mn(II) is thermodynamically unstable in oxygenated waters and is oxidized to insoluble Mn(III) and, above all, Mn(IV) oxides (Calvert and Pedersen, 1993, 1996). The Mn(IV) solid phases, referred to as Mn-oxyhydroxides, are mainly MnO_2 and MnOOH. Reactive Mn is delivered to the ocean as oxide coatings on particulate material delivered by winds or rivers and by diffusion out of shelf sediments (in addition to hydrothermal fluxes). Dissolved Mn is present in low concentrations in seawater, although it is somewhat enriched in surface waters relative to deep waters, from which it is actively scavenged (Calvert and Pedersen, 1993, 1996). Below the oxic–anoxic interface, the reductive dissolution of oxyhydroxide particles releases soluble Mn(II) that may diffuse upward and downward within the sediment (Brumsack, 1986; Middelburg et al., 1987; Brumsack, 1989; Rajendran et al., 1992), partly because dissolved Mn is not taken up significantly by any organic or sulfide phase (Huerta-Diaz and Morse, 1992; Algeo and Maynard, 2004). The downward diffusion of Mn^{2+} can lead to $MnCO_3$ precipitation in case of pore water supersaturation with respect to rhodochrosite (Pedersen and Price, 1982; Morford et al., 2001). This phenomenon has been shown to occur under oxic bottom waters (Calvert and Pedersen, 1993; Caplan and Bustin, 1999, 2001). The upward diffusion of Mn^{2+} can result in either Mn^{2+} escape to the water column (particularly in anoxic basins) or oxidation and precipitation of Mn oxides when pore water oxygen is encountered (Cruse and Lyons, 2004 and references herein). The high solubility of Mn^{2+} in sediments deposited under reducing conditions may result in Mn being depleted in the sediment if fixation in carbonate minerals does not occur (Hild and Brumsack, 1998).

Due to the difference in solubility of Mn(II) and Mn (IV) species, Mn displays an active biogeochemical cycle across redox boundaries that can lie below, at or above the sediment–water interface (Canfield et al., 1993). Thus, dissolved Mn concentrations are usually relatively high in stratified water columns immediately below the chemocline (i.e., O_2–H_2S interface). This distribution is due to the reductive solution of particulate oxyhydroxides settling from a particle concentration maximum immediately above the chemocline, which is itself created by the oxidative precipitation of upward-diffusing Mn^{2+} from anoxic waters (Calvert and Pedersen, 1996). Owing to rapid settling, some fraction of particulate Mn-oxyhydroxides reaches the sediment–water interface even under anoxic water columns. The trace metals adsorbed onto Mn-oxyhydroxides are then released upon reductive dissolution of the host particles at or below the water–sediment interface and become available for new reactions—e.g., capture in solid solutions by authigenic sulfides, such as pyrite. Mn redox cycling if of primary importance for trace-metal enrichment in suboxic–anoxic systems because it can trigger and/or accelerate the transfer of trace elements from seawater to the sediment as well as the diagenetic remobilization of trace elements within the sediment (e.g., Morford et al., 2005 and references therein). Fe exhibits a similar pattern of redox cycling to Mn although with a significant difference: iron is systematically involved in iron-sulfide precipitation within reducing sediments and waters and is sequestered in Fe-carbonates (i.e., siderite) only under special conditions (Canfield et al., 1993). In addition, Mn^{2+} and Fe^{2+} behave differently with regard to their relative oxidation kinetics (Calvert and Pedersen, 1993, 1996). The primary trace elements influenced by Mn–Fe cycling are Ni, Cu, Zn, Co, Pb (as "$^{2+}$cations"), as well as Mo, V and Cr (as ionic species such as MoO_4^{2-}, VO^{2+} and $Cr(OH)_2^{+}$, respectively). Basically, the trace metals adsorb onto Fe–Mn-oxyhydroxides, are exported to the sediment and then released upon reductive dissolution of the oxyhydroxides at or below the water–sediment interface (depending on the position of the chemocline). The trace metals are then available for new reactions—e.g., capture in solid solutions by authigenic sulfides, such as pyrite, in reducing environments.

To conclude, because Mn is very mobile in reducing sediments, it can either escape back to the water column or be trapped in authigenic Mn-carbonates or as oxides. Thus, Mn cannot be used as a redox proxy, even if a negative correlation is frequently observed between Mn and total organic carbon (TOC) contents in OM-rich sediments and sedimentary rocks. Conversely, its main role is the transfer of trace metals from the water column to the sediment. Mn oxides trap trace metals from diffusing to overlying waters. Trace-metal adsorption to Mn-oxyhydroxides provides a potentially mobile reservoir of trace metals in the sediment that can return to the aqueous phase or become fixed in authigenic mineral phases depending on the redox history of the sediment.

6. Trace-metal applications to paleoenvironmental analysis

6.1. Redox proxies with minimal detrital influences

Uranium in seawater is present mainly as U(VI) in the conservative form of uranyl ions that bind to carbonate ions, forming $UO_2(CO_3)_3^{4-}$. In oxic marine settings, dissolved U(VI) is neither reduced to the thermodynamically favored U(IV) nor is it scavenged by particulates (Anderson et al., 1989). Reduction of U(VI) to U(IV) occurs under conditions similar to those of Fe(III) to Fe(II) reduction for the ranges of pH and alkalinity values characteristic of seawater (Klinkhammer and Palmer, 1991; Crusius et al., 1996; Zheng et al., 2000; Morford et al., 2001; Chaillou et al., 2002; McManus et al., 2005). Authigenic U enrichment is considered to take place primarily in the sediment and not in the water column, because U(VI) to U(IV) reduction is decoupled from the amount of free H_2S and is not directly influenced by redox cycling of Fe and Mn in the water column (Algeo and Maynard, 2004; McManus et al., 2005; although Zheng et al., 2002a,b hypothesized that U authigenesis could be regulated by the combined rates of iron and sulfate reduction). Consequently, in the sediments, the main U-enrichment process is $UO_2(CO_3)_3^{4-}$ diffusion from the water column, reduction reactions and adsorption or precipitation as UO_2 (uraninite, the most frequent form), U_3O_7 or U_3O_8 (e.g., Klinkhammer and Palmer, 1991; Crusius et al., 1996; Zheng et al., 2000; Morford et al., 2001; Chaillou et al., 2002; McManus et al., 2005). Since the enrichment takes place within the sediment and not in the water column, the oxygen penetration depth and the sedimentation rate may play a role, in that slower sedimentation rates allow more time for diffusion of uranyl ions from the water column into the sediment (Crusius and Thomson, 2000). In the reduced state, removal of U from the water column to the sediment may be accelerated by the formation of organometallic ligands in humic acids (Klinkhammer and Palmer, 1991; Zheng et al., 2002a,b; McManus et al., 2005). Wignall and Maynard (1993) and Algeo and Maynard (2004) also discussed the enhancing influence of organic substrates on U uptake by the sediments. The accumulation is at least partly mediated by bacterial sulfate reduction reactions, because without bacterial activity, the reduction process would be very slow (Zheng et al., 2002a,b; Sundby et al., 2004; McManus et al., 2005). As the intensity of sulfate reduction activity is linked to the abundance of reactive organic matter, U abundance usually shows a good correlation with the organic carbon rain rate (McManus et al., 2005) and with the organic-carbon content in anoxic (non-sulfidic) facies (Algeo and Maynard, 2004).

