

Definition of new trace-metal proxies for the controls on organic matter enrichment in marine sediments based on Mn, Co, Mo and Cd concentrations

Tim Sweere^{1,2,3*}, Sander van den Boorn³, Alexander J. Dickson¹ and Gert-Jan Reichart^{2,4}

¹Department of Earth Sciences, University of Oxford, South Parks Rd, OX1 3AN Oxford, United Kingdom,

²Department of Earth Sciences, Utrecht University, Heidelberglaan 2, 3584 CS Utrecht, Netherlands,

³Shell Global Solutions International, Kessler Park 1, 2288 GS Rijswijk, Netherlands,

⁴Royal Netherlands Institute for Sea Research, Texel, Netherlands

*tim.sweere@seh.ox.ac.uk

Abstract

Trace metal enrichments in sedimentary deposits are of prime interest because they are governed by processes that also control the production and preservation of organic matter. Consequently, trace metals have been used in reconstructions of the (palaeo)depositional environment of organic-rich deposits, but most of these studies have primarily focused on hydrographically restricted basins and the response of trace metals to changing redox conditions whereas the role of trace metals in the nutrient cycle and primary productivity in upwelling settings remains relatively unexplored.

In this study we present a comprehensive database of published trace metal concentration data in modern organic-rich deposits from a variety of marine settings. Scrutiny of the compiled dataset has resulted in the development of novel trace metal based proxies that allow the distinction between two marine end-member depositional settings that are associated with enhanced organic carbon burial: open marine settings on the continental margin associated with upwelling (e.g. Namibian Margin) and hydrographically restricted marginal marine basins (e.g. Black Sea).

It is shown that high Cd/Mo values are typical for sediments from continental margin upwelling settings whereas Co and Mn concentrations (expressed as Co*Mn values) are high in samples from hydrographically restricted marine basins. The Cd/Mo ratios are thought to track the relative importance of productivity versus preservation with high values in productivity driven systems attributed to the transfer of Cd to the sediments from re-mineralised plankton biomass. Co*Mn values, on the other hand, are believed to reflect the supply and reactive behaviour of Co and Mn and can be used to assess circulation patterns in the water column and the relative contribution of deep versus surface/river water influx to the basin. It is demonstrated that the combined use of the Cd/Mo and Co*Mn proxies provides a highly effective way to distinguish modern/recent marine sedimentary environments, which holds promise for its use in palaeo-environmental reconstructions.

Highlights

- A database for trace metal concentrations in modern sediments has been compiled.
- Two new trace metal-based proxies (Cd/Mo and Co*Mn) are proposed.
- The new elemental proxies distinