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## CONTROLS ON TRACE METAL AUTHIGENIC ENRICHMENT IN REDUCING SEDIMENTS: INSIGHTS FROM MODERN OXYGEN-DEFICIENT SETTINGS

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**ABSTRACT.** Any effort to reconstruct Earth history using variations in authigenic enrichments of redox-sensitive and biogeochemically important trace metals must rest on a fundamental understanding of their modern oceanic and sedimentary geochemistry. Further, unravelling the multiple controls on sedimentary enrichments requires a multi-element approach. Of the range of metals studied, most is known about the behavior of Fe, Mn, and Mo. In this study, we compare the authigenic enrichment patterns of these elements with a group whose behavior is not as well defined (Cd, Cu, Zn, and Ni) in three oxygen-poor settings: the Black Sea, the Cariaco Basin (Venezuela), and the Peru Margin. These three settings span a range of biogeochemical environments, allowing us to isolate the different controls on sedimentary enrichment. Our approach, relying on the covariation of elemental enrichment factors [EF, defined for element X as:  $EF_X = (X/Al)_{\text{sample}} / (X/Al)_{\text{lithogenic}}$ ], has previously been applied to Mo and U to elucidate paleoenvironmental information on, for example, benthic redox conditions, the particulate shuttle, and the evolution of water mass chemistry. We find two key controls on trace metal enrichment. First, the concentration of an element in the lithogenic background sediment (used in calculating  $EF_X$ ) controls the magnitude of potential enrichment. Maximum enrichment factors of 376 and 800 are calculated for Mo (~1 ppm in detrital sediments) and Cd (~0.3 ppm), respectively, compared to values not greater than 17 in any setting for the other five metals (~45 ppm to ~4.5 wt.% in detrital sediments). Second, there is a relationship between the aqueous concentration of the element in overlying seawater and its degree of enrichment in the sediment. We further identify four important processes for delivery of trace metals to the sediment. These are: (1) cellular uptake (especially important for Zn and Cd), (2) interaction/co-precipitation with sulfide (Mo, Cu, and Cd), (3) passive scavenging via the traditional particulate shuttle (Mo, Ni, and Cu), and (4) an association with the benthic Fe redox shuttle (Mn, Ni). Finally, we summarize the oceanic mass balance of Cd and Mo and place the first constraints on the contribution of reducing sediments to the oceanic mass balance of Cu, Zn, and Ni. We show that reducing sediments are the ultimate repository for up to half the total output flux of these elements from the oceanic dissolved pool.

Keywords: reducing sediments, trace metals, authigenic enrichment, euxinia, ocean redox, mass balance

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## INTRODUCTION

Trace metals are fundamental for a range of biogeochemical processes in the ocean. Some elements (for example, Fe and Zn) are thought to limit productivity in regions of the ocean replete with major nutrients, such as the high-latitude Southern Ocean, with ramifications for carbon cycling (for example Boyd and Ellwood, 2010; Sinoir and others, 2012). Others are both bioessential and redox sensitive (for example, Mo, Fe, and Cu), for which sediments deposited under reducing conditions represent a significant fraction of their oceanic output and are one control on their bioavailability (for example Morford and Emerson, 1999). The oceans have been subject to large shifts in redox over Earth history, with parallel shifts in the marine inventories of these redox-sensitive trace metals (for example Canfield, 2005; Reinhard and others, 2013; Lyons and others, 2014). These shifts in turn have been implicated in the pattern of biological evolution on Earth (for example Saito and others, 2003; Dupont and others, 2010).

The potential for using trace metal concentrations as a means to probe present and past Earth-surface conditions has been recognized since Goldschmidt's early observation that these elements are typically enriched in organic-rich sediments (Goldschmidt, 1954). Organic-rich sediments are considered indicators of low bottom water oxygen concentrations, with two contrasting models proposed for their accumulation in the modern and past ocean (see review by Meyer and Kump, 2008). In one end-member process, upwelling-driven productivity is accompanied by high organic carbon export rates, leading to high rates of oxygen utilization in the deep ocean (Suess and Thiede, 1983)—that is, anoxia is controlled by O<sub>2</sub> sinks. In a second model, restricted circulation reduces the input of oxygen from the atmosphere and is accompanied by water column anoxia and commonly euxinia (free HS<sup>-</sup> in the water column), such as observed in the modern Black Sea (Demaison and Moore, 1980). In the latter case, organic richness is tied at least in part to enhanced preservation under O<sub>2</sub>-free conditions. Unravelling the relative roles of these two processes in the deposition of ancient black shales remains a challenge (for example Brumsack, 2006). However, if the differing responses of transition metals to changes in water column chemistry, primary production, and diagenetic processes could be further clarified, a new generation of multi-tracer approaches offers the opportunity to disentangle the relative roles of these and other processes through time.

Reducing conditions can be subdivided into those that are anoxic but non-sulfidic and those that are euxinic. This study considers the possible controls on the authigenic enrichment of a suite of trace metals (Fe, Mn, Mo, Cd, Ni, Cu, and Zn) from a range of reducing sedimentary environments. Though subsets of these elements from a more limited range of oceanographic settings have been considered before in this context (for example Francois, 1988; Calvert and Pederson, 1993; Morford and Emerson, 1999; Nameroff and others, 2002; Böning and others, 2004; Tribovillard and others, 2006; Algeo and Maynard, 2008; Algeo and Tribovillard, 2009), there has been no comprehensive treatment of them all as a group. We present new data for elemental enrichment factors from three modern study sites that bridge the two end-member mechanisms introduced above for the accumulation of organic-rich sediments in reducing conditions. We compare these data with existing results for similar settings (Francois, 1988; Calvert and Pedersen, 1993; Lyons and others, 2003; Böning and others, 2004; Algeo and Maynard, 2004; McManus and others, 2006). The data from this study are then used to place new constraints on the elemental oceanic mass balance of Ni, Cu, Zn, Mo, and Cd, with an emphasis on the significance of the size of the reducing sedimentary sink.

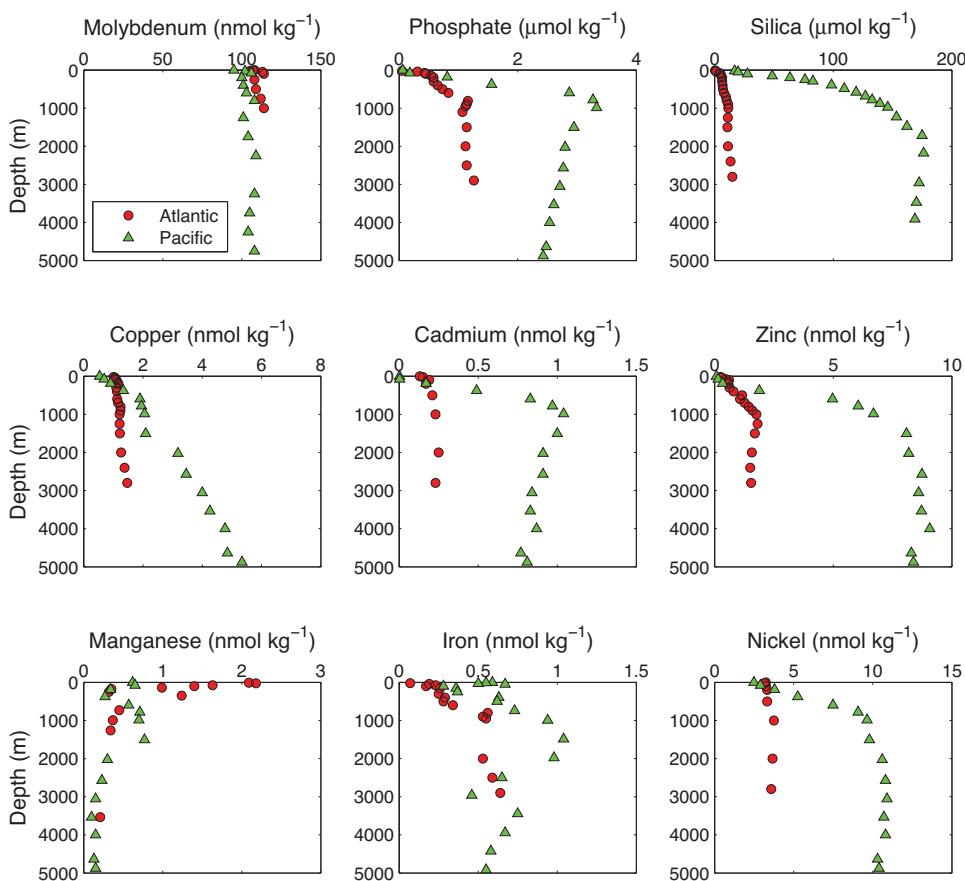


Fig. 1. Typical dissolved trace element distributions in oxic seawater: Atlantic, circles, and Pacific, triangles. Data sources: Morris, 1975; Bruland, 1980; Landing and Bruland 1980; Hynes 1983; Danielsson and others, 1985; Orians and Bruland, 1986; Statham and Burton, 1986; Sohrin and others, 1987; Martin and others, 1989; Martin and others, 1993; Ezoe and others, 2004.

#### BACKGROUND: THE GEOCHEMICAL BEHAVIOR OF TRACE METALS

##### *The Geochemical Behavior of Fe and Mn*

Iron and Mn behave geochemically similarly. In oxic seawater, both Fe(III) and Mn(III and IV) precipitate as Fe and Mn oxyhydroxides. As a result, average seawater concentrations of Fe and Mn are  $<1$  nM. The distribution of dissolved Fe in oxic seawater is unusual; it has a nutrient-type profile but with little intra-basinal fractionation (fig. 1) and a short residence time (*ca.* 100 yrs). The processes responsible for this distribution are reviewed in Johnson and others (1997). Dissolved Mn displays a typical scavenged-type element distribution (fig. 1), with high concentrations close to external sources in surface waters and near hydrothermal vents (reviewed in Bruland and Franks, 1983). Both Fe and Mn exhibit a dissolved maximum in the Pacific correlative with the development of oxygen minimum zones, either due to *in-situ* dissolution of oxide particles and/or to diffusion of Fe(II) and Mn(II) out of reductive sediments along continental margins (for example Klinkhammer and Bender, 1980; Landing and Bruland, 1987; Johnson and others, 1997; McManus and others, 2012). In anoxic

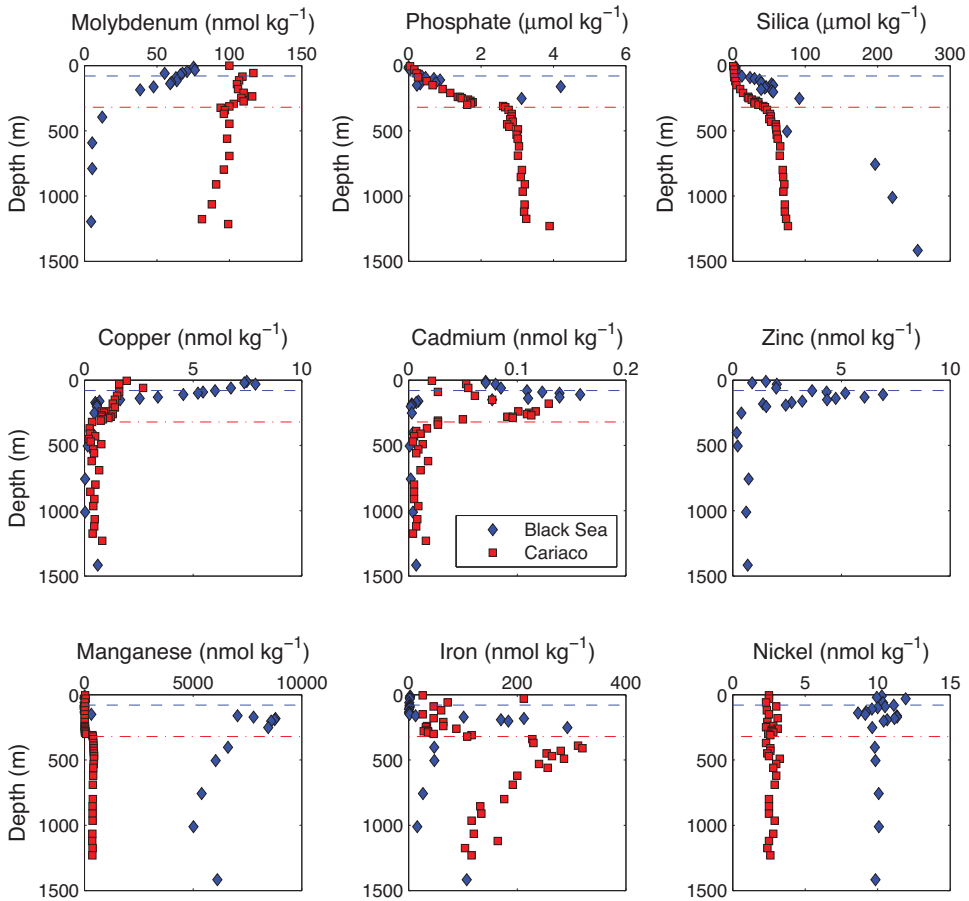


Fig. 2. Dissolved trace element distributions in the Black Sea, diamonds, and the Cariaco Basin, squares. Dashed (Black Sea) and dashed dot (Cariaco Basin) lines illustrate the depth of the oxic-anoxic interface in each basin. Data sources: Jacobs and others, 1987; Emerson and Husted, 1991; Tankéré and others, 2001.

water columns such as the Black Sea or Cariaco Basin, Fe and Mn exhibit a more pronounced maximum at the redoxline (fig. 2). The maximum in dissolved Fe occurs somewhat deeper than that for dissolved Mn due to the earlier onset of Mn versus Fe reduction (Froelich and others, 1979; Lewis and Landing, 1991; Landing and Lewis, 1991; Tankéré and others, 2001). Below the redox boundary in the Black Sea, concentrations of dissolved Fe and Mn decrease but remain high compared to oxic conditions (figs. 1 and 2).