In addition to the factors that deliver U to the sediments, this element can be remobilized within the sediments if oxygen penetrates to a depth where authigenic U has accumulated (Morford et al., 2001; Zheng et al., 2002a,b; McManus et al., 2005). Such an increase in the oxygen penetration depth can be caused either through an increase in bottom water oxygen abundance or a decrease in organic matter flux (or both) or seasonal variations in the depth of bioturbation/bioirrigation. This reoxidation process can either erase a primary U signal (e.g., through loss of U from the sediments to the overlying water column) or result in the vertical migration of the initial U peak to another location in the sediments where conditions favoring reprecipitation are met (McManus et al., 2005).

Vanadium. In oxic waters, vanadium is present as V (V) in the quasi-conservative form of vanadate oxyanions (HVO_4^{2-} and $H_2VO_4^-$). In pelagic and hemipelagic sediments, vanadium is tightly coupled with the redox cycle of Mn (Hastings et al., 1996). Vanadate readily adsorbs onto both Mn- and Fe-oxyhydroxides (Calvert and Piper, 1984; Wehrly and Stumm, 1989) and possibly kaolinite (Breit and Wanty, 1991). Under mildly reducing conditions, V(V) is reduced to V(IV) and forms vanadyl ions (VO^{2-}), related hydroxyl species $VO(OH)_3^-$ and insoluble hydroxides $VO(OH)_2$. This reaction is favored by the presence of humic and fulvic acids. In marine environment, the V(IV) ionic species may be removed to the sediment by surface adsorption processes or by formation of organometallic ligands (Emerson and Huested, 1991; Morford and Emerson, 1999). Wanty and Goldhaber (1992) suggested that oxalates probably play a role in transporting vanadyl ions. Under more strongly reducing–i.e., euxinic–conditions, the presence of free H_2S released by bacterial sulfate reduction causes V to be further reduced to V(III), which can be taken up by geoporphyrins or be precipitated as the solid oxide V_2O_3 or hydroxide $V(OH)_3$ phase (Breit and Wanty, 1991; Wanty and Goldhaber, 1992). Additionally, H_2S inhibits competing ions such as Ni from binding with organic complexes (Breit and Wanty, 1991). The two-step reduction process of V may lead to the formation of separate V carrier phases of contrasting solubilities under non-sulfidic anoxic versus euxinic conditions (Calvert and Pedersen, 1993; Algeo and Maynard, 2004).

Vanadium is thus probably not trapped in solid solution by Fe-sulfides (Algeo and Maynard, 2004) and may be removed from pore waters below the level of Mn–Fe-oxyhydroxides reduction (Hastings et al., 1996; Morford and Emerson, 1999).

In the diagenetic environment, V(III) readily substitutes for aluminum in the octahedral sites of authigenic clay minerals or in recrystallizing clay minerals (Breit and Wanty, 1991).

Molybdenum is present mainly in the form of molybdate (MoO_4^{2-}; Broecker and Peng, 1982). It is sufficiently abundant relative to biological requirement that its distribution is conservative, contrasting starkly with the "nutrient-like" distributions characteristic of many other bioessential trace elements (Collier, 1985). Mo is not concentrated by ordinary plankton nor is it readily adsorbed by most types of natural particles, and it displays little affinity for the surfaces of clay minerals, $CaCO_3$ and Fe-oxyhydroxides at marine pH values (Brumsack, 1989; Goldberg et al., 1998). By contrast, molybdenum is easily captured by Mn-oxyhydroxides, generally at the sediment surface (Bertine and Turekian, 1973; Calvert and Pedersen, 1993; Crusius et al., 1996; Erickson and Helz, 2000; Zheng et al., 2000). Subsequent reduction of these phases liberates adsorbed Mo to pore waters (Crusius et al., 1996). This phenomenon can enhance Mo enrichment in the shallow burial environment: dissolved Mn refluxing from the sediment has the potential to absorb and concentrate MoO_4^{2-} at or near the sediment–water interface, when the oxic–anoxic interface is encountered (Berrang and Grill, 1974; Adelson et al., 2001). Although this process can concentrate Mo in surficial sediments, it does not explain the mechanism of Mo fixation within the sediment. A reduction step was thought to be necessary for Mo fixation, with Mo being scavenged directly from the water column or captured from pore waters supplied diffusively with Mo from the water column (François, 1988; Emerson and Huested, 1991; Huerta-Diaz and Morse, 1992; Calvert and Pedersen, 1993; Crusius et al., 1996, Zheng et al., 2000). Other models favor a direct role played by sulfide: Helz et al. (1996) and Vorlicek et al. (2004) suggested that fixation in the presence of dissolved sulfide does not simply result from MoS_2 or MoS_3 formation, but instead mineralization occurs through organic thiomolybdates and inorganic Fe–Mo–S cluster complexes possibly occurring as solid-solution components in Fe-sulfides. Helz et al. (1996) introduced the concept of a geochemical switch, through which H_2S/HS^- transforms Mo from a conservative element to particle-reactive species, in marine depositional environments. The oxygen atoms in MoO_4^{2-} are susceptible to replacement by soft ligands, such as S donors. According to Erickson and Helz (2000), a key step in this inorganic pathway is the reaction $MoO_4^{2-} \rightarrow$thiomolybdates (MoO_xS_{4-x}, $x=0–3$), which are particle-reactive and thus prone to scavenging. The sulfide activation of the switch depends on H_2S activity (Erickson and Helz, 2000; Zheng et al., 2000). Because each successive sulfidation reaction is about one order of magnitude slower than the previous one, dithio-↔trithio- and trithio-↔tetrathiomolybdate equilibria might not be achieved in seasonally or intermittently sulfidic waters (Erickson and Helz, 2000). Persistently sulfidic conditions seem to be required. In the sediments, the transformation reactions are catalyzed by proton donors or in the presence of some active-surface minerals such as kaolinite (Erickson and Helz, 2000; Vorlicek and Helz, 2002).