The oxic-anoxic boundary in the Black Sea is at *ca.* 100 m water depth, far above the sediment. As a result, the particulate Fe and Mn oxides that are formed in the oxic layer, and which may sorb other trace metals, dissolve in the thick anoxic layer beneath (for example Yiğiterhan and others, 2011). In contrast, in an oxic water column with a redox boundary either in or just above the sediment, these Fe and Mn oxide particles deliver their sorbed trace metal complement directly to the sediment. This process has been termed the ‘particulate shuttle’. It is most efficient for elements like Mo that have a strong affinity for Fe-Mn oxides and has been used to explain strong Mo and weak U enrichments in some sediments (Algeo and Tribouillard, 2009; Scholz and others,

2013). The shuttle is particularly efficient in places like the Peru Margin (Algeo and Tribovillard, 2009).

Studies of Fe/Al ratios in the Black Sea record reactive Fe enrichment, where the reactive Fe fraction of marine sediments is defined as that portion of the total Fe pool that is reactive towards hydrogen sulfide on short diagenetic time scales (for example Canfield and others, 1996; Lyons, 1997; Raiswell and Canfield, 1998; Lyons and Severmann, 2006). This enrichment has been attributed to a second type of shuttle, the 'benthic Fe redox shuttle' (for example Canfield and others, 1996; Wijsman and others, 2001; Anderson and Raiswell, 2004; Lyons and Severmann, 2006). On oxic to suboxic shelves, where TOC levels are high enough to drive the system to anaerobic respiration but low enough to limit sulfide production by sulfate reduction, particulate Fe (III) oxides are solubilized in the upper levels of the sediment (Froelich and others, 1979). The Fe(II) produced is soluble in the anoxic pore waters and diffuses into local bottom waters. It can then be transported into the euxinic portion of the basin, where it reacts with dissolved sulfide and is rained out into sediment (Wijsman and others, 2001; Anderson and Raiswell, 2004). An analogous process may explain parallel authigenic enrichments of Mn in the Black Sea (Lyons and Severmann, 2006). Thermodynamic modeling of the euxinic Black Sea water column indicates that both Fe and Mn are saturated with respect to a sulfide phase (Mn with  $\text{MnS}_2$  and Fe with FeS or  $\text{Fe}_3\text{S}_4$ ; Landing and Lewis, 1991) and numerous data point to a predominance of water-column pyrite formation (for example Lyons, 1997; Wilkin and others, 1997). The 'benthic Fe/Mn redox shuttle' requires a mechanism to transport the solubilized Mn(II) and Fe(II) from anoxic pore waters on the shelf across the redoxcline to the deep basin. One means to achieve this transport may be via organic complexation (for example Hallberg and Larsson, 1999), but Mn forms relatively weak organic complexes in oxic seawater (Bruland and Franks, 1983). Alternatively oxides may re-precipitate, but as nano-particulates that continue to be advected basinward (Lyons and Severmann, 2006). This latter hypothesis is supported in the Black Sea by the presence of a Mn-rich 'fine particle layer', which forms on the shelf and spreads throughout the basin (Tank  re and others, 2001; Dellwig and others, 2010).

#### *The Geochemical Behavior of Mo, Cd, Zn, Ni, and Cu*

The absolute dissolved concentration of a trace metal in the water column is likely to exert a primary control on the degree to which it is enriched in the sediment (Algeo and Lyons, 2006). Many trace metals are less soluble under anoxic than oxic conditions and are thus present at lower concentrations (compare figs. 1 and 2), particularly in the presence of dissolved sulfide. Equilibrium thermodynamic predictions of metal-sulfide complexation suggest equilibrium metal(II)-sulfide species decrease in stability in the order  $\text{Cu} \gg \text{Cd} = \text{Pb} > \text{Zn} > \text{Fe} = \text{Co} > \text{Ni} > \text{Mn}$  (Al-Farawati and Van den Berg, 1999, and references therein).

In the sediment, authigenic enrichment requires both supply of the trace metal of interest and a diagenetic process to sequester the metal once delivered. Supply can occur via active uptake by plankton and delivery in cellular organic carbon or by passive scavenging to particulate organic carbon or other surfaces such as oxides (for example Balistrieri and others, 1981). In the presence of free  $\text{HS}^-$ , equilibrium thermodynamics predict that most trace metals will form insoluble monosulfide phases (for example Drever, 1997), and such pure metal sulfide phases are often assumed to control trace metal solubility (for example Emerson and others, 1983; Davies-Colley and others, 1985; Landing and Lewis, 1991). However, such settings are far from equilibrium environments (for example Simpson and others, 1998). By far the dominant sulfide phase precipitated is pyrite, and co-precipitation of other metals as a trace constituent in pyrite enhances supply to and fixation in the sediment (for example Huerta-Diaz and Morse, 1992; Large and others, 2014). This process is

reflected in a high degree of trace metal pyritization (DTMP), where DTMP is operationally defined as:

$$\text{DTMP} = \text{Pyrite} - \text{Me} / (\text{Pyrite} - \text{Me} + \text{Reactive} - \text{Me}) \quad (1)$$

(Huerta-Diaz and Morse, 1990, 1992). Sediment observations illustrate a decreasing order of DTMP for trace metals as follows: Mo > Cu = Fe > Co > Ni  $\gg$  Mn > Zn > Pb > Cd. Morse and Luther (1999) explain this pattern, in part, by suggesting that a metal with a slower reaction rate than Fe will tend to be incorporated as a trace constituent in pyrite (and hence have a high DTMP). Zinc and Cd are not incorporated in pyrite and instead appear to preferentially form their own sulfide phases, as observed in contaminated environments (Luther and others, 1980; Lee and Kittrick, 1984), though there remains little direct observational evidence for other metal sulfide phases in sediments (for example Morse and others, 1987; Zaggia and Zonta, 1997). Furthermore, metals are very likely associated with sulfur-rich organic phases in sulfide containing sediments, the behavior of which is also poorly known and may vary by location (for example Morse and others, 1987; Simpson and others, 1998).

*Molybdenum.*—Molybdenum is a trace component of the solid Earth, with low concentrations in detrital sediments (1–1.5 ppm, table 1; Wedepohl, 1991; Rudnick and Gao, 2003). In contrast, it is present at uniformly high concentrations of  $\sim 105$  nM in oxic seawater (fig. 1, table 1; Collier, 1985), where it exists predominantly as the molybdate anion ( $\text{MoO}_4^{2-}$ ). The high ratio of  $[\text{Mo}]_{\text{sw}} / [\text{Mo}]_{\text{average shale}}$  (table 1) is key in generating high degrees of authigenic Mo enrichment.

Removal of Mo in oxic settings is controlled by slow adsorption to Mn and Fe oxyhydroxides, with delivery to the sediment via active uptake into plankton likely of only minor importance (for example Brumsack, 1980; Böning and others, 2004). Mo/P and total Mo concentrations in plankton are low (table 1) and Mo shows no strong depletion in the photic zone of the oxic ocean (fig. 1; Nakagawa and others, 2012). In water columns that are stratified, but where the lower anoxic layer is thin compared to the upper oxic layer, Mo is significantly enriched via the particulate shuttle (Algeo and Tribouillard, 2009). Manganese or Fe oxide particles adsorb molybdate anion in the upper oxic part of the water column and sink to the sediment, where their reduction occurs at or close to the sediment-water interface. This process releases Mo to be sequestered in sulfidic bottom or pore waters (Crusius and others, 1996; Scholz and others, 2013).

In anoxic seawater Mo is considerably more reactive, as illustrated by the Black Sea where it is strongly depleted below the  $\text{O}_2$ - $\text{H}_2\text{S}$  chemocline (fig. 2; Emerson and Huested, 1991). It is also depleted below the chemocline in the Cariaco Basin, though its removal here is less marked (fig. 2; Emerson and Huested, 1991). This difference may be due to the lower sulfide concentrations in the Cariaco Basin, or to the less restricted hydrographic setting (Algeo and Lyons, 2006; Algeo and Maynard, 2008). Removal of Mo from the water column in euxinic settings was thought to occur via direct reduction of Mo(VI) (for example Francois, 1988; Emerson and Huested, 1991; compare Dahl and others, 2013). However, Helz and coworkers (1996) explained Mo removal in sulfidic environments by proposing a geochemical sulfide ‘switch’. In the presence of dissolved  $\text{HS}^-$ , replacement of the oxygen atoms in  $\text{MoO}_4^{2-}$  with sulfur occurs stepwise, forming reactive thiomolybdate species in which the redox state remains as Mo(VI). Above a threshold value (the ‘switchpoint’) of  $\sim 11$   $\mu\text{M}$   $[\text{H}_2\text{S}]_{(\text{aq})}$ , conversion of Mo to tetrathiomolybdate is quantitative (that is, complete; Helz and others, 1996; Erickson and Helz, 2000). The precise mechanism(s) of thiomolybdate removal to sediment is uncertain. A recent study found Mo(IV)-S compounds in sediments from a euxinic lake, which they cite as evidence for Mo reduction along the post-thiomolybdate burial pathway (Dahl and others, 2013). In other studies, a strong

TABLE 1  
*Summary of trace metal concentrations in average shale, seawater, and plankton, and calculated seawater/shale and plankton/shale ratios*

Metal ion	Atomic Weight	[Me] <sub>shale</sub> Wedepohl, 1991 ppm	[Me] <sub>seawater</sub> Nozaki, 1997 nM	ppm	Mean Me/P plankton* mmol/mol	Me/C plankton mmol/mol	[Me] <sub>plankton</sub> ppm	[Me] <sub>seawater</sub> /[Me] <sub>shale</sub> ( $\times 10^{-4}$ )	[Me] <sub>plankton</sub> /[Me] <sub>shale</sub>
Mn	54.94	850	0.36	$2.0 \times 10^{-5}$	1.02	0.0097	44	0.0002	0.05
Fe	55.85	47200	0.54	$3.0 \times 10^{-5}$	5.19	0.049	228	0.00001	0.005
Ni	58.69	68	8.2	$4.8 \times 10^{-4}$	0.80	0.0075	37	0.07	0.54
Cu	63.55	45	2.4	$1.5 \times 10^{-4}$	0.43	0.0040	21	0.03	0.47
Zn	65.38	95	5.4	$3.5 \times 10^{-4}$	3.79	0.036	195	0.04	2.1
Mo	95.94	1.3	105	0.010	0.03	0.0003	2.3	77	1.7
Cd	112.41	0.3	0.65	$7.5 \times 10^{-5}$	0.40	0.0037	35	2.4	117

\* Mean Me/P ratios in plankton calculated from available published data compiled in Appendix table 2, and converted to C assuming a C/P ratio in plankton of 106.

positive correlation between  $[\text{Mo}]_{\text{black shale}}$  and TOC has been observed in both modern and ancient black shales, suggesting that organic matter is the dominant phase involved in the transfer of Mo to sediment in euxinic environments (Algeo and Maynard, 2004; Tribovillard and others, 2004; Algeo and Lyons, 2006; Lyons and others, 2009, and references therein). Other studies propose that transfer to sediment is related to Fe-Mo-sulfide precipitation (Huerta-Diaz and Morse, 1992; Helz and others, 1996; Piper and Issacs, 1996; Morse and Luther, 1999). There are several lines of evidence (chemical and x-ray based) that support a strong Fe-Mo relationship in nature (see Helz and others, 2011, and references therein), yet there is often little evidence for correlation of  $[\text{Mo}]_{\text{black shale}}$  with pyrite S or total S (Lyons and others, 2003; Algeo and Maynard, 2004). Recent high spatial resolution analysis has suggested that pyrite plays a relatively minor role as a host for Mo in black shales (Chappaz and others, 2014).

*Cadmium.*—Cadmium is present in trace concentrations of 0.1 to 0.3 ppm in detrital sediments (table 1; Wedepohl, 1991; Rudnick and Gao, 2003). Deep-water concentrations are also low, at  $\sim 0.3$  nM in the North Atlantic compared with  $\sim 0.9$  nM in the North Pacific (fig. 1; Bruland, 1980; Bruland and Franks, 1983). Despite these low dissolved concentrations, Cd has a  $[\text{Me}]_{\text{sw}}/[\text{Me}]_{\text{average shale}}$  ratio two orders of magnitude higher than those of Zn, Ni, and Cu, though it is a factor of about 30 to 40 less than for Mo (table 1). Cadmium concentrations in organic matter are three orders of magnitude higher than in average shale (table 1) and it exhibits a strong nutrient-type distribution in oxic seawater; its near 1000-fold variation from surface to deep waters is the highest of any trace metal (fig. 1; Boyle and others, 1976; Bruland and Franks, 1983).

In anoxic seawater Cd forms strong complexes with bisulfide in anoxic seawater (Dyrssen, 1988; Zhang and Millero, 1994; Luther and others, 1996; Al-Farawati and Van den Berg, 1999). Removal of Cd associated with sulfide is observed in both the Black Sea and Cariaco Basin, with concentrations at both locations reduced from maxima of  $\sim 120$  pM close to the redoxcline to  $\sim 5$  to 10 pM beneath it (fig. 2; Jacobs and others, 1987; Haraldsson and Westerlund, 1991). Biological uptake probably remains a significant removal process in the oxic layer of euxinic basins and may be supplemented by sorption to Mn oxides precipitating above the redoxcline supplied by upwards diffusion of dissolved  $\text{Mn}^{2+}$ . Cadmium is not strongly scavenged by degrading organic material (John and Conway, 2014). Supply of Cd to sediments is thus likely via a combination of coprecipitation with sulfide and/or delivery in organic material. In the sediment Cd is released on degradation of organic matter to pore waters, where it is fixed by precipitation as insoluble CdS (Elderfield and others, 1981; Gobeil and others, 1987; Pederson and others, 1989; Rosenthal and others, 1995) or possibly by adsorption to newly precipitated Fe oxides (in suboxic-oxic sediments; McCorkle and Klinkhammer, 1991).

*Zinc.*—Zinc, like Cd, displays nutrient-type behavior in oxic seawater, with a relatively deep maximum in concentration correlated with silica (Bruland, 1980; Lohan and others, 2002). Deep-water Zn concentrations are *ca.* 2 and 10 nM in the deep Atlantic and Pacific, respectively (fig. 1). Free  $\text{Zn}^{2+}$  concentrations in surface waters can be very low and potentially bio-limiting (Morel and others, 1991)—due not only to uptake but also to complexation by organic ligands (Bruland, 1989). In the Black Sea, organic complexation of Zn is also high in surface waters, particularly near the shelf edge (Muller and others, 2001). Thermodynamic predictions and experimental measurements indicate that Zn-sulfide complexes are of intermediate strength compared to the other metals discussed here (Al-Farawati and Van den Berg, 1999). Like Cd, Zn shows a maximum in concentration close to the oxic/anoxic interface of the Black Sea (of  $\sim 7$  nM). Removal above could be due to phytoplankton uptake,



adsorptive removal onto Mn oxides, or a combination of the two. Removal below the redoxcline results in concentrations dropping to  $\sim 0.5$  nM (Haraldsson and Westerlund, 1991; Tankéré and others, 2001).

Zinc is present at concentrations of 70 to 95 ppm in average detrital sediments (Wedepohl, 1991; Rudnick and Gao, 2003). As a result, the  $[\text{Zn}]_{\text{sw}}/[\text{Zn}]_{\text{average shale}}$  ratio is low, and its authigenic enrichment is restricted. One exception to this limited enrichment is in the Framvaren Fjord, Norway, where enrichment factors for Zn reach  $\sim 100$  (Skei, 1983; Jacobs and others, 1985). Deep-water sulfide concentrations in Framvaren are much higher than, for example, in the Black Sea, at 7 to 8 mM, as are reported deep-water Zn concentrations (30 nM, table 2). In the Saanich Inlet, Canada, Francois (1988) concluded that excess Zn in sediment is due to transfer in or in association with planktonic material, consistent with high Zn/P and absolute Zn contents in average plankton (table 1). Zinc may also be delivered to the sediment via a particulate shuttle, as described for Mo.

*Nickel.*—Nickel also displays nutrient-type regeneration in seawater (Bruland, 1980; Twining and others, 2012, fig. 1). Deep-water Ni concentrations increase from  $\sim 4$  nM in the deep Atlantic (Yeats and Campbell, 1983; Danielsson and others, 1985) to  $\sim 10$  nM in the deep Pacific (Bruland, 1980). Nickel is the only metal (of those considered here) to exhibit a conservative dissolved profile in anoxic basins (fig. 2, Jacobs and Emerson, 1982; Jacobs and others, 1987; Haraldsson and Westerlund, 1991; Balistrieri and others, 1994; Tankéré and others, 2001). Equilibrium Ni-sulfide complexes have low conditional stability constants (Al-Farawati and Van den Berg, 1999) and no decrease in Ni concentrations is observed in the oxic surface layers of anoxic basins (fig. 2).

Unexpectedly, Ni is moderately to significantly enriched in the sediments of euxinic basins (Skei, 1986; Francois, 1988; Calvert and Pedersen, 1993). The reasons for Ni enrichment in the sediment in these cases are not clear. The conservative profile of Ni in a sulfidic water column seems to require that any removal of Ni to enrich sediment must be balanced by an input of Ni external to the euxinic portion of the basin. Nickel is incorporated in pyrite, unlike Cd and Zn (Huerta-Diaz and Morse, 1992). Recent studies have shown that many trace elements are commonly incorporated in pyrite as micro-inclusions, while Ni is stoichiometric in the pyrite mineral structure (for example Large and others, 2007, 2014). The resulting high level of Ni-DTMP may in part explain authigenic Ni enrichments.

*Copper.*—Copper exhibits the most complex geochemical behavior of the trace metals considered here. It can exist in multiple valence states (0, I, II) and forms diverse aqueous complexes and solid phases. It is bioessential yet toxic to all photosynthesizing microorganisms at  $\text{Cu}^{2+}$  ion concentrations of  $>10^{-13}$  M. Hence phytoplankton are proposed to exude a class of strong organic ligands that dominate its aqueous speciation in natural waters, both oxic and anoxic (for example Coale and Bruland, 1988, 1990; Muller and others, 2001; Bruland and Lohan, 2003; Moffett and Dupont, 2007; Buck and others, 2012). In oxic seawater, Cu exhibits approximately linearly increasing concentrations with depth, described as intermediate between scavenged and nutrient-type profiles (fig. 1; Boyle and others, 1977; Bruland and Lohan, 2003). Alternatively, a one-dimensional modeling study has shown that this profile shape can be well described by a simple reversible scavenging type process (Little and others, 2013). Deep Atlantic concentrations are  $\sim 1.5$  nM, compared with  $\sim 4.5$  nM in the deep Pacific. Copper also forms strong complexes with dissolved sulfide (Dyrssen, 1988; Zhang and Millero, 1994; Al-Farawati and Van den Berg, 1999), though it is not clear whether Cu is complexed as Cu(I), Cu(II), or both by sulfide (for example Haraldsson and Westerlund, 1991; Mountain and Seward, 1999). Removal in association with sulfide results in the stripping of Cu from the Black Sea and the

TABLE 2  
Physical and geochemical characteristics of sites\*

A: Physical Characteristics									
	Volume km <sup>3</sup>	Sill depth m	Chemocline depth m	Total depth m	Deepwater age years	Bulk sediment burial flux g m <sup>-2</sup> yr <sup>-1</sup>	Organic C burial flux g m <sup>-2</sup> yr <sup>-1</sup>		
Black Sea	541000	33	50-150	2240	400	10-200	1-10		
Cariaco Basin	8000	146	250-375	1425	50-100	80-250	10-60		
Peru Margin	na	none	none	na	~0	110-350	40		
Framvaren Fjord	0.33	2	18-20	183	1600	50-120	12-24		
Saanich Inlet	5.4	70	150-240	238	~1.5	420-4800	20-110		
B: Geochemical Characteristics									
	Deep-water [HS <sup>-</sup> ] (μM)			Deep-water trace metal concentrations** (nM)					
	[HS <sup>-</sup> ]	[Mo]	[Cu]	[Zn]	[Ni]	[Cd]			
Black Sea	350	3	0.2	0.7	9	0.006			
Cariaco Basin	60	90	0.4	nd	2.6	0.007			
Peru Margin	0	105	4.5	8.5	10.5	0.9			
Framvaren Fjord	6000-8400	18	1.2	30	9.5	0.01			
Saanich Inlet	25	90	2	nd	6	0.05			

\* Compilation in Algeo and Lyons, 2006; see references therein.

\*\* Jacobs and others, 1982, 1985, 1987; Haraldsson and Westerlund, 1991; Landing and Lewis, 1991; Dryssen and others, 1996; Tankere and others, 2001.

Cariaco Basin water columns, which have average deep-water Cu concentrations of 0.2 to 0.4 nM (fig. 2). Copper does not exhibit surface minima in anoxic water columns (unlike Cd and Zn), indicating that biological uptake is not a strong control on its distribution here.

In oxic sediments, Cu is strongly associated with Mn oxides and may be enriched in sediments via a traditional particulate shuttle. In reducing sediments, Cu is incorporated in pyrite despite a high rate of reaction relative to Fe (Morse and Luther, 1999). This anomaly has been explained as the result of its complex redox behavior; several different Cu sulfide minerals can coexist, and metastable phases may be important in anoxic sediments (for example Pattrick and others, 1997). Despite its strong removal from anoxic water columns, Cu exhibits variable degrees of enrichment in the anoxic basins investigated to date (Francois, 1988; Calvert and Pedersen, 1993; Algeo and Maynard, 2004; Brumsack, 2006). Its enrichment is most significant in those basins with a low detrital flux, principally because Cu concentrations are high, at 25 to 75 ppm, in detrital sediments (Wedepohl, 1991; Rudnick and Gao, 2003).

#### SITE AND SAMPLE SELECTION

##### *Black Sea*

The Black Sea is the world's largest permanently anoxic basin (423,000 km<sup>2</sup>), the result of restricted inflow and outflow to the Mediterranean Sea via the narrow (0.76–3.6 km) and shallow (13–110 m) Bosphorus Strait, in combination with a positive water balance and moderate primary production. The water column is strongly stratified with respect to salinity, with a thin upper oxic layer (~100 m thick) overlying a suboxic intermediate layer and anoxic, strongly sulfidic deeper waters (Murray and others, 1989). Total sulfide concentrations increase to a maximum of 380 μM at 2200 m (Murray and others, 1989). Pore-water sulfide concentrations in the deep basin are similar to those of the overlying water column (Lyons and Berner, 1992). Bulk sediment (10–200 g m<sup>-2</sup> yr<sup>-1</sup>) and organic carbon (1–10 g m<sup>-2</sup> yr<sup>-1</sup>) accumulation rates are generally low and increase towards the basin margins (table 2; Arthur and others, 1994). The samples analyzed in this study come from four sites (fig. 3). Two basinal sites, stations 9 and 14, underlie the strongly euxinic part of the water column. Organic C contents at these two stations are *ca.* 5 weight percent (Lyons and Berner, 1992). Station 16 is from the oxic shelf margin, with a predominantly detrital influence, while station 16B is also oxic but from close to the modern day chemocline. Lyons (1991) provides additional details regarding the sedimentological characteristics of these samples. In addition, the euxinic samples have been studied previously for their carbon-sulfur-iron systematics (Lyons and Berner, 1992), sulfur isotope trends (Lyons, 1997), Fe isotopes (Severmann and others, 2008), and Mo concentrations and isotopes (Arnold and others, 2004; Algeo and Lyons, 2006). The samples from stations 16 and 16B have been the subject of a chemocline study in Lyons and others (1993). Further geochemical data for all four stations can be found in Lyons and Severmann (2006). We present a large trace element dataset (Fe, Mn, Ni, Cu, Zn, Mo, and Cd) for 31 samples from the upper ~20 cm of sediment from each station.

##### *Cariaco Basin*

The Cariaco Basin is the world's second largest modern anoxic basin and is located on the northern continental shelf of Venezuela. Its setting and hydrodynamic properties have been described in detail elsewhere, with deep waters (below 300 m) that are anoxic-sulfidic due to the restricted circulation of ocean waters coupled with high productivity (for example Jacobs and others, 1987; Lyons and others, 2003; Algeo and Lyons, 2006). Water column stratification is maintained by a strong thermocline. Total sulfide concentrations are lower than those observed in the Black Sea, peaking at

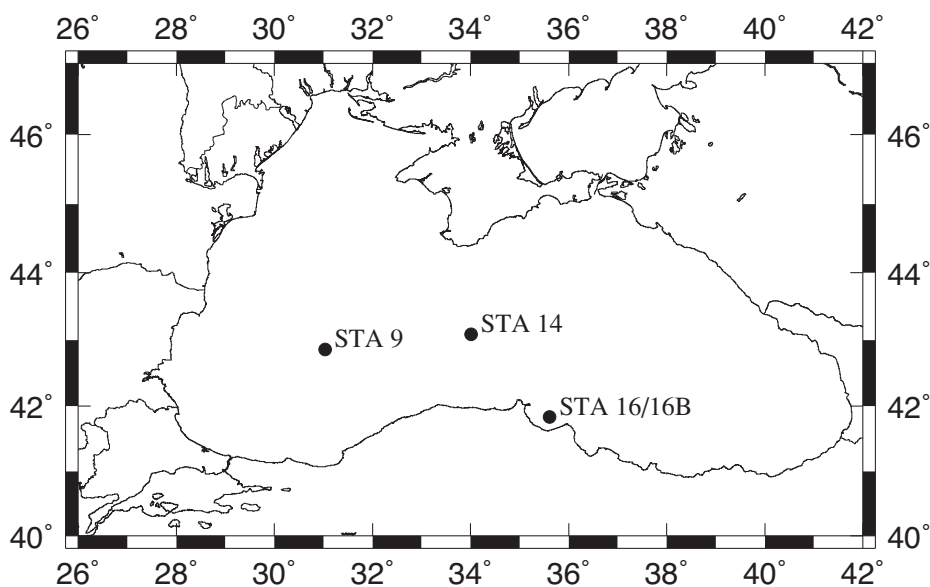


Fig. 3. Map illustrating the location of the four sites in the Black Sea (map generated using GMT). Stations 9 and 14 underlie the euxinic portion of the water column.

$\sim 65 \mu\text{M}$  (Scranton and others, 1987; Li and others, 2010; Li and others, 2011). Basin waters are fully marine. Pore-water sulfide concentrations increase from  $\sim 0.1 \text{ mM}$  at the sediment-water interface to a maximum of  $\sim 8 \text{ mM}$  at 250 cm depth and then decrease gradually to values near 0 mM at 6 m (Werne and others, 2003). Bulk sediment accumulation rates are moderate ( $80\text{--}250 \text{ g m}^{-2} \text{ yr}^{-1}$ ), as are those for organic carbon ( $10\text{--}60 \text{ g m}^{-2} \text{ yr}^{-1}$ , table 2; Peterson and others, 2000; Piper and Dean, 2002). Organic carbon contents peak at 6 weight percent in the upper part of the sediment column. Sediments in this study come from Site 1002 of Leg 165 of the Ocean Drilling Program ( $10^{\circ}42.4' \text{ N}$ ,  $65^{\circ}10.2' \text{ W}$ ), described in Lyons and others (2003). The Cariaco Basin has been euxinic since the key hydrographic changes that occurred during the last deglaciation. Our 22 drill-core samples include four from below the abrupt shift from oxic to euxinic conditions at the 14.5 ka glacial-interglacial transition (Haug and others, 1998; Dean and others, 1999; Peterson and others, 2000) and eighteen from above. These samples have previously been studied for their sulfur, iron, carbon, molybdenum and chromium geochemistry (Lyons and others, 2003; Werne and others, 2003; Lyons and Severmann, 2006; Reinhard and others, 2014).