Once the thiomolybdate switch has been achieved, Mo is scavenged by forming bonds with metal-rich (notably Fe) particles, sulfur-rich organic molecules (Helz et al., 1996; Tribovillard et al., 2004b) and iron sulfide (Vorlicek et al., 2004). The work by Helz et al. (1996) suggests the formation of compact, monocrystalline Fe–Mo–S cluster compounds, which are capable of surviving over geologic time periods. Bostick et al. (2003) showed that the clusters are retained on pyrite surfaces, and Vorlicek et al. (2004) argued that a reduction step is favorable, if not necessary, in that case. Organic detritus will also scavenge Mo. One role of OM is simply as a carrier for Fe and other trace metals. The second role is more direct: organic O–S groups attached to macromolecular detritus may insert directly into the MoO_4^{2-}, resulting in covalent bonding between Mo and the macromolecule. Helz et al. (1996) also emphasized the role of thiols (including humic-bound thiol groups) that can activate Mo. According to Adelson et al. (2001), the organic thiomolybdates are presumed to be formed by replacement of oxygen in the first coordination sphere of Mo by S, producing covalent S bonds between Mo and sulfidized macromolecules.

Owing to generally strong enrichment in organic-rich marine facies deposited under anoxic conditions, sedimentary Mo concentrations have been widely used as a proxy for benthic redox potential (e.g., Meyers et al., 2005 and references therein). However, recent investigation (Algeo, 2004; Algeo and Lyons, in press) revisited the use of Mo as a paleoredox proxy in restricted (silled) depositional environments. These studies highlight the role of the so-called “basin reservoir effect”: increasing restriction results in lower deepwater aqueous Mo concentrations, owing to rates of Mo removal to the sediment in excess of resupply, and in lower sediment Mo/TOC ratios with decreasing aqueous Mo concentrations. The key factor is the degree of watermass restriction environments with unrestricted or weakly restricted deepwater masses, in which no measurable drawdown of aqueous Mo concentrations occurs, should exhibit the paradigmatic relationship between sedimentary Mo enrichment and declining benthic redox potential. Environments with moderately to strongly restricted deepwater masses, in which aqueous Mo is depleted through the basin reservoir effect, may exhibit either no systematic relationship between sedimentary Mo abundance and redox potential or the converse of the paradigmatic relationship—i.e., Mo enrichment associated with increasing redox potential (i.e., less intensely sulfidic conditions). Thus, Algeo and Lyons (in press) concluded that the use of Mo concentrations as a paleoredox proxy needs to be justified through (1) comparison with other, independent paleoredox proxies (see below) and (2) hydrographic analysis of the paleoenvironment of interest—i.e., assessment of its basinal configuration, circulation patterns and other factors influencing the chemistry and degree of restriction of its subpycnoclinal watermass. Of course, such assessments may prove difficult in that many anoxic paleoenvironments have incompletely known paleogeographic dimensions and underwent complex paleoredox histories.

Lastly, Mo and V are present in nitrogenase—i.e., an enzyme used by nitrogen-fixing bacteria (Premovic et al., 2002; Anbar and Knoll, 2002; Anbar, 2004; Grosjean et al., 2004 and references therein). However, because the fluxes of these elements as micronutrients are far smaller than their fluxes in other roles, it is unlikely that their presence in OM influences their general patterns of sedimentary concentration.

6.2. Redox proxies with strong detrital influence

Chromium. In oxygenated seawater, chromium is present primarily as Cr(VI) in the chromate anion, CrO_4^{2-} and, to a much lesser extent as Cr (III) in the aquahydroxyl ion, $Cr(H_2O)_4(OH)_2^+$ (Calvert and Pedersen, 1993). Under normal seawater conditions, the chromate anion is soluble, but under anoxic conditions, Cr(IV) is reduced to Cr(III), forming aquahydroxyl cations and hydroxyl cations ($Cr(OH)_2^+$, $Cr(OH)_3$, (Cr, Fe)$(OH)_3$), which can readily complex with humic/fulvic acids or adsorb to Fe- and Mn-oxyhydroxides (Breit and Wanty, 1991; Algeo and Maynard, 2004). Thus, Cr is exported to the sediments. Because of structural and electronic incompatibilities with pyrite, Cr(III) uptake by authigenic Fe-sulfides is very limited (Huerta-Diaz and Morse, 1992; Morse and Luther, 1999). In addition, Cr is not known to form an insoluble sulfide (Morse and Luther, 1999). Consequently, upon OM remineralization by sulfate-reducing bacteria, Cr is not readily trapped within the sediments in the form of a sulfide and may be lost to the overlying water column by diffusive/advective transport during sediment compaction. Furthermore, Cr may be transported to the sediment with the land-derived clastic fraction (e.g., chromite, clay minerals, ferromagnesian minerals in which Cr substitutes readily for Mg; François, 1988;

Brumsack, 1989; Hild and Brumsack, 1998). Thus, the complexities of Cr transport and enrichment limit its paleoenvironmental utility.

Cobalt. In oxic environments, cobalt is present as the dissolved cation, Co^{2+} or is complexed with humic/fulvic acids (Saito et al., 2002; Whitfield, 2002; Achterberg et al., 2003). In anoxic waters, Co forms the insoluble sulfide CoS, which can be taken up in solid solution by authigenic Fe-sulfides (Huerta-Diaz and Morse, 1992). Nevertheless, very slow kinetics limit CoS incorporation into authigenic sulfides. Finally, the distribution Co in sediments is more strongly tied to the abundance of clastic material, which limits its use as a reliable redox proxy.

6.3. Productivity proxies and their relationships to redox control

Phosphorus is essential to all forms of life on Earth, as it plays a fundamental role in many metabolic processes and is a major constituent of skeletal material. Phosphorus is a structural element in DNA and RNA, as well as in many enzymes, phospholipids and other biomolecules. Phosphorus is present with an average crustal abundance of 0.01%, but it shows a higher content in most marine sediments and sedimentary rocks (Mackenzie et al., 1993; Trappe, 1998). Although distributions of P in sediments or sedimentary rocks are linked to the supply of OM, possibly resulting from high productivity, the use of P as a proxy is not straightforward, as explained below.

The main source of P to the sediments is the phytoplankton necromass that reaches the sediment–water interface, plus fish scales and bones. Usually, P is released as PO_4^{3-} from decaying OM during oxic, suboxic and anoxic bacterial degradation below the sediment–water interface. This remineralization of P is illustrated by the equations in Table 2. Generally speaking, the P remineralized to pore waters can either escape from the sediment back to the water column or be precipitated and trapped within the sediment (e.g., Span et al., 1992; Louchouarn et al., 1997; Kidder et al., 2003; Sannigrahi and Ingall, in press).

P escape. The bacterial reactions consuming sedimentary OM regenerate organically bound P to aqueous PO_4^{3-}. Under anoxic conditions, phosphorus then generally diffuses upward from the sediment and returns to the water column. This P cycling is very efficient: it has been estimated that only 1% of organic phosphorus escapes cycling and is trapped in sediments and sedimentary rocks (Benitez-Nelson, 2000). Phosphorus thus released to bottom water can return to the photic zone and support phytoplankton productivity (e.g., Tyson and Pearson, 1991; Ingall et al., 1993; Van Cappellen and Ingall, 1994; Ingall and Jahnke, 1997; Vink et al., 1997; Filippelli, 1997, 2001; Slomp et al., 2003; Sannigrahi and Ingall, in press). Large-scale P cycling has been invoked to explain unusual periods of intense productivity coupled with anoxic bottom water conditions prone to P regeneration (e.g., Föllmi, 1996; Kim et al., 1999; Benitez-Nelson, 2000; Murphy et al., 2000a,b; Hoppie and Garrison, 2001). In this situation, high productivity may develop in surface waters without the sediments recording any P enrichment.

P trapping. Under certain conditions, P released to pore water can reach relatively high concentrations and authigenic phases can then precipitate. The authigenic precipitation is conditioned by alkalinity, pH, Eh and bacterial activity (Reimers et al., 1996; Benitez-Nelson, 2000). The principal authigenic phases belong to the apatite family, e.g., the carbonate-fluorapatite mineral called francolite. Francolite can precipitate either rapidly (directly or more probably replacing a short-lived and poorly crystallized precursor) or slowly (usually replacing calcite; Jarvis et al., 1994; Trappe, 1998; Piper and Perkins, 2004). The P concentration must be high enough to support francolite supersaturation. This enrichment may result from a high OM supply in highly productive marine environments such as upwelling areas, but high productivity is not always a prerequisite. In low-productivity portions of the oceans, it is often considered that P enrichment can be effectuated through redox cycling of iron, with P sorption onto iron-oxyhydroxide coatings and Fe–P co-precipitation (e.g., Jarvis et al., 1994; Piper and Perkins, 2004; n.b., manganese also can be involved in P enrichment; Wang and van Cappellen, 1996). An alternative mechanism for P retention may be uptake by bacterially precipitated polyphosphates (Sannigrahi and Ingall, in press).

Thus, in the case of P trapping, the abundance of P is not necessarily indicative of a high OM flux, because P may be enriched efficiently even in the absence of high surface-water productivity.

To summarize, the degree to which remineralized organic P is retained as a reactive fraction in sediments depends on the redox conditions of the depositional system. In environments with at least intermittently oxic bottom waters, redox cycling of Fe within the sediment limits the diffusive flux of remineralized P to the overlying water column: Fe-oxyhydroxides that scavenge phosphate from sediment pore waters are precipitated above the oxic/anoxic interface and dissolved below it, leading to retention of P for a period sufficient to permit slow growth of authigenic phosphate phases.

In permanently anoxic environments with sulfidic bottom waters, Fe-oxyhydroxides do not precipitate within the sediment, reducing the potential for adsorption and complexation of remineralized organic P. Consequently, P is not a reliable redox or productivity proxy for short scale reconstructions. However, as P loss/retention from the sediment is closely tied to redox conditions, P distribution may be useful for global paleoredox budgets I (e.g., Ingall et al., 1993). For instance, Algeo and Ingall (submitted for publication) use it to propose a curve of atmospheric pO_2 variation through the Phanerozoic.

Phosphorites. The phosphate content of sediments may reach high values forming phosphorite deposits in the extreme case. The high P content of phosphorites is usually enhanced by hydrodynamically induced winnowing of francolite-rich sediments. A large literature is devoted to phosphorites (Schmitz et al., 1997; Schuffert et al., 1998; see the recent synthesis by Glenn et al., 2000 and references therein). Phosphorites are not discussed in detail here, but they exert strong influences on the distributions of some other trace metals.

The francolite family may be represented by the formula: $Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_{x-y-z}(CO_3{\cdot}F)_y(SO_4)_zF_2$. Because of the “open” structure of francolite, many substitutions can occur in the two Ca sites and the PO_4 and F sites (Jarvis et al., 1994). These substitutions affect major and trace elements. Some trace metals show marked enrichments in phosphorites, compared to average shales. These elements are mainly Ag, Cd, Mo, Se, U, Y and Zn, as well as rare earth elements and accessory Br, Cu, Cr, I, Pb and V (Prévôt and Lucas, 1980, 1986; Lucas et al., 1990; Jarvis et al., 1994; Nathan et al., 1997). However, the trace elements are not necessarily located within the apatite structure itself but may be adsorbed onto crystal surfaces or may be related to other minerals (mainly sulfides) and OM (see Jarvis et al., 1994 for discussion). Though there remains considerable uncertainty regarding the real mineralogical affinities of the trace elements toward francolite and the incorporation mechanisms involved, it is observed that Cd and U are strongly enriched in phosphorites (Middelburg and Comans, 1991). In many modern marine sediments, Cd shows the closest correspondence to PO_4 profiles among all the trace elements and this has led to the suggestion that the Cd content of foraminiferal calcite may be used as a paleoproductivity proxy (Jarvis et al., 1994; Van Geen et al., 1995). The foraminiferal Cd/Ca ratio has thus been used in a number of paleoenvironmental studies (e.g., Oppo and Rosenthal, 1994; Rosenthal et al., 1997; Henderson, 2002, and references herein). Uranium in the form U^{4+} substitutes for Ca in the structures of many apatites, but U is dominantly complexed by OM and is not always present in the apatite lattice in significant quantities (Jarvis et al., 1994). Jarvis et al. (1994) and Trappe (1998) argued that, because of efficient U redox cycling, high U content in phosphorites does not necessarily indicate that francolite precipitated under reducing or strong productivity conditions. The fact that some trace elements widely used as paleoredox proxies are enriched in phosphorites indicates the importance of determining the primary phases of residence of each element, before drawing inferences regarding the environmental significance of its enrichment.