#### *Peru Margin*

The Peru Margin is an unrestricted continental margin setting with high upwelling-driven productivity, resulting in an extensive oxygen minimum zone at water depths of  $\sim 50$  to 650 m on the shelf and upper slope (Emeis and others, 1991; Lückge and Reinhardt, 2000). Reported  $\text{O}_2$  concentrations in the bottom waters are low ( $< 10 \mu\text{M}$ ). More recent work suggests that these waters can be sporadically sulfidic (Schunck and others, 2013). Free sulfide is present at levels of  $> 1 \text{ mM}$  in pore waters within the upper 20 cm of the sediment pile, driven by sulfate reduction (Mossmann and others, 1991; Böning and others, 2004). Sediment accumulation rates ( $110\text{--}350 \text{ g m}^{-2} \text{ yr}^{-1}$  generally, specifically  $250 \text{ g m}^{-2} \text{ yr}^{-1}$  in our core; DeMaster, 1981; McManus and others, 2006) and organic carbon accumulation rates (*ca.*  $40 \text{ g m}^{-2} \text{ yr}^{-1}$ ; Müller and

Suess, 1979) are high (table 2), as are solid phase sulfur concentrations (Böning and others, 2004) and organic carbon contents (~14 wt%; Böning and others, 2004; McManus and others, 2006). The study site, from which data from 10 samples in one core is presented, is at 264 m water depth, within the oxygen minimum zone (OMZ) at 13.7° S, 76.7° W (described in McManus and others, 2006).

#### ANALYTICAL METHODS AND CALCULATION OF TRACE METAL ENRICHMENT FACTORS

##### *Sample Digestion and Metal Concentration Analyses*

All acids and reagents used in this study were either ultrapure or were purified by double sub-boiling distillation. All work was carried out under clean laboratory conditions using trace metal cleaned Savillex PFA labware. Fifty to 100 mg of each sample were first treated with dilute nitric acid to dissolve carbonate and then digested in a 3:1 mix of concentrated hydrofluoric and nitric acid. Samples were then treated three times with concentrated HNO<sub>3</sub> to remove residual fluoride salts before final dissolution in 7M HCl.

Elemental analysis was carried out on an aliquot of these solutions on a Finnigan Element 2, single collector, fast scanning magnetic-sector ICPMS at the Bristol Isotope Group, University of Bristol. Concentrations of relevant solutes were calculated using a primary artificial element standard prepared in house. Accuracy and reproducibility (on average 12-13%, 2RSD, see table 3 for details) were monitored using three commercially available reference materials.

Most of the organic carbon data presented here (table 4) are derived from the literature (Lyons and Berner, 1992; Lyons and others, 2003). Values for the Peru Margin sediments are newly presented here and were determined via a high temperature combustion technique (Hedges and Stern, 1984).

##### *Modes of Trace Metal Normalization*

The use of trace element concentrations to reconstruct paleoenvironmental conditions requires some means to evaluate their relative enrichment or depletion in the sediment. The first step in this process usually involves normalization of the trace metal concentration to Al, which is used as a tracer of the detrital contribution to a sediment (for example Brumsack, 1989; Calvert and Pedersen, 1993). After this step, an authigenic enrichment factor (EF) is calculated for the given trace metal (TM) by comparison with a reference material, traditionally 'average shale' (Wedepohl, 1991):

$$EF_{\text{element}} = (\text{element}/\text{Al})_{\text{sample}} / (\text{element}/\text{Al})_{\text{reference}} \quad (2)$$

An EF greater than 1 implies authigenic enrichment of the trace metal, while a value less than 1 indicates depletion. A disadvantage of calculating enrichment factors in this fashion is the possibility that uncorrelated variables may acquire spurious correlations when normalized to Al (Van der Weijden, 2002). This is most likely a problem when the Al fraction of the sediment under study has a wide range in Al content, which is not the case for the sediments considered here. Alternatively, one may calculate the non-detrital, 'excess' trace metal content (TM<sub>XS</sub>), as follows:

$$TM_{XS} = TM_{\text{sample}} - Al_{\text{sample}} \cdot (TM/Al)_{\text{reference}} \quad (3)$$

In this study, enrichment factors and TM<sub>XS</sub> concentrations are calculated as per equations (2) and (3) but *not* using 'average shale' as a reference material, because this is unlikely to be representative of the true background sedimentation. Instead, the lithogenic background is approximated using the minimum Me/Al elemental ratios measured in proximal oxic sediments, where available (as recommended by Böning and others, 2012). Thus, the lithogenic background for calculating Black Sea enrich-

TABLE 3  
Elemental reproducibilities for three secondary standards used over the period during which data presented herein were collected

	SLRS-5 n = 46			BCR-2 n=6			SLR-1640* n = 40		
	Certified	Accuracy (%)	2RSD (%)	Certified	Accuracy (%)	2RSD (%)	Certified	Accuracy (%)	2RSD (%)
27 Al	1.83µM (LR)	104%	9%	8.4ppm	121%	13%	<i>0.19µM (LR)</i>	140%	80%
55 Mn	78.8nM (LR)	100%	13%	179.5ppb	118%	12%	219nM	99%	15%
56 Fe	1.63µM	108%	18%	11.4ppm	113%	14%	<i>0.06µM (LR)</i>	106%	35%
60 Ni	8.11nM	96%	12%	ncv	/	9%	46.3nM	93%	12%
63 Cu	274nM	103%	9%	<i>2.2ppb</i>	<i>104%</i>	<i>18%</i>	133nM	97%	10%
66 Zn	12.9nM	94%	14%	15.0ppb	113%	18%	80.6nM	104%	28%
95 Mo	ncv	/	11%	29.3ppb	108%	14%	48.3nM	90%	12%
111 Cd	<i>0.05nM</i>	<i>139%</i>	<i>37%</i>	<i>(&lt;0.5ppb)</i>	/	<i>97%</i>	20.1nM	98%	13%
Mean		101%	12%		115%	13%		97%	15%
1σ		5%	3%		5%	3%		5%	7%

Low concentration of element in standard (not included in mean and st dev calculations).

Values in italics reflect low concentrations. ncv = no certified value. All analyses were carried out in medium resolution, unless stated (LR=low res).

\* SLR-1640 is less reproducible for Al and Fe than the other standards, due to their lower concentrations in this standard, and for Zn. The reason for the latter is not clear, but this standard is included in the compilation because it is the only one to have appreciable concentrations of Cd.

TABLE 4  
Results. Metal/Al ratios and enrichment factors calculated as per equation 2

Sample depth (cm)	C <sub>org</sub> (1,2,3) wt%	All ratios (except Fe) × 10 <sup>-4</sup>													
		Ni/Al	Cu/Al	Zn/Al	Mo/Al	Cd/Al	Mn/Al	Fe/Al	EFNi	EFZn	EFMo	EFMn	EFFe		
Average Shale (4)	nd	7.6	5.1	10.7	0.15	0.03	95.6	0.53	na	na	na	na	na	na	
<b>Black Sea Stations</b>															
Oxic	0	nd	14	5.6	11	0.11	0.05	85	0.58	1.1	1.2	1.1	1.4	1.6	1.2
Station 16	2	nd	15	5.4	9.8	0.10	0.03	72	0.54	1.1	1.1	1.0	1.3	1.1	1.0
	4	nd	13	5.2	9.4	0.08	0.04	78	0.50	1.0	1.1	1.0	1.1	1.3	1.1
	6	nd	14	5.5	10	0.09	0.03	79	0.55	1.1	1.1	1.1	1.1	1.0	1.1
	10	nd	13	5.4	9.5	0.08	0.03	77	0.54	1.0	1.1	1.0	1.1	1.1	1.1
	12	nd	13	5.1	9.7	0.08	0.03	74	0.53	1.0	1.1	1.0	1.0	1.0	1.0
	14	nd	13	4.8	9.4	0.08	0.03	75	0.51	1.0	1.0	1.0	1.0	1.1	1.0
	16	nd	15	5.1	10	0.08	0.04	83	0.56	1.2	1.1	1.1	1.1	1.3	1.2
Chemocline	0	nd	12	6.1	13	0.20	0.04	73	0.50	0.9	1.3	1.4	2.7	1.3	1.0
Station 16B	2	nd	13	5.9	13	0.39	0.04	78	0.52	1.0	1.2	1.4	5.1	1.5	1.1
	4	nd	15	6.8	15	0.35	0.04	71	0.63	1.2	1.4	1.6	4.6	1.5	1.0
	6	nd	14	5.7	12	0.13	0.03	76	0.55	1.1	1.2	1.3	1.8	0.9	1.1
	8	nd	21	8.0	17	0.20	0.04	75	0.74	1.6	1.7	1.8	2.7	1.5	1.1
	12	nd	18	6.4	14	0.14	0.03	83	0.65	1.4	1.3	1.5	1.8	1.1	1.2
	14	nd	12	5.3	11	0.10	0.03	77	0.49	1.0	1.1	1.1	1.4	1.0	1.1
	18	nd	11	4.9	10	0.09	0.03	81	0.47	0.9	1.0	1.1	1.3	1.1	1.1
	20	nd	12	4.9	11	0.10	0.02	78	0.47	0.9	1.0	1.1	1.3	0.8	1.1
<i>Min oxic Me/Al for normalization:</i>															
			13	4.8	9.4	0.08	0.03	72	0.50						
Euxinic Station 9	4	5.3	18	19	27	9	0.65	172	0.85	1.4	4.0	2.8	122	22	2.4
	8	5.6	20	23	21	11	0.50	197	0.98	1.6	4.8	2.2	148	17	2.7
	10	7.0	24	26	23	13	0.53	198	1.06	1.9	5.5	2.4	177	18	2.8
	14	3.4	30	35	23	19	0.68	358	1.16	2.4	7.2	2.5	257	23	5.0
	16	5.7	28	28	22	16	0.56	231	1.14	2.2	5.8	2.3	211	19	3.2
	18	5.7	27	25	21	16	0.47	221	1.10	2.1	5.2	2.2	217	16	3.1
	22	4.5	32	29	84	25	0.59	284	1.09	2.5	5.9	8.9	335	20	4.0
	24	5.6	37	30	20	28	0.60	261	1.08	2.9	6.2	2.2	376	20	3.6





TABLE 4  
(continued)

Sample depth (cm)	C <sub>org</sub> (1,2,3) wt%	All ratios (except Fe) × 10 <sup>-4</sup>													
		Ni/Al	Cu/Al	Zn/Al	Mo/Al	Cd/Al	Mn/Al	Fe/Al	EFNi	EFCu	EFZn	EFMo	EFCd	EFMn	EFFe
<b>Peru Margin, site MC82</b>															
<i>Peru andesite for normalization (5):</i>															
0.5	15.5	48	27	36	26	18	53	0.4	17.0	5.9	3.8	106	607	0.7	0.8
1.0	16.0	47	24	32	24	17	54	0.4	16.4	5.5	3.4	98	571	0.7	0.8
1.7	15.7	47	24	32	25	18	53	0.4	16.3	5.4	3.4	103	624	0.7	0.8
2.4	15.4	46	23	31	26	19	53	0.4	16.2	5.2	3.2	108	658	0.7	0.8
4.8	14.5	44	23	31	30	21	52	0.4	15.5	5.3	3.3	122	724	0.7	0.8
8.2	12.8	44	22	31	31	21	53	0.4	15.4	4.9	3.2	127	729	0.7	0.8
15.0	11.7	44	22	27	26	23	52	0.4	15.5	4.9	2.8	109	800	0.6	0.8
15.7	12.1	43	21	24	23	20	54	0.4	15.1	4.7	2.6	95	688	0.7	0.8
18.4	14.4	41	19	23	22	20	50	0.4	14.4	4.4	2.4	90	683	0.6	0.8
19.1	14.8	45	21	25	21	19	51	0.4	15.8	4.7	2.6	86	659	0.6	0.8

Average shale (Wedepohl, 1991) is given for comparison with the local lithogenic Me/Al ratios used in enrichment factor calculations (in italics). Organic C contents included for reference. nd = not done, na = not applicable.

References: (1) Lyons and Berner, 1992; (2) Lyons and others, 2003; Anomalous value in gray for one Station 9 Zn/Al measurement assumed contaminated. (3) McManus, J., personal communications; (4) Wedepohl, 1991; (5) Sarbas and Nohl, 2009.

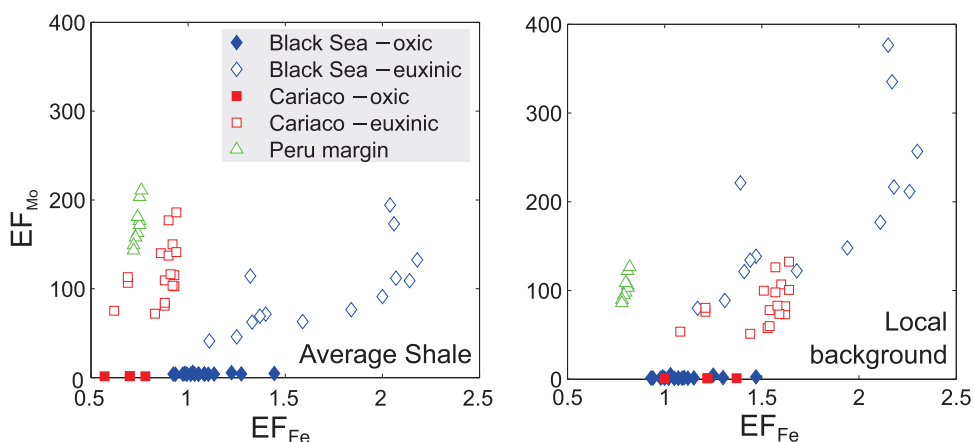


Fig. 4. Cross plots of calculated enrichment factors for Fe and Mo for the three study sites. Left: normalization carried out relative to average shale composition (Wedepohl, 1991). Right: normalization relative to the best estimate of the local lithogenic background (as discussed in the text).

ment factors was taken to be the minimum measured Me/Al ratios from Black Sea Station 16 and for the Cariaco Basin to be the minimum measured ratios from the oxic section of the sediment core (these lithogenic background values are defined in table 4). In the case of the Peru Margin samples, for which we measured no equivalent oxic sediments, the lithogenic background has previously been approximated to be closest to that of a Peruvian andesite (Böning and others, 2004; Scholz and others, 2011). For these samples, enrichment factors were calculated relative to average andesite from the Central Volcanic Zone of Peru (see table 4: values derived from the GEOROC data base of the Max-Planck Institute for Chemistry, Mainz, Germany, Sarbas and Nohl, 2009).