Barium is present in marine sediments mainly in detrital plagioclase crystals and in the form of barite ($BaSO_4$; Bishop, 1988; Rutsch et al., 1995). The formation of authigenic barite in surface water is related to bio-induced processes but is not fully understood. As seawater is undersaturated with respect to barite (Monnin et al., 1999; Jeandel et al., 2000), it has been proposed that acantharia, promote barite precipitation during dissolution of their Ba-containing celestite skeleton within microenvironments such as OM-rich particles, foram chambers and fecal pellets (McManus et al., 1994). More probable is the role of the decaying phytoplankton biomass. Live phytoplankton incorporate Ba (actively or passively ; i.e., metabolic uptake or adsorption) and Ba released during phytoplanktonic necromass decay may precipitate as barite in micro-environments where Ba-sulfate reaches supersaturation (Dehairs et al., 1980, 1987, 1991, 1992; Dymond et al., 1992; Kenison Falkner et al., 1993). The barite crystals can be protected from partial or total dissolution during particle settling in the undersaturated water column, thanks to the protective role of intraparticle microenvironments (Dehairs et al., 1991; Stroobants et al., 1991; Lea and Spero, 1994). The apparent relationship between the abundance of biogenic barite and OM and the refractory nature of barite in sediments where no intense sulfate reduction takes place have given support to the consideration of biogenic barium and barite as proxies for paleoproductivity (e.g., Dehairs et al., 1980, 1991; Dymond et al., 1992; François et al., 1995; McManus et al., 1998a,b, 1999; Cardinal et al., 2005; Sanchez-Vidal et al., 2005). Many studies have examined the link between surface productivity, export of OM from the photic zone and the biogenic Ba abundance in the water column (e.g., Dymond et al., 1992; Gingele and Dahmke, 1994; Monnin et al., 1999; Jeandel et al., 2000), as well as in surface sediments (e.g., Paytan et al., 1996, 2003; Paytan and Kastner, 1996; Prakash Babu et al., 2002). Others have employed biogenic Ba as a paleoproductivity proxy in older sediments (Brumsack and Gieskes, 1983; Brumsack, 1986, 1989; von Breymann et al., 1992; Tribovillard et al., 1996; Bonn et al., 1998; McManus et al., 1998a,b, 1999; Jacot des Combes et al., 1999; Martinez-Ruiz et al., 2000; Kasten et al., 2001; Joachimski et al., 2002; Weldeab et al., 2003; Tribovillard et al., 2004b; Riquier et al., 2005). However, Ba concentration and barite abundance must be considered cautiously for this purpose (e.g., Kumar et al., 1996; Monnin et al., 1999; van Beek et al., 2003; Reitz et al., 2004). This caveat is particularly true in the case of sediments characterized by intense sulfate reduction, which led to barite dissolution and Ba migration through pore waters (Van Os et al., 1991; Torres et al., 1996; van Santvoort et al., 1996). Thus, barite (or Ba-rich oxyhydroxide) migration fronts may form within sediments in which authigenic Ba sulfate precipitate where oxidizing conditions are met (a behavior somewhat similar to that of Mn, with which Ba can be involved; Dymond et al., 1992). In other words, Ba may be delivered to the sediments with a high OM flux but it can migrate during early diagenesis and precipitate in sediments deposited in the absence of high productivity. Such sulfate-reducing conditions usually develop rapidly in OM-rich sediments; consequently and paradoxically, Ba abundance cannot be used confidently as a paleoproductivity in organic-rich sediments, typically present in high-productivity platform. Rather, effective use of Ba as a paleoproductivity marker may be restricted to marine sediments deposited in portions of the ocean with low to moderate productivity.

Nickel. In oxic marine environments, Ni behaves as a micronutrient and may be present as soluble Ni^{2+} cations or $NiCl^+$ ions but it is mostly present as a soluble Ni carbonate ($NiCO_3$) or adsorbed onto humic and fulvic acids (Calvert and Pedersen, 1993; Whitfield, 2002; Algeo and Maynard, 2004). Complexation of Ni with OM will accelerate scavenging in the water column and thus sediment enrichment (Piper and Perkins, 2004; Nameroff et al., 2004; Naimo et al., 2005). Upon OM decay, Ni may be released from organometallic complexes to pore waters. In moderately reducing sediments, Ni is cycled from the sediment into the overlying waters because sulfides and Mn oxides are absent. Under (sulfate-) reducing conditions, Ni may be incorporated as the insoluble NiS into pyrite (solid solutions), even if the kinetics of the process are slow (Huerta-Diaz and Morse, 1990, 1992; Morse and Luther, 1999). Occasionally, the Ni brought to the sediments by OM may also be incorporated into tetrapyrrole complexes and may be preserved as Ni-geoporphyrins under reducing (anoxic/euxinic) conditions (Lewan and Maynard, 1982; Grosjean et al., 2004).

Copper. In oxic marine environments, Cu is dominantly present as organometallic ligands and, to a lesser degree, $CuCl^+$ ions present in solution (Calvert and Pedersen, 1993; Whitfield, 2002; Achterberg et al., 2003; Algeo and Maynard, 2004). Copper behaves only partly as a micronutrient but is also scavenged from solution in deep water (Calvert and Pedersen, 1993). Complexation of Cu with OM, as well as adsorption onto particulate Fe–Mn-oxyhydroxides, will accelerate scavenging and sediment enrichment (Fernex et al., 1992; Sun and Püttmann, 2000; Nameroff et al., 2004; Naimo et al., 2005). Upon OM decay and/or reductive dissolution of Fe–Mn-oxyhydroxides, Cu may be released to pore waters. Under reducing conditions (notably bacterial sulfate reduction conditions), Cu(II) is reduced to Cu(I) and may be incorporated in solid solution in pyrite, or it may even form its own sulfide phases, CuS and CuS_2 (Huerta-Diaz and Morse, 1990, 1992; Morse and Luther, 1999). In (hemi-)pelagic sediments with slow sedimentation rates, Cu may be diagenetically fixed by authigenic nontronite or smectite minerals (Pedersen et al., 1986).

Zinc. In oxic marine environments, Zn behaves as a micronutrient and may be present as soluble Zn^{2+} cations or $ZnCl^+$ ions but it is mostly present as complexes with humic/fulvic acids (Calvert and Pedersen, 1993; Algeo and Maynard, 2004). Zinc may also be adsorbed onto particulate Fe–Mn-oxyhydroxides (Fernex et al., 1992). Upon OM decay, Zn may be released from organometallic complexes to pore waters. Under reducing conditions (notably in the bacterial sulfate reduction zone), Zn may be incorporated as ZnS as a solid solution phase in pyrite or, to a lesser degree, it may form its own sulfides, sphalerite ([Zn,Fe]S) (Huerta-Diaz and Morse, 1992; Daskaladis and Helz, 1993; Morse and Luther, 1999).

Cadmium. Contrary to Ni, Cu and Zn discussed above, Cd is present in only one coordination state (Cd (II)) in the water column and sediments and has a nutrient-like behavior, which implies a relatively short residence time (Boyle, 1981, 1988; Rosenthal et al., 1995, 1997; Morford and Emerson, 1999). Cadmium is delivered to marine sediment mainly in association with OM (Piper and Perkins, 2004) and is released to interstitial waters during OM decay and authigenically enriched in sediments, probably in the form of a sulfide (Gobeil et al., 1997; Morford and Emerson, 1999; Morford et al., 2001). In the presence of H_2S, Cd likely forms a separate insoluble sulfide phase (CdS) rather than coprecipitating with FeS (Huerta-Diaz and Morse, 1992). Cadmium is enriched in both mildly and strongly reducing sediments (Calvert and Pedersen, 1993; Rosenthal et al., 1995; Russell and Morford, 2001; Chaillou et al., 2002). Lastly, Cd is strongly enriched in phosphorites because it substitutes readily for Ca in hydroxyapatite (Middelburg and Comans, 1991; Jarvis et al., 1994).

7. Remobilization of authigenically enriched trace metals during diagenesis

Inferences regarding paleoenvironmental conditions based on trace-metal data are commonly unreliable if single element distributions are used, because trace-metal concentrations are influenced by many factors and mechanisms. Factors that influence trace-element enrichment include the detrital siliciclastic flux, primary productivity rate and OM provenance, which can vary quasi-independently of the degree of deepwater restriction. The trace elements presented here can be used as proxies for paleoproductivity and paleoredox conditions only if the hydrogenous signal is recognizable, as is generally the case if the seawater-derived fraction exceeds inputs from other sources (e.g., detrital or hydrothermal; see above). In addition, one must be cognizant of the possibility of trace-element mobility during diagenesis, which can produce elemental distributions that do not reflect primary (i.e., paleoenvironmental) controls.

Sedimentary accumulations of trace elements may be hosted by various phases, e.g., metal sulfides, in solid solution in pyrite, insoluble oxides and oxyhydroxides, phosphate, sulfate, organometallic complexes and adsorbed onto organic or mineral surfaces. Consequently, the behavior of different trace elements is highly variable during diagenesis, depending on the specific pH and Eh conditions of the burial environment.

In the absence of postdepositional replenishment of oxidizing agents, sulfides are stable and the elements engaged in or coprecipitated with (iron-) sulfides typically do not move during diagenesis. This immobility is generally the case with Mo, V, Cd, Ni, Co, Cu, Zn and Pb. These elements show varying tendency to be incorporated into pyrite. This range is illustrated by the degree of trace-metal pyritization studied by Huerta-Diaz and Morse (1992). These authors, together with Thomson et al. (1993, 1998) and Morse and Luther (1999), suggested the following hierarchy for sensitivity to pyritization: $Hg > As = Mo > Cu = Fe > Co > Ni \gg Mn > Zn > Cr = Pb > Cd$. In addition to forming insoluble sulfides, Zn, Pb and Cd may form strong, soluble complexes with reduced S species (Huerta-Diaz and Morse, 1990, 1992). Consequently, these soluble complexes increase the mobility of the elements in anoxic sediments, leaving them free to diffuse across the sediments. Depending on the H_2S concentration, diffusion in the direction of the sediment–water interface can result in coprecipitation of these metals with iron and manganese oxides or reprecipitation in the form of solid sulfides.

7.1. Postdepositional reoxygenation

In the typical sequence of diagenetic events (Section 2), once the pools of oxidizing agents (electron acceptors) are exhausted by abiogenic oxidation reactions or bacterial OM oxidation, reducing conditions develop irreversibly in the sediment. However, under some conditions, oxidizing agents can be replenished from above after the development of reducing conditions. Of course, this does not affect deeply buried sediments but it may be observed when environmental conditions vary (relatively) abruptly, such as glacial–interglacial transitions (Dean et al., 1997; Lyons et al., 2003; McManus et al., 2005), or when turbidites are deposited in low-oxygen settings (e.g., Van Os et al., 1991; Van Santvoort et al., 1997; Cowie et al., 1998; de Lange, 1998; Jarvis et al., 1998; Thomson et al., 1998; Wehausen and Brumsack, 1999; Rinna et al., 2002). The influence of postdepositional oxygen replenishment is greater when the penetration depth into the sediments is large. In particular, this oxygen replenishment may lead to uranium remobilization if oxygen penetrates to a region where authigenic U has accumulated (see Section 7.1). Other trace elements such as V, Cd and Mo might also be affected by the reoxidation process but to a lesser extent than U (Morford et al., 2001). However, Thomson et al. (1998) noted no migration for Cd and V, and only short-distance (<5 cm) migration for Co, Cu, Ni and Zn in the turbiditic systems they studied. In cases where significant enrichments in V, Cr, Cd and Mo are observed with U being enriched only at a lesser degree, it must be hypothesized that small quantities of dissolved oxygen may have caused the solubilization and loss of U from sediments that had previously experienced reducing conditions.

8. Multi-proxy trace-element patterns

Because trace elements respond in largely predictable ways to redox variation, analysis of environmental redox conditions is best undertaken using a suite of trace elements rather than a single elemental proxy. As suggested above, some elements may have several origins (Cr, Co, Ba) and/or move more or less easily after deposition and burial (P, Ba, Zn, Pb, Cd); consequently, the discussions that follow emphasize an integrated approach centered on those elements least vulnerable to primary and secondary complications—i.e., U, V, Mo, Ni and Cu. It should be emphasized that the trace-element patterns discussed below are representative mainly of sediments with relatively simple redox histories and that trace-element patterns in sediments with complex or unusual redox histories are not easily generalized.