## RESULTS

### *Choice of Normalizing Reference Material*

The impact of normalizing to the local lithogenic background rather than ‘average shale’ can be significant, as illustrated in the cross-plots of Fe versus Mo enrichment factors (fig. 4). In this case, normalizing to the local background has two major effects:

1. The degree of Mo enrichment increases significantly in the Black Sea but decreases significantly in the Peru Margin.
2. The degree of Fe enrichment increases significantly in the Cariaco Basin.

As a result, the Cariaco Basin samples plot on the same trend as those of the Black Sea when normalized to their local lithogenic background, rather than two distinct trends when normalized to average shale (fig. 4). Interpretation of these types of cross-plots is a major topic of the discussion that follows, but figure 4 is included at this stage to emphasize the importance of selecting the correct background sediment composition when calculating authigenic enrichment (see also Böning and others, 2004, 2009, 2012).

### *Overview of Elemental Concentrations and Calculated Enrichment Factors*

Absolute concentrations of each element are given in Appendix data table A1. This discussion will focus on the enrichment factors presented in table 4, which are

largely consistent with previous work while considerably expanding the published dataset (Calvert, 1990; Calvert and Pederson, 1993; Böning and others, 2004; Lüschen, ms, 2004; Lyons and Severmann, 2006).

Significant enrichments in Fe and Mn are observed in the euxinic sites of the Black Sea (fig. 5A, average EF Fe = 1.8, EF Mn = 2.7), while the euxinic samples of the Cariaco Basin sediment core are weakly enriched in Fe compared to the assumed oxic background (average euxinic EF Fe = 1.5). In the Peru Margin, both Mn and Fe show depletions compared to the andesitic lithogenic background (average EF Mn = 0.65, EF Fe = 0.80).

Molybdenum is strongly enriched at all three locations (fig. 5F). Molybdenum enrichment factors increase in the order Cariaco Basin < Peru Margin < Black Sea ( $90 < 104 < 188$ ; table 4). Low absolute Mo concentrations (Appendix data table A1) in the Black Sea sediments are due to dilution by the high carbonate content (*ca.* 50%) of these sediments and to the restricted basin setting (Lyons, 1991; Algeo and Lyons, 2006). High enrichment factors thus result from the low Mo/Al ratio of the local lithogenic background (background Mo/Al of Black Sea = 0.08, compare Cariaco Basin = 0.21 and Peru Margin = 0.24; table 4). Lower Mo enrichment factors for the Cariaco Basin compared to the Peru Margin are due to the higher calculated detrital Mo fraction of Cariaco Basin sediments. The low detrital fraction of the Peru Margin sediments (mean Al content of Peru Margin = 3.0 wt% compare Cariaco Basin = 6.4 wt%) is attributed to their high opal content (Böning and others, 2004).

Cadmium is significantly enriched at all three locations but greatly so in the Peru Margin sediments (fig. 5B). Cadmium concentrations increase from  $0.9 \pm 0.5$  ppm in the Black Sea to  $8 \pm 10$  ppm in the Cariaco Basin and  $58 \pm 16$  ppm on the Peru Margin (Appendix data table A1). Enrichment factors increase in the same order: from  $15 < 28 < 674$  (table 4).

Absolute Cu concentrations represent similar, modest degrees of enrichment for Cu in the Black Sea and Peru Margin (fig. 5E). Mean enrichment factors in these sediments (relative to the local background) are 4.7 and 5.1, respectively (table 4). Note that Böning and others (2004) considered even the relatively low Cu/Al ratio of Peruvian andesite to be an overestimation of the true value for background sediment in this region, which they later estimate to be between 0 and 2.8 (Böning and others, 2012). The reported Cu EF for Peru Margin sediments analyzed in this study (of 5.1) can thus be considered a lower bound on Cu enrichment in these sediments. A previous study, normalizing to average shale, found no enrichment in Cu in Cariaco Basin sediments (Calvert and Pederson, 1993). However, the minimum Cu/Al ratio for the oxic part of the Cariaco Basin sediment column is 3.1 (compared to average shale Cu/Al = 5.1, table 4), indicating that the background sediment source for this basin is depleted in Cu relative to Al compared to average shale (Wedepohl, 1991). Using this local oxic background Cu/Al ratio, we find measurable Cu authigenic enrichment in the euxinic samples, with a maximum EF of 1.9 and an average of 1.4.

Modest authigenic Ni enrichment in the Black Sea is observed, with an average EF of 1.8. Much more significant enrichment is seen in the Peru Margin samples, with an average EF for Ni of 15.8 (using the andesite Ni/Al reference of 2.9). As described for Cu, this value may be an underestimation. Böning and others (2012) calculated values of 0 to 3.3 for the Ni/Al ratio of background sediments in the Peru Margin region. Nickel concentrations in the Peru Margin sediments are the highest of the samples analyzed, at  $132 \pm 29$  ppm. Similarly, the enrichment of Ni in the Cariaco Basin sediments has previously been underestimated because the local lithogenic background has a Ni/Al ratio enrichment factor considerably lower than that of average shale (Ni/Al = 4.0 cf. 7.6).

Absolute concentrations of Zn in the Cariaco Basin are the highest of the three locations, at  $111 \pm 64$  ppm. Average Zn enrichment factors range from 1.6 for the Cariaco Basin, to 2.6 for the Black Sea, to 3.1 for the Peru Margin (table 4).

#### *Oceanic Mass Balance Calculations*

The new trace element data presented in this study, in combination with previously published data, allow us to make new estimates of the oceanic mass balance of Cu, Ni, Zn, Cd, and Mo, presented in table 5. In particular, the significance of reducing settings to the removal of Cu, Zn, and Ni, is calculated here for the first time by comparison with published models for Mo and Me/Mo data from this study.

*Oceanic output fluxes.*—Output fluxes are calculated for (1) pelagic sediments (the ‘oxic sink’), (2) euxinic sediments, and (3) continental margin sediments (table 5). Estimates for the magnitude of the oxic sink (pelagic sediments) are calculated in three ways. The first compares the authigenic enrichment observed in pelagic clays with concentrations in average shale (Martin and Whitfield, 1983; compare Wedepohl, 1991). The second relies on a comparison with Mn, using Me/Mn ratios in pelagic clay and Fe-Mn crusts and an estimated burial flux of Mn of  $3.8 \times 10^{10}$  mol/year (Martin and Whitfield, 1983; Manheim and Lane-Bostwick, 1989; Li and Shoonmaker, 2003; Rehkämper and Nielson, 2004). The third is based on a comparison with Mo, using published Me/Mo ratios in pelagic clay and Fe-Mn crusts, and assuming a burial flux of Mo of  $9 \times 10^8$  mol/yr (Martin and Whitfield, 1983; Manheim and Lane-Bostwick, 1989; Morford and Emerson, 1999; Li and Shoonmaker, 2003; Little and others, 2014). With the exception of Cu, the estimates from the three approaches agree within a factor of three (a factor of four for Cu).

Together, euxinic and continental margin sediments make up the reducing sedimentary sink. Continental margin sediments are further subdivided based on the contrasting redox behavior of Cd and Mo. Suboxic sediments with *suboxic pore waters*, where ‘suboxic’ is here defined as negligible concentrations of both oxygen and sulfide, are a sink for Cd (Van Geen and others, 1995; Morford and Emerson, 1999). However, these sediments are a source for Mo (Morford and Emerson, 1999) and, we assume by extension in this study, for Cu, Ni, and Zn. By contrast, sediments underlying *suboxic bottom waters* but with significant *pore water sulfide* are a sink for Mo and Cd (for example McManus and others, 2006) and, we assume by extension in this study, for Cu, Ni, and Zn. Ideally, a quantitative assessment of the aerial extent and redox state of continental margin sediments would be attempted, for example, via a diagenetic model, but that is beyond the scope of this contribution. We settle with the coarse differentiation of continental margin sediments into two subtypes: (a) truly ‘suboxic’ sediments with suboxic pore waters (that is, negligible oxygen and sulfide), which we assume are a source of Mo, Cu, Ni, and Zn (see oceanic inputs) but sink of Cd, and (b) ‘anoxic-suboxic’ sediments with significant pore water sulfide beneath suboxic bottom waters, which we assume are a sink for all five metals.

Estimates of the magnitude of the reducing sedimentary sink for Cu, Ni, and Zn are calculated from published Mo fluxes using authigenic Me/Mo ratios from data presented in this study. The Peru Margin site is chosen as representative of the anoxic-suboxic continental margin sediment type, and the Black Sea is representative of euxinic sediments. We use the most recent published Mo mass balance calculation, which suggests that continental margin settings are responsible for  $9 \times 10^8$  mol/yr Mo removal, with euxinic settings a minor contributor, at  $<0.1 - 0.2 \times 10^8$  mol/yr (Poulson Brucker and others, 2009). We find that the reducing sedimentary sink is responsible for between 10 and 50 percent of the removal of Cu, Zn, and Ni from the oceans. This sink is similar to or slightly less than the reducing sink’s estimated importance for Mo and Cd (~50%: for example van Geen and others, 1995; Poulson Brucker and others, 2009).

TABLE 5

Summary of oceanic mass balance of Mo, Cd, Ni, Cu and Zn, estimated from published data and from data presented in this study (in bold)

	Mo	Cd	Ni	Cu	Zn	References
<b>Concentrations</b>						
Ocean, dissolved (nmol/kg)	104	0.6	8.2	2.4	5.3	(1)
River, dissolved (nmol/kg)	6	0.1-0.4	13.5	19	16	(2)
Upper crust (ppm)	1.1	0.09	55	28	67	(3)
Shale (ppm)	1.3	0.3	68	45	95	(4)
Riverine particulate (ppm)	3.0	?	88	102	353	(5)
Pelagic clay (ppm)	8	0.23	200	200	120	(6)
Fe-Mn crust (ppm)	370	3	3900	380	540	(7)
<b>Source fluxes (<math>10^8</math> mol/yr)</b>						
River	1.8-2.3	0.04-0.14	3.6-5.1	6-8.7	3.5-8.3	(2)
Dust	n	0.02-0.11	0.07	0.5	0.7	(2)
Hydrothermal	n	(0.02-0.26)	?	(3-13)	(12-32)	(8)
Suboxic margin sediments	0.08-0.17	n	<b>2.4-12</b>	<b>0.7-3.2</b>	<b>0.4-2.5</b>	(9)
<b>Total source</b>	<b>1.88-2.47</b>	<b>0.06-0.25</b>	<b>6.1-17.2</b>	<b>7.2-12.4</b>	<b>4.6-11.5</b>	
<b>Sink fluxes (<math>10^8</math> mol/yr)</b>						
Sediments	<b>0.3-0.9</b>	n	<b>5.5-17</b>	<b>1.6-9.7</b>	<b>0.8-3.2</b>	(10)
Oxic	n	0.03-0.23	n	n	n	(9)
suboxic margin	0.2-0.9	<b>0.09-0.36</b>	<b>2.2</b>	<b>0.9</b>	<b>1.0</b>	(11)
anoxic margin	0.1	n	<b>0.4</b>	<b>0.5</b>	<b>0.3</b>	(11)
euxinic	0.04-0.17	(0.02-0.26)	?	(3-13)	(12-32)	(12)
Hydrothermal	<b>1.34-1.9</b>	<b>0.04-0.59</b>	<b>8.1-19.6</b>	<b>3-11.1</b>	<b>2.1-4.5</b>	
<b>Total sink</b>	<b>650</b>	<b>55</b>	<b>9.5</b>	<b>3.3</b>	<b>9.0</b>	
Steady state residence time (kyr)	w.r.t. input	26	8.0	4.6	22	
	w.r.t. output					

Values in parentheses for hydrothermal fluxes are assumed to be removed quantitatively close to the vent, and are not included in total source/sink additions. n = negligible, ? = unknown.

References: (1) Chester and Jickells, 2012; (2) Archer and Vance 2008; van Geen and others, 1995; Vance and others, 2008; Little and others, 2014; Gaillardet and others, 2003; Cameron and Vance, 2014; (3) Rudnick and Gao, 2003; (4) Wedepohl, 1991; (5) Martin and Meybeck, 1979; (6) Martin and Whitfield, 1983; (7) Li and Shoonmaker, 2003; (8) Elderfield and Schultz, 1996; Von Damm and others, 1985; (9) van Geen and others, 1995; Morford and Emerson, 1999; (10) Morford and Emerson, 1999; Little and others, 2014; this study; (11) Poulson Brucker and others, 2009; van Geen and others, 1995; (12) Trefry and others, 1994; Elderfield and Schultz, 1996.