8.1. Suboxic–anoxic vs. euxinic

A suite of trace elements can exhibit somewhat different sensitivities to redox conditions along an oxic to sulfidic gradient. Basically, Cr, U and V are reduced and can accumulate under denitrifying conditions, whereas Ni, Co, Cu, Zn, Cd and Mo are enriched mainly under sulfate-reducing conditions alone (see Section 2). Using the contrasting behavior of these two groups of trace elements, it may be possible to recognize redox gradations in some sedimentary systems. For example, in the case of U and V enrichment without Mo enrichment, suboxic/anoxic depositional without free H_2S can be inferred. Conversely, sediments exhibiting concurrent enrichments in U, V and Mo reflect euxinic conditions at the sediment–water interface or in the water column (Algeo and Maynard, 2004; Tribovillard et al., 2004b, 2005). The two-step reduction of certain trace elements, e.g., V(V)→V(IV)→V(III), may provide another means of assessing small redox variations in paleoenvironments (Fig. 1).

Nevertheless, it must be noted that what is exposed above may look an over simplification in some complex sedimentological settings. For instance, Nameroff et al. (2002) demonstrated that, in the case of the oxygen-minimum zone of the eastern tropical North Pacific, a trace-metal sediment signature that indicates anoxic conditions is not necessarily attributable to an anoxic water column.

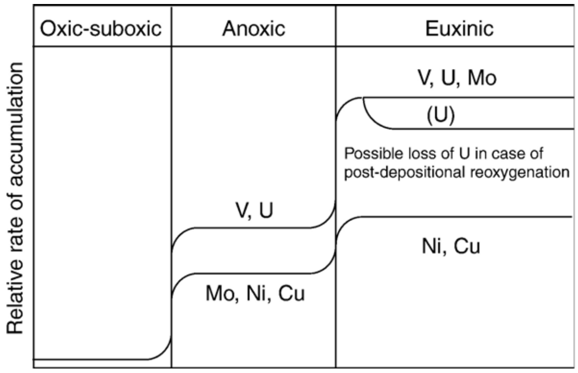


Fig. 1. Schematic behavior of Ni, Cu, Mo, U and V as a function of the redox status of the depositional environment (modified from Algeo and Maynard, 2004).

8.2. Tracers for OM abundance

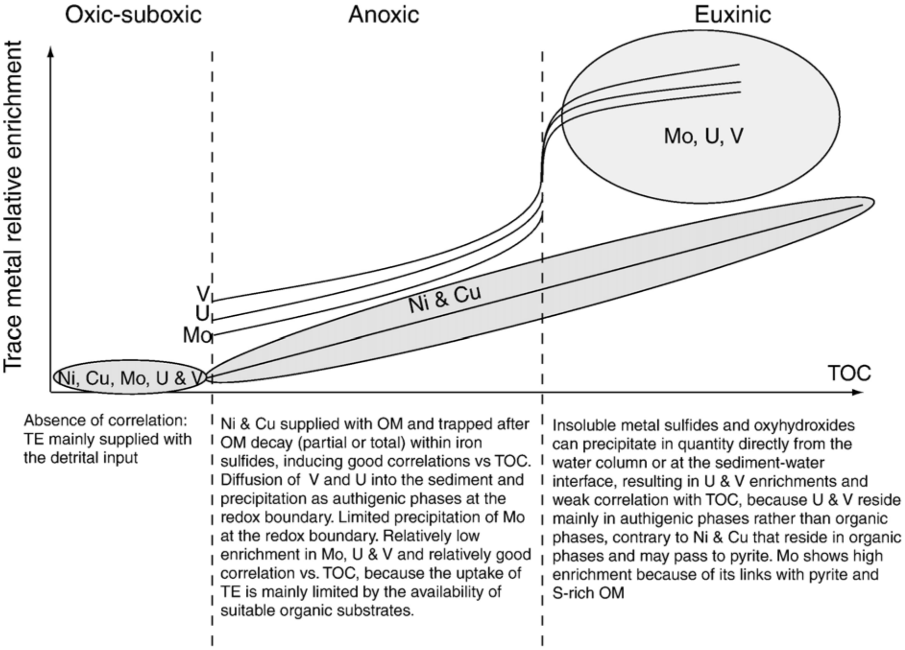
In addition to their variable behavior in response to different redox conditions, trace elements can be distinguished through their relations to OM. For instance, contrary to U and V, Ni and Cu are dominantly delivered to the sediments in association with OM (organometallic complexes). These elements are often referred to as 'sulfide forming' and they are generally not considered to be markers of organic fluxes to the sediment. They are released through OM decay and can be trapped by pyrite if sulfate-reducing conditions prevail (Huerta-Diaz and Morse, 1992; Fernex et al., 1992; Nameroff et al., 2002, 2004; Piper and Perkins, 2004; Algeo and Maynard, 2004). Thus, if Ni and Cu are not scavenged by settling organic particles, they are not observed to be significantly enriched in sediments even if reducing conditions develop rapidly. Consequently, a high content in Ni and Cu indicates (1) that a high OM flux brought these elements to the sediments in great abundance and (2) that reducing conditions were met, allowing Ni and Cu fixation within the sediments. Thus, we emphasize that Ni and Cu abundance can serve as a marker of a relatively high OM flux, whereas U, V and Mo can be used to decipher paleoredox conditions (Fig. 1). Furthermore, Ni and Cu may be retained within the sediments, being hosted by pyrite (most frequently), whereas OM may be remineralized by bacterial activity. Consequently, Ni and Cu may speak to the original presence of OM even if it is partially or totally lost after deposition. In that way, we consider that Cu and Ni are better proxies to OM abundance than P and Ba.

8.3. Bottom water oxygenation and/or organic matter flux?

Based on the considerations above, it may be possible to discriminate depositional environments where reducing conditions developed (as evidenced by enrichments in U and V, plus Mo in the case of euxinic conditions) in the presence of sedimentary OM (Ni and Cu enrichment) or in the absence of OM (no marked enrichment in Ni and Cu. In the latter case, it is deduced that anoxia was not triggered by intense OM degradation but may instead be explained by restricted watermass renewal or even stagnation (see examples in Tribovillard et al., 2004b; Riquier et al., 2005, in press). In the former case (anoxia and OM), it is not always possible to decipher whether anoxia was caused by intense OM degradation or whether anoxia prevailed prior to OM deposition and prevented partial or total OM degradation, because in most anoxic environments, there is an interplay between productivity and benthic anoxia that is difficult to separate. In addition, trace elements cannot easily help decipher whether the chemocline was at the sediment–water interface or above it within bottom waters. Solving this point requires other proxies that can detect the presence of syngenetic pyrite in sediments. Pyrite can form syngenetically if the chemocline lies above the sediment–water interface, or diagenetically if the chemocline lies at or below the sediment–water interface. Syngenetic pyrite consists of fine-grained, euhedral crystals, whereas diagenetic pyrite is typically composed of larger, spherical framboids. Consequently, the grain-size analysis of pyrite grains can be used to identify water-column euxinicity (Wilkin et al., 1996; Wijsman et al., 2001; Lyons et al., 2003; Cruse and Lyons, 2004). A detectable iron enrichment (i.e., an increase in the Fe/Al ratio) also may indicate an additional, syngenetic pyrite source of iron for the sediment (e.g., Wilkin et al., 1996; Lyons, 1997; Raiswell and Canfield, 1998).