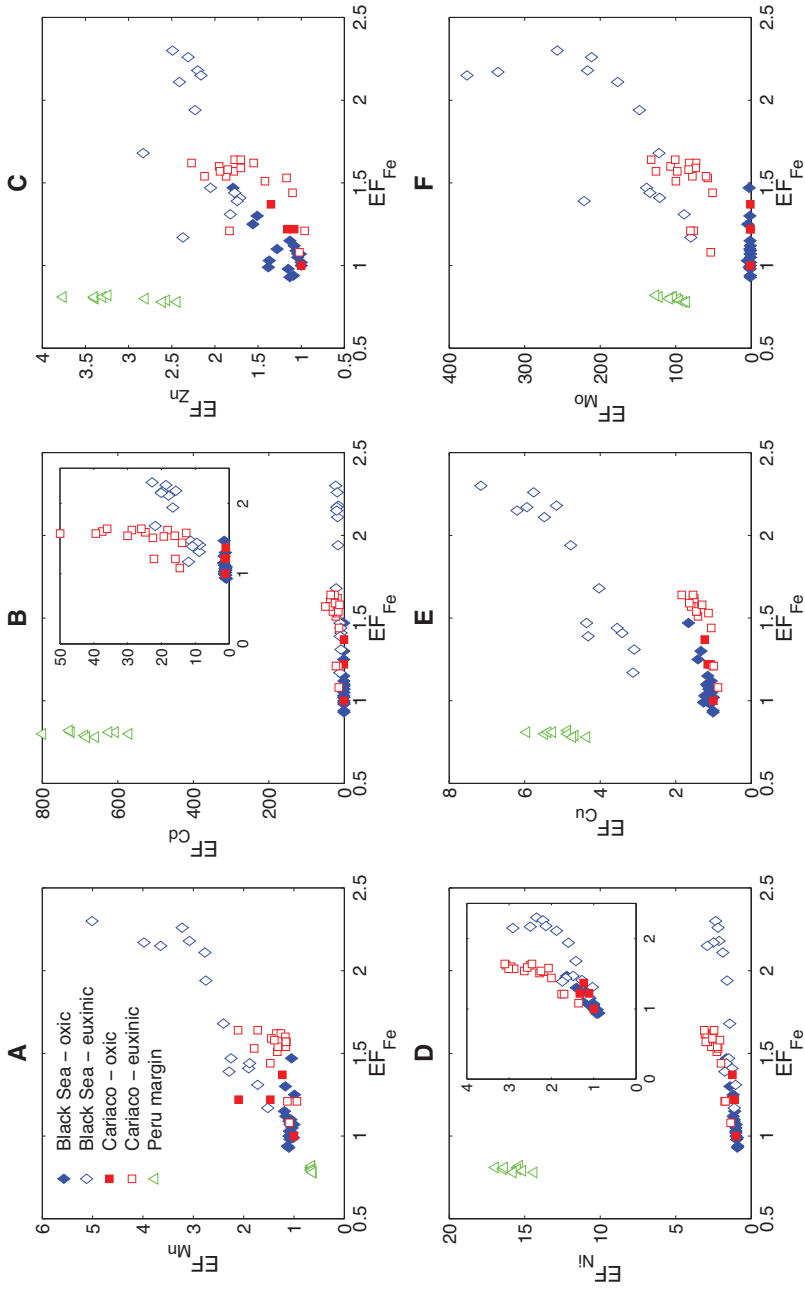


Fig. 5. Covariation diagrams of Fe enrichment factors versus other trace metal enrichment factors for the three study sites. Symbols are as illustrated in the key for plot A (Mn). Additional panels for Cd (plot B) and Ni (plot D) show expanded y-scale.

TABLE 6  
Coefficients of determination ( $R^2$  values) between elements for the Black Sea and Cariaco Basin sites.

		Black Sea →						
		Cu	Zn	Ni	Mo	Cd	Fe	Mn
	Cu		<b>0.76</b>	<b>0.76</b>	<b>0.91</b>	<b>0.93</b>	<b>0.88</b>	<b>0.93</b>
Cariaco	Zn	0.51		0.49	0.59	<b>0.86</b>	0.69	0.62
Basin ↓	Ni	<b>0.72</b>	0.57		<b>0.83</b>	0.64	<b>0.84</b>	<b>0.77</b>
	Mo	0.45	0.35	<b>0.75</b>		<b>0.81</b>	<b>0.76</b>	<b>0.85</b>
	Cd	0.47	0.35	<b>0.81</b>	<b>0.82</b>		<b>0.81</b>	<b>0.85</b>
	Fe	<b>0.75</b>	0.51	<b>0.77</b>	0.47	0.42		<b>0.85</b>
	Mn	0.07	0.01	0.01	0.00	0.01	0.09	

Strong correlations are in bold type-face, no correlation in italics.

*Oceanic input fluxes.*—Inputs to the oceans are assumed to be predominantly from rivers and aeolian dust (table 5; Morford and Emerson, 1999; Gaillardet and others, 2003; Vance and others, 2008, Little and others, 2014; Cameron and Vance, 2014). The importance of benthic fluxes out of suboxic continental margin sediments is not well known. One estimate exists for Mo ( $0.08\text{--}0.17 \times 10^8$  mol/yr; Morford and Emerson, 1999). The magnitude of analogous benthic sources of Cu, Zn, and Ni can be estimated by comparison with this published flux for Mo, using published Me/Mo ratios from Fe-Mn crusts (Manheim and Lane-Bostwick, 1989; Little and others, 2014). A second estimate is obtained assuming Cu, Zn, and Ni are mobilized with Mn in accordance with their Me/Mn ratio in Fe-Mn crusts. The flux of Mn out of suboxic sediments is estimated at  $2.1 - 6.8 \times 10^{10}$  mol/yr (Morford and Emerson, 1999; Rehkämper and Nielson, 2004; McManus and others, 2012).

#### DISCUSSION

##### *Covariation of the Enrichments of Mn, Cd, Mo, Cu, Ni, and Zn with that of Fe*

Due to the multiple controls on trace metal authigenic enrichment, concentration measurements of single elements are insufficient to identify specific enrichment processes. Comparison of the enrichment patterns of several elements offers this possibility (for example Algeo and Tribovillard, 2009).

For example, the covariation of the enrichment of Fe and Mn in the Black Sea is consistent with the suggestion that both are enriched via the benthic Fe/Mn redox shuttle—from the shelf to the basin interior (fig. 5A; Lyons and Severmann, 2006). Excluding the chemocline site, Fe and Mn exhibit a strong positive correlation, with an  $R^2$  of 0.88 (table 6). The Peru Margin site does not exhibit any evidence for a benthic redox shuttle, with no enrichment (rather, depletion) in Fe or Mn due to their reduction at or close to the sediment-water interface and diffusion into the water column (Noffke and others, 2012; compare Scholz and others, 2014). In the Cariaco Basin, evidence for a benthic redox shuttle is less definitive than in the Black Sea, likely because of its higher sedimentation rate (Lyons and Severmann, 2006). The lower Mn-to-Fe ratios observed in the Cariaco Basin sediments may relate to the lower sulfide concentrations in the Cariaco Basin water column, given that Mn forms weak complexes with sulfide (Al-Farawati and Van den Berg, 1999). In addition, deep-water concentrations of dissolved Mn are an order of magnitude lower in the Cariaco Basin

compared to those in the Black Sea, while Fe concentrations are higher in the Cariaco Basin than in the Black Sea (fig. 2).

The patterns of authigenic enrichment of the other metals compared to Fe point to additional processes (figs. 5B–5F). Most noticeable is the extreme enrichment in Cd in the Peru Margin sediments (fig. 5B). This enrichment is possible for three reasons. Firstly, Cd concentrations in detrital sediments are very low, and Cd has a high  $[\text{Cd}]_{\text{sw}}/[\text{Cd}]_{\text{average shale}}$  ratio (table 1; Wedepohl, 1991; Rudnick and Gao, 2003). Secondly, deep-water concentrations are highest for Cd in the Pacific, at 0.9 nM—a factor of five higher than dissolved Cd in the intermediate Atlantic water supplying the Cariaco Basin. Further, the continental margin setting is unrestricted, with associated high rates of water advection past the site; thus, trace metal supply to the Peru Margin sediments is not limited by slow rates of bottom-water renewal (compare low overall enrichments in Cd in the Black Sea). This is the ‘basin reservoir effect’ previously discussed in reference to Mo (Algeo and Lyons, 2006). The third reason for high Cd enrichments in the Peru Margin is the high organic carbon flux in this upwelling region (table 2; Böning and others, 2004).

Nickel covariation with Fe in the Black Sea and Cariaco Basin is similar to Mn (figs. 5A and 5D). The maintenance of a conservative Ni profile with depth in the sulfidic part of the Black Sea appears to require a source of Ni from outside the euxinic portion of the basin. We suggest that this source of Ni, and perhaps other trace metals, could arise via the benthic Fe/Mn redox shuttle in restricted basins. The transport of Fe and Mn from the shelf to the open basin may occur via nano-particulate oxides, which will carry sorbed trace metals. This suggestion is supported by the presence of a fine particle layer that forms on the shelf via reoxidation of reduced dissolved Mn and Fe and spreads laterally throughout the Black Sea. This layer is rich in Mn, Fe, and other trace metals (including particulate Ni, Cu, and Zn; Tankéré and others, 2001). Given the evidence for pyrite formation in the water column of the Black Sea (for example Lyons, 1997; Wilkin and others, 1997), it is plausible that a small amount of water column removal of Ni is occurring via incorporation into pyrite and that its ‘conservative’ dissolved profile is thus maintained by the addition of Ni to sulfidic deep waters (for example via the benthic redox shuttle) at approximately the same rate at which it is removed to sediment.

Copper, like Ni, exhibits a strong correlation with Fe in both the Black Sea and Cariaco Basin sediments (Ni-Fe  $R^2 = 0.84$  and  $0.77$ , Cu-Fe  $R^2 = 0.88$  and  $0.75$ , respectively, table 6) and may similarly be supplied to euxinic deeper waters in association with the benthic Fe/Mn redox shuttle. However, a significant difference appears between the Fe-Ni and Fe-Cu plots. For Cu, there is a pronounced step to higher Cu-Fe ratios for the Black Sea euxinic stations relative to the oxic sites (fig. 5E). This step is probably explained by the fact that, unlike Ni, dissolved Cu is strongly removed from a sulfide-containing water column (fig. 2). Such a step to higher Me-Fe enrichment ratios for the euxinic sediments of both the Black Sea and Cariaco Basin is also observed for Mo and Cd. The absence of a significant step in enrichment in Cu between the euxinic and oxic Cariaco Basin samples implies that the drawdown of Cu from the Cariaco Basin water column (fig. 2) is masked, presumably by the high sedimentation rates in this setting.

The pattern of covariation of Zn with Fe for the three regions is not dissimilar to that of Cd and Ni but with more modest total enrichments (fig. 5C). This less exaggerated enrichment in Zn is due to its high concentration in detrital sediments (95 ppm in average shale; Wedepohl, 1991), which is 300 to 400 times that of Cd, for example. The greatest Zn enrichment is seen in the Peru Margin sediments, where Fe is not enriched. This enrichment can be observed in absolute terms via the calculation of  $\text{Zn}_{\text{XS}}$  concentrations (as per eq. 3, Appendix data table A1). The mean  $\text{Zn}_{\text{XS}}$  for the



Peru Margin samples is 53 ppm, which is almost indistinguishable from that of Cd (57 ppm). The  $Cd_{XS}/Zn_{XS}$  ratio in these sediments is thus  $\sim 1$ , a factor of five greater than that in ‘average plankton’ (table 1). Therefore, if Zn enrichment is controlled solely by its delivery in organic material, Cd must additionally be enriched via another process, for example direct diffusion from the water column into the sediments or preferential retention of Cd over Zn in the sediment once it is delivered there.

Lastly, Mo exhibits strong enrichment in all three settings (fig. 5F). In a first order sense, this enrichment is because Mo is present at high concentrations in seawater relative to sediment. On average, Mo concentrations in seawater are 20 times higher than those for Zn and 10 to 15 times greater than for Ni (table 1). In addition, detrital sediment concentrations of Mo are low, at 1 to 1.5 ppm (Wedepohl, 1991; Rudnick and Gao, 2003). Together, these two factors mean Mo is 100 to 200 times easier to enrich Mo in sediment than Zn, Cu, and Ni.

#### *Covariation of the Enrichment of Mo, Cu, Ni, Zn, and Cd with TOC*

A striking result of this study is the high Mo enrichments in the Peru Margin sediments, despite the absence of persistent free sulfide in the water column at this locality (compare Schunck and others, 2013). Algeo and Lyons (2006) suggest that the strong correlation of Mo with organic carbon (TOC) across a wide range of euxinic environments is evidence for scavenging by TOC (compare Helz and others, 2011, and references therein). They also find that, in silled-basin environments, decreasing Mo/TOC ratios correlate with increasing water column restriction and therefore decreasing deep-water renewal, leading to lower aqueous Mo concentrations. This ‘basin reservoir effect’ explains relatively low total  $Mo_{XS}$  enrichments in the Black Sea (for example, this study; Algeo and Tribovillard, 2009). The Cariaco Basin, with a more open setting, has Mo enrichments that are generally higher (for example, this study; Algeo and Tribovillard, 2009). The completely unrestricted hydrographic setting of the Peru Margin allows for high  $[Mo]_{aq}$ . The high Mo enrichment we observe in this setting likely reflects this high Mo supply, along with delivery to the sediment in association with the particulate shuttle, and additional scavenging in association with high organic C fluxes. Fixation in the sediment may also be enhanced by high concentrations of sulfide in pore waters and episodic fluxes of sulfide into bottom waters (Schunck and others, 2013).