8.4. Interpreting paleoredox conditions from trace element–TOC covariation patterns

From many studies of sedimentary rocks (e.g., Tribovillard et al., 1994; Riboulleau et al., 2003; Cruse and Lyons, 2004; Algeo and Maynard, 2004; Tribovillard et al., 2004b; Tribovillard et al., 2005) or recent sediments (Robinson et al., 2002; Algeo and Lyons, in press), it is observed that U, V, Mo, Ni and Cu abundances plotted versus TOC illustrate many of the points discussed above (Fig. 2). For sediments or sedimentary rocks showing a large range of TOC (<1% to >15–20%), except for the lowest TOC values, good positive correlations between Ni–Cu enrichments and TOC are observed whatever the redox status (suboxic to euxinic). However, again except for the lowest TOC concentrations, U and V show good correlations with TOC when TOC stays below a certain threshold value, but the correlation disappears above the threshold. Above the threshold a significant Mo enrichment accompanies the U–V enrichment, evidencing the development of euxinic conditions. Thus, the threshold marks the limit between anoxic and euxinic conditions. The TOC value of this threshold can be highly variable: It is approximately 1.0–1.5% in the modern Cariaco Basin and ~2.5–3.5% in the modern Saanich Inlet, but it can be much higher in ancient sediments, e.g., ~7% TOC for the Kimmeridge Clay Formation of Western



Absence of correlation: TE mainly supplied with the detrital input

Ni & Cu supplied with OM and trapped after OM decay (partial or total) within iron sulfides, inducing good correlations vs TOC. Diffusion of V and U into the sediment and precipitation as authigenic phases at the redox boundary. Limited precipitation of Mo at the redox boundary. Relatively low enrichment in Mo, U & V and relatively good correlation vs. TOC, because the uptake of TE is mainly limited by the availability of suitable organic substrates.

Insoluble metal sulfides and oxyhydroxides can precipitate in quantity directly from the water column or at the sediment-water interface, resulting in U & V enrichments and weak correlation with TOC, because U & V reside mainly in authigenic phases rather than organic phases, contrary to Ni & Cu that reside in organic phases and may pass to pyrite. Mo shows high enrichment because of its links with pyrite and S-rich OM

Fig. 2. Schematic diagram illustrating the relative enrichment of Ni, Cu, Mo, U and V versus total organic carbon (TOC). TE stands for trace elements and OM stands for organic matter.

Europe (Ramanampisoa and Disnar, 1994; Tribovillard et al., 1994, 2005) and ~10% TOC for the upper Pennsylvanian cyclothemic core shales of Kansas (Algeo and Maynard, 2004).

Our interpretation of the trace element–TOC covariation pattern shown in Fig. 2 is that, under oxic–dysoxic conditions (sediment TOC generally <2%), trace elements are deposited mainly in association with the detrital fraction of the sediment resulting in no covariation with TOC. Under anoxic but non-sulfidic conditions, Ni and Cu are deposited largely in the form of organometallic complexes with more limited diffusion of U and V into the sediments and precipitation as authigenic phases at redox boundary. These conditions can result in variable TOC values but favor strong TOC–trace element correlations because the uptake of trace elements is mainly limited by the availability of suitable organic substrates (Algeo and Maynard, 2004). Under euxinic conditions, in which free H_2S is present and trace elements are generally reduced to their lowest valence state, insoluble metal sulfides and oxyhydroxides can precipitate in quantity directly from the water column or at the sediment–water interface. These conditions result in strong U and V enrichments and weak correlations with TOC because U and V reside mainly in authigenic mineral phases rather than organic phases (Algeo and Maynard, 2004), contrarily to Ni and Cu that reside in organic phases and may pass to pyrite (Figs. 1 and 2). Mo shows high enrichment because of its links with pyrite and sulfur-rich OM (Tribovillard et al., 2004b). These trace element–TOC covariation patterns are probably typical only of open-marine systems, where the dissolved trace-element inventory of seawater is not depleted through sedimentation (e.g., Algeo and Maynard, 2004). In hydrographically restricted marine systems, in which the sink flux of trace elements to the sediment may exceed the source flux associated with deepwater renewal, different relationships between sedimentary TOC and trace elements appear to exist (Algeo, 2004; Algeo and Lyons, in press; Algeo et al., submitted for publication).

9. New tracks for the near future?

The marine molybdenum isotope budget appears to be redox-sensitive (Siebert et al., 2003; Arnold et al., 2004) and Mo isotopic composition seems to be a promising proxy to reconstruct the paleoredox status of the global ocean on time scales longer than one million years (Anbar, 2004). Till now Mo isotope composition proved to be a good paleoredox proxy for the early Earth (Arnold et al., 2004; Anbar, 2004; Siebert et al., 2005), but expected progresses should allow to use this proxy on smaller time scales (Siebert et al., 2006; Algeo et al., submitted for publication).

10. Conclusions

This synthesis of the geochemical behavior of certain trace elements and of works that use them for paleoenvironmental reconstructions allows us to select some trace metals to be used as proxies for paleoredox and paleoproductivity conditions. These elements can be used provided their concentrations result from hydrogenous sources and not from detrital or hydrothermal sources. One of the principal results of this contribution is that a combined used of U, V and Mo enrichments can allow distinguishing suboxic environments from anoxic–euxinic ones. This distinction can be facilitated by the fact that the enrichments in these elements can be markedly different below or above a certain TOC threshold value. This threshold value depends on many factors, among them the sedimentation rate, OM nature and sediment fabrics. However, concerning reducing depositional conditions, trace elements cannot always help determine whether the chemocline was located at the sediment–water interface or above it. To answer this point, the iron concentrations and size of pyrite grains may be a great help. Another result is that Ni and Cu can have a value as paleoproductivity proxies and these elements do not suffer from the limitations affecting P and Ba in that use.

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