The covariation of Zn with TOC shows that the Cariaco Basin and Peru Margin samples fall on the same positive trend (fig. 6B). This single trend implies that an association of Zn with organic C is the only significant source of Zn to the sediment in all locations. The question, therefore, is whether this relationship is born out of primary *uptake* by phytoplankton or rather is the result of secondary scavenging by organic C (or a combination of the two). To distinguish between these two possibilities, and to explore this relationship for other metals, an estimate of the extent to which direct biological uptake can account for the observed authigenic enrichment can be made simply by multiplying the measured organic C content of the sediment (table 4) by the concentration of a metal in average phytoplankton (table 1):

$$TM_{Bio} = C_{org} \times [Me]_{plankton} \quad (4)$$

These data were calculated from published molar Me/P ratios converted to Me/C assuming a Redfield C/P ratio of 106 (Appendix data table A2). Thus, the proportion of the total authigenic metal content of a sediment ( $TM_{XS}$ ) that can be explained by direct phytoplankton uptake ( $TM_{Bio}$ ), illustrated in figure 7, can be calculated as:

$$\text{Fraction } TM_{Bio} \text{ contribution to } TM_{XS} = TM_{Bio}/TM_{XS} \quad (5)$$

Given oxidation of organic matter in sediment and loss of  $CO_2$ , while metals, once released from their organic carbon host, are commonly fixed in sediment (for example

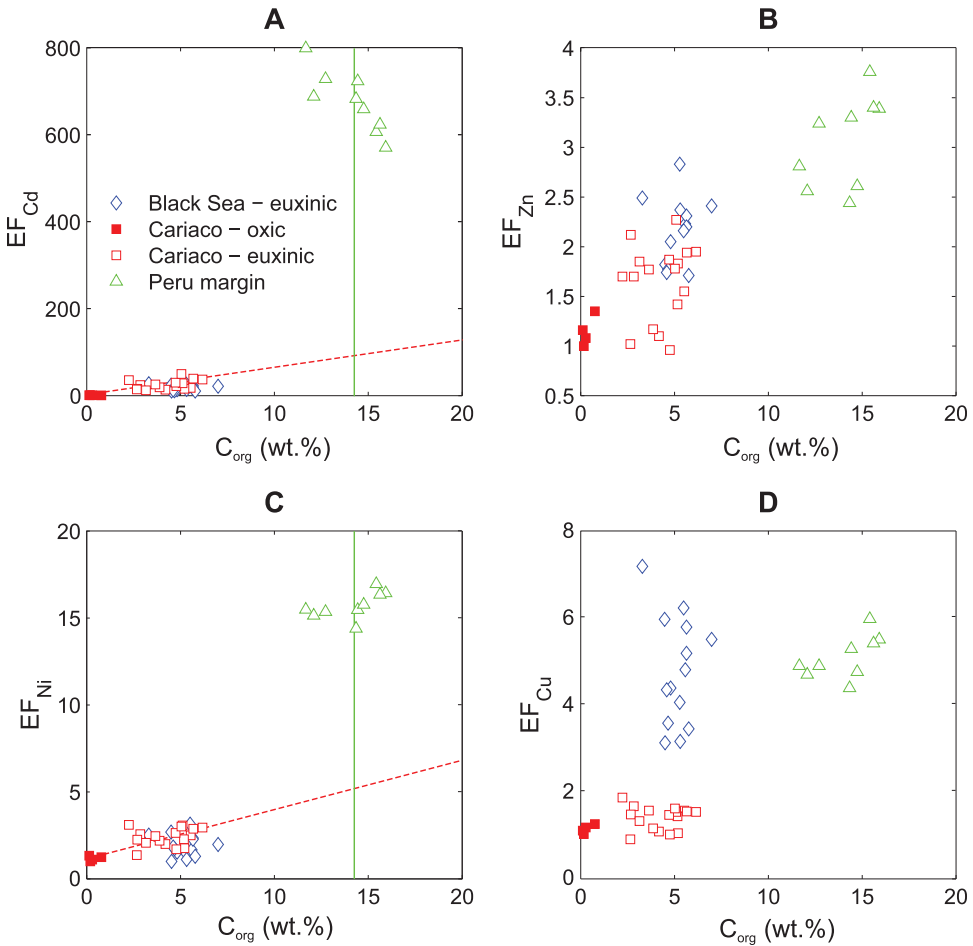


Fig. 6. Covariation diagrams of organic carbon content (wt.%) versus enrichment factors of Cd, Zn, Cu and Ni. Dashed dot lines for Cd and Ni are linear lines of best fit to the Cariaco Basin data, extrapolated for comparison with the enrichment observed at the  $C_{org}$  content of the Peru margin samples (14 wt%—solid lines)—see text for discussion. Note lack of  $C_{org}$  data for the oxic stations of the Black Sea, other symbols as used previously.

Shaw and others, 1990; Rosenthal and others, 1995), the mean and ranges (reflecting ranges in published Me/P ratios) given in figure 7 should be considered minimum estimates for the fractional contribution of direct biological uptake to trace metal concentrations. Nevertheless, some key conclusions can be drawn. First, as expected, only trivial enrichments in Mo can be explained by direct uptake in phytoplankton. Second, it appears that significant enrichments in Zn *can* be explained as the result of direct uptake in plankton. Copper and Ni are somewhere between the extremes of Zn and Mo, while the results for Cd are ambiguous, mainly because plankton Cd contents are variable (Appendix data table A2).

For Cd, Ni, and Cu, a more complex set of processes than that postulated for Zn must explain their enrichment patterns compared to TOC. For Cd and Ni, a positive correlation exists between EF and TOC for the Cariaco Basin samples, where high productivity is proposed to be important in maintaining anoxia at depth. The appar-

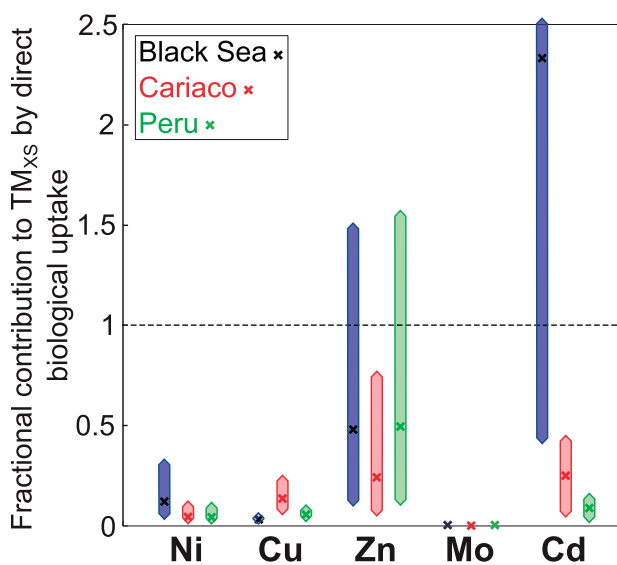


Fig. 7. Fractional contribution of direct biological uptake to the total authigenic enrichment ( $TM_{XS}$ ) observed for the five trace metals in the three study sites. A fractional contribution of 1 (or above) indicates that the entire authigenic trace metal content of the sediment can be explained by primary biological uptake. Calculation uses the average and range of published Me/P ratios in plankton (Appendix data table A2), converted to C given the Redfield C/P ratio of 106, in combination with measured sedimentary organic C contents (see also text).

ently simple relationship for Zn-TOC, assuming that it is explained principally by the delivery of Zn to the sediment *in* organic matter, provides a method to evaluate the relative contribution of Cd and Ni in the Peru Margin site linked to delivery in organic C—specifically, extrapolating the Cariaco Basin Cd:TOC and Ni:TOC correlations to Peru Margin TOC values (figs. 6A and 6C). Doing so, the Peru Margin samples are enriched by a factor of  $\sim 3$  (Ni) and  $\sim 7$  (Cd) above the predicted enrichment based on their respective Cariaco Basin correlations, indicating that there is at least one additional factor involved in generating the high authigenic enrichment of both metals at this site. This is also evident from figure 7 and is consistent with the observation that  $Cd_{XS}/Zn_{XS}$  and  $Ni_{XS}/Zn_{XS}$  ratios in Peru Margin sediments are more than a factor of five higher than those in plankton. The explanation must relate either to additional delivery of Cd and Ni to the sediment in this location, for example, via scavenging by organic matter and/or via the particulate shuttle, or to the preferential retention of Cd and Ni in the sediment relative to Zn. In the case of Cd, scavenging on organic matter is not thought to be a major control on its oceanic distributions (for example John and Conway, 2014). Cadmium is very reactive towards sulfide, however, and water column Cd concentrations are the highest of the three study sites in the Peru Margin. It is plausible, therefore, that diffusion into and fixation of Cd in pore waters is occurring in this open-water setting, bolstering already high authigenic Cd contents that are the result of delivery to the sediment in organic matter.

For Cu, no significant correlation exists with TOC in the Cariaco Basin ( $R^2 = 0.1$ , fig. 6D), and there is no surface depletion in Cu in either the Cariaco Basin or Black Sea (fig. 2). Active uptake in phytoplankton appears to be of relatively minor importance for Cu delivery to the sediment (fig. 7).

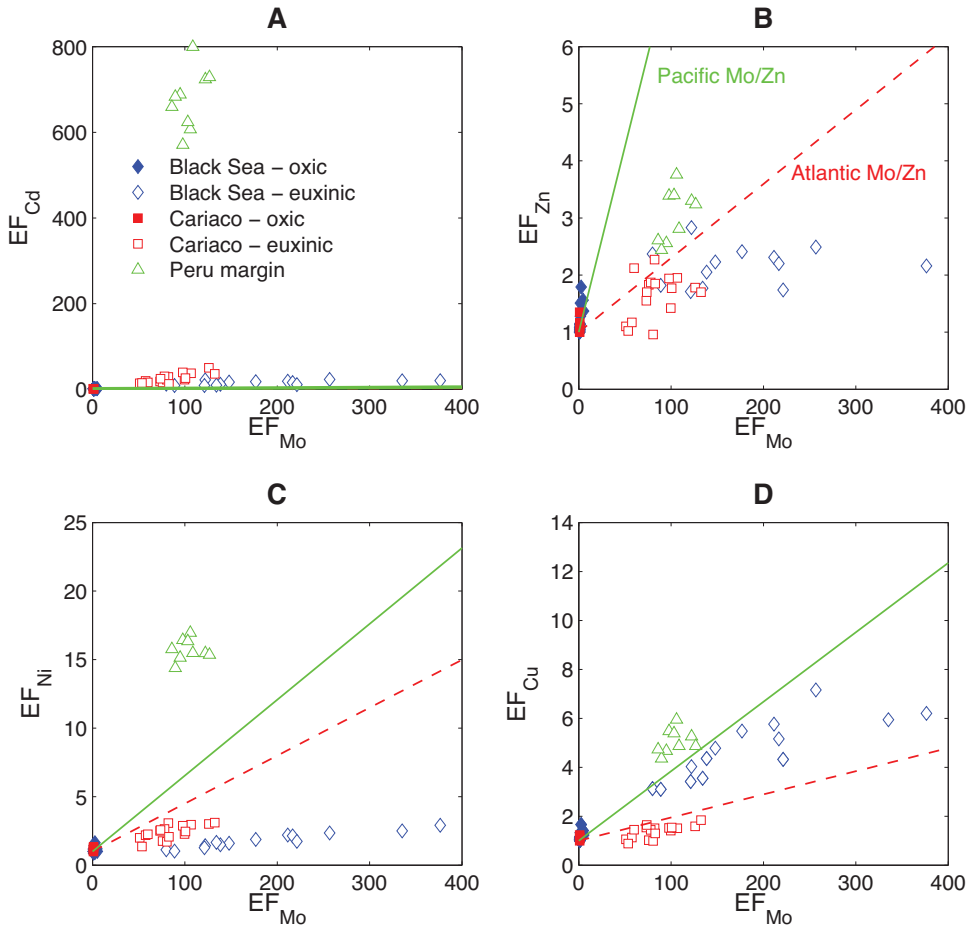


Fig. 8. Covariation plots of Mo EFs with those of Cd, Zn, Ni, and Cu. Dashed and solid lines represent the average deep-water Atlantic (compare Cariaco data) and Pacific (compare Peru margin data) Mo/Me seawater ratios respectively (by weight), plotted through an intercept of (1,1), given that an enrichment factor of 1 indicates no enrichment above detrital sediment concentrations. Enrichment patterns following these lines indicate simultaneous control of the enrichment of the two metals by their aqueous concentration, and by advection of seawater past the site. Deviation from seawater ratios (for example plot A: Mo/Cd) indicates a more complicated relationship (see text for discussion).

*Covariation of the Enrichment of Cd, Zn, Ni, and Cu with that of Mo, and Comparison to Seawater Mo/Me Ratios*

Aqueous, bottom water Mo concentrations can exert a strong control on Mo enrichment (Algeo and Lyons, 2006). Hence, enrichment of Cd-Zn-Cu-Ni in accordance with the seawater Mo/Me ratio would indicate a similar control on the enrichment of these metals by their dissolved concentrations (fig. 8).

Cadmium enrichment is much higher than that predicted by the Mo/Cd ratio of seawater, particularly in the Peru Margin (fig. 8A). The Peru Margin samples are ~300 times more enriched in Cd than predicted from the Pacific Mo/Cd seawater ratio. By comparison, and assuming that the Atlantic Mo/Cd ratio is a good estimate for the input waters to the Cariaco Basin, the Cariaco samples are ~150 times more enriched in Cd than is predicted by the Atlantic ratio. There are three possible explanations for

TABLE 7

*Summary of processes controlling trace element authigenic enrichment in black shales. Elements in parentheses are thought to be affected by the given process, but the impact is considered minor compared to that of some other process.*

<u>Magnitude of enrichment:</u>	
Low detrital sediment concentrations	Cd, Mo
Aqueous concentrations ("basin reservoir effect")	Cd, Mo, (Cu), (Zn)
<u>Delivery to sediment:</u>	
Cellular organic C (uptake)	Zn, Cd, (Ni), (Cu)
Interaction with sulfide (water column/sediment)	Fe, Mn, Mo, Cu, Cd, (Zn)
Particulate shuttle / passive scavenging (oxides, POC, other)	Cu, Mo, Ni (Zn)
Benthic Fe redox shuttle	Mn, Ni, (Cu), (Zn), (Mo)
<u>Fixation in the sediment:</u>	
High degree of trace metal pyritization (DTMP)	[Fe], Mo, Ni, Cu
Fixation in metal sulfide / sulfur-rich organic phase	Cd, Zn, Cu
Carbonates	Mn

this observation: (1) preconcentration of Cd in organic material, (2) more efficient removal of Cd relative to Mo from the water column, particularly in a water column that is non-sulfidic, and (3) more efficient trapping of Cd relative to Mo in sediment. Algeo and Tribovillard (2009) find that, under suboxic conditions (where, again, here suboxic is defined as the absence of both oxygen and sulfide), U is enriched in preference to Mo because U(VI) is reduced at the Fe(II)-Fe(III) redox boundary, while Mo enrichment is controlled by the establishment of significant levels of sulfate reduction and the concomitant accumulation of significant sulfide. Rosenthal and others (1995), in a study of Cd and U behavior in suboxic pore waters, observed a strong coupling between the authigenic enrichment of Cd and U. They propose that fixation of Cd occurs in suboxic sediments via CdS precipitation in the presence of only trace levels of sulfide (Rosenthal and others, 1995). Thus, the onset of authigenic Cd enrichment may, like U, precede (and therefore exceed) that of Mo in continental margin settings.

The clearest relationship in figure 8 is between dissolved seawater Mo and Cu concentrations and Mo and Cu authigenic enrichment, consistent with two elements that are not strongly associated with biological cycling in the water column and which behave in a similar fashion in the presence or absence of sulfide (fig. 8D). Both metals are likely associated with a traditional particulate shuttle. Neither the Ni-Mo plot (fig. 8C) nor the Zn-Mo plot (fig. 8B) show any clear relationship with authigenic Me enrichment and seawater Me/Mo ratios.

#### SUMMARY AND CONCLUSIONS

##### *Patterns of Trace Metal Authigenic Enrichment*

By comparing the patterns of enrichment of Cu, Zn, Ni, Cd, and Mn with those of Mo and Fe for a range of modern anoxic settings, we find two first-order controls on the magnitude of calculated enrichment factors (table 7). The first is the element's background concentration in detrital sediments. The potential for authigenic enrichment is much greater for Cd and Mo because their background concentrations are low,

and this is borne out in their maximum calculated enrichment factors (Cd: 800; Mo: 376; cf. Cu: 7; Ni: 17, Zn: 4). The second is the concentration of the element in overlying seawater. In this study, enrichment factors for three of the five trace elements (Cd, Zn, and Ni) are greatest in the Peru Margin site, where overlying seawater concentrations are the highest of the three study sites (figs. 1 and 2).

Molybdenum is strongly enriched in all three anoxic settings—whether euxinic or from an open continental margin oxygen minimum zone. Its enrichment does not have a simple relationship with water column sulfide concentration, with lowest absolute concentrations observed at the site with the most sulfidic water column—the Black Sea (this study; Algeo and Lyons, 2006). This counterintuitive relationship has been explained as a result of the ‘basin reservoir effect’, whereby deep-water removal of Mo is not matched by resupply (Algeo and Lyons, 2006). Nevertheless, high Mo enrichments in the Peru Margin sediments challenges the notion that euxinia is required for large Mo enrichment (for example Scott and Lyons, 2012). Algeo and Tribovillard (2009) propose the simultaneous use of U and Mo concentrations as a means to distinguish mechanisms of enrichment, based on the predisposition of U to enrichment under less reducing conditions compared to Mo (for example Morford and Emerson, 1999). Cadmium enrichment likely also precedes that of Mo; in this study Cd is enriched over and above that predicted by the seawater Cd/Mo ratio in all settings (fig. 8). Cadmium, like U, is fixed in sediments with suboxic pore waters (van Geen and others, 1995; Rosenthal and others, 1995; Morford and Emerson, 1999), while Mo enrichment does not occur until the onset of significant sulfate reduction (and concomitant build up of pore water sulfide). The exaggerated enrichment of Cd in the Peru Margin compared to its limited enrichment in the restricted Black Sea illustrates the potential to use Cd concentrations, in combination with other tracers, as a tracer of an open ocean margin setting with oxygen depletion driven by high productivity.

A novel suggestion of this study is that the benthic Fe (and Mn) redox shuttle, operating by nanoparticulate Fe and Mn oxides (Lyons and Severmann, 2006), scavenges a range of other trace metals and delivers them to euxinic deeper waters. This mechanism is necessary to explain Ni enrichments in Black Sea sediments, with its apparent ‘conservative’ water column profile maintained by a balance between supply in association with the benthic Fe/Mn redox shuttle and removal in pyrite.

A proxy for the presence of appreciable sulfide in the water column is marked enrichment in Cu. Maximum Cu enrichments are measured for the Black Sea, where Cu is removed from the water column, presumably by co-precipitation with sulfide (fig. 2). The contrast with muted Cu enrichments in the Cariaco Basin may simply reflect a high detrital input in this setting (and associated dilution), and/or that sulfide concentrations in the Cariaco Basin are insufficiently high to generate high Cu enrichments. In general, moderate-to-high enrichments in Cd and Mo but limited enrichments in elements with high detrital contents (Cu, Ni, and Zn), as seen in the Cariaco Basin, are indicative of an anoxic setting with significant detrital input, where untangling the detrital and authigenic contributions to the sediment is consequently more difficult.

Finally, the Zn enrichment factors calculated in this study show a single, straightforward, relationship with TOC. This conclusion is supported by a calculation of the fractional contribution of direct biological uptake to  $TM_{XS}$  concentrations, which is most significant for Zn (fig. 7).

#### *Implications for Oceanic Mass Balance*

The reducing sedimentary sink (including sediments deposited under euxinic and under ‘anoxic-suboxic’ conditions, the latter defined here as sediments with sulfidic porewaters underlying suboxic bottom waters) is responsible for between 10

and 50 percent of the removal of Cu, Zn, and Ni from the oceans. This calculation is similar to or slightly less than the reducing sink's estimated importance for Mo and Cd (~50%: for example van Geen and others, 1995; Poulson Brucker and others, 2009). A thorough consideration of the quantitative effect of varying the magnitude of the reducing sedimentary sink on the oceanic inventory of the trace metals studied here is beyond the scope of this paper (see, for example Reinhard and others, 2013). However, we note that the oceanic residence times of Cu, Zn, and Ni are significantly shorter than that of Mo and shorter than that of Cd (Emerson and Husted, 1991; Morford and Emerson, 1999; Little and others, 2014; this study). Variations in the area of reducing sediments are thus likely to have had a larger impact over glacial-interglacial timescales on the oceanic concentrations of Cu and Ni, in particular, than on those of Mo and Cd, given significant glacial-interglacial variation in marine redox (for example Haug and others, 1998). Ultimately, better constraints on the oceanic mass balance of these trace metals will come from the inclusion of the isotopic compositions of the various input and output fluxes in the calculations (for example Siebert and others, 2003; McManus and others, 2006; Poulson Brucker and others, 2009; Little and others, 2014).

#### ACKNOWLEDGMENTS

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TABLE A1  
(continued)

Sample depth cm	Ni ppm	Cu ppm	Zn ppm	Mo ppm	Cd ppm	Al wt%	Nixs ppm	Cuxs ppm	Znxs ppm	Moxs ppm	Cdxs ppm	C <sub>org</sub> wt. %	S <sub>pyrite</sub> wt. %	DOP	C <sub>org</sub> /S <sub>p</sub>
Cariaco Basin, core 1002A-B															
Oxic	680	29	91	2.1	0.5	8.7	12	2.3	4	0.3	0.12	0.8	1.82	nd	0.45
	710	42	132	2.4	0.5	11	10	7.9	23	0.1	0.00	0.2	2.65	nd	0.09
	755	35	135	2.4	0.5	11	0.0	0.0	24	0.1	0.08	0.3	0.18	nd	1.83
	770	40	142	2.3	0.5	11	5.0	5.2	31	0.0	0.03	0.2	0.18	nd	0.94
Euxinic	20	29	78	91	4.5	6.0	36	10	18	90	4.3	5.6	1.34	0.52	4.16
	35	49	77	109	4.9	5.3	28	6.9	25	108	4.7	5.2	1.39	0.54	3.76
	85	45	20	145	98	4.1	6.3	19	0.4	83	3.9	5.3	1.29	0.54	4.07
	115	42	19	101	102	5.6	6.2	-0.2	40	101	5.4	4.8	1.46	0.53	3.30
	200	55	22	85	71	3.9	6.8	2.7	1.4	18	70	4.2	1.59	0.56	2.66
	245	59	23	85	79	5.3	6.7	2.7	1.9	78	5.0	3.9	1.57	0.56	2.50
	305	89	34	162	122	8.6	7.2	11	91	120	8.3	5.2	1.55	0.55	3.32
	320	87	37	152	131	10	8.2	11	71	130	9.8	4.8	1.53	0.55	3.12
	340	97	38	157	179	13	8.2	13	77	177	12	6.2	1.56	0.55	3.98
	360	94	38	156	163	13	8.1	12	75	162	13	5.7	1.55	0.55	3.69
	400	77	31	112	164	13	6.3	12	49	163	13	5.1	1.18	0.53	4.31
	420	84	33	70	147	25	3.8	21	32	146	25	4.9	1.21	0.58	4.02
	440	46	23	75	67	4.5	4.5	8.8	31	66	4.4	2.9	0.92	0.56	3.14
	490	46	23	106	62	3.3	5.1	7.1	56	61	3.1	2.7	1.18	0.56	2.31
	510	71	35	72	68	7.8	4.6	16	11	67	7.5	2.7	1.17	0.53	2.32
	530	56	27	123	114	3.5	6.7	6.4	56	113	3.2	3.2	1.22	0.52	2.62
	570	78	38	138	163	8.4	4.6	13	60	161	8.1	3.7	1.93	0.64	1.92
	610	81	37	109	177	9.6	5.5	17	45	175	9.4	2.3	2.29	nd	1.00
Average proportion of Me <sub>es</sub> possible from direct biological uptake (%):															
Peru Margin	0.52	130	71	95	69	47	2.7	59	70	69	47	15.5	nd	nd	na
	1.04	133	69	91	67	47	2.8	56	64	67	47	16.0	nd	nd	na
	1.74	134	69	92	72	52	2.9	56	65	71	52	15.7	nd	nd	na
	2.43	139	70	92	79	57	3.0	57	63	79	57	15.4	nd	nd	na
	4.82	129	68	91	87	61	2.9	55	63	86	61	14.5	nd	nd	na
	8.21	115	57	80	81	55	2.6	45	55	80	55	12.8	nd	nd	na

TABLE A1  
(continued)

Sample depth cm	Ni ppm	Cu ppm	Zn ppm	Mo ppm	Cd ppm	Al wt%	Nixs ppm	Cuxs ppm	Znxs ppm	Moxs ppm	Cdxs ppm	Other Geochemical Data (1,2,3) C <sub>org</sub> <sup>wt.%</sup>	S <sub>pyrite</sub> wt.%	DOP	C <sub>org</sub> /S <sub>p</sub>
14.99	112	55	67	67	59	2.5	105	44	43	66	59	11.7	nd	nd	na
15.68	123	59	69	66	57	2.9	115	47	42	65	57	12.1	nd	nd	na
18.38	148	70	83	79	71	3.6	138	54	49	78	71	14.4	nd	nd	na
19.07	161	75	88	75	68	3.6	150	59	54	74	68	14.8	nd	nd	na
Average proportion of Me <sub>ss</sub> possible from direct biological uptake (%):															
							4	6	49	0	9				

TM<sub>ss</sub> values are calculated using local lithogenic Me/Al ratios defined in table 4, as per equation (3). The proportion of the TM<sub>ss</sub> in the reducing sediment samples that can be accounted for by direct biological uptake is calculated using the TM content of 'average plankton' (table 1, Appendix data table 2) and the measured organic carbon content of the sediment. Other geochemical data are given for reference. nd = not done. na = not applicable.

References: (1) Lyons and Berner, 1992; (2) Lyons and others, 2003; (3) McManus, J., personal communication.

TABLE A2  
*Compilation of published elemental compositions of cultivated (Ho and others, 2003) and collected (others) plankton from the coastal and open oceans.*

Metal	Martin and Knauer 1973 a	Martin and others 1976 b	Collier and Edmond 1984 c	Kuss and Kremling 1999 d	Twining and others 2004 e	Twining and others 2010 f	Twining and others 2011 g	Ho and others 2003 h	Ho and others 2007 i	Ho and others 2007 j	Mean Plankton* (excl. i, j)
Mn/P	0.39	0.38	0.52	1.59	0.24	0.65	0.62	3.8	149	9.3	1.02
Fe/P	5.2	5	11.1	4.5	0.63	5	2.6	7.5	6520	323	5.19
Ni/P	0.21	0.35	0.75	0.88	0.53	2.2	0.67	—	5	1.4	0.80
Cu/P	0.18	0.38	0.78	0.42	—	—	—	0.38	6.8	4.8	0.43
Zn/P	0.84	1.8	7.4	1.5	3.9	12	2.1	0.8	32.7	10.7	3.79
Mo/P	—	—	—	—	—	—	—	0.03	—	—	0.03
Cd/P	0.07	0.46	0.71	0.53	—	—	—	0.21	—	—	0.40

Particulate trace metal (Me) concentrations are quotas normalized to phosphate (P) and have the same unit: mmol-Me/mol-P. (Adapted from Yüçerhan and others, 2011).

\* 'Mean Plankton' is an average of published values, excluding the China Sea data for which anthropogenic contamination is likely.

References:

a: North Pacific Monterey Bay, b: North Pacific, Stn. 54–88, c: Average of bulk plankton from Antarctic, Galapagos, Central Tropical Pacific, d: Biogenic samples from NE, e: Average of diatom, autotrophic flagellates and heterotrophic flagellates plankton from Southern Ocean, f: average of three mesoscale eddies in the Sargasso Sea, g: Average of bulk, diatom, autotrophic flagellates, heterotrophic flagellates and pico plankton from Equatorial Pacific, h: Average culture, i: Southern China Sea Pearl, River mouth 2–30 m depth interval, j: S.E. Asia time-series site 25–200 m depth interval.

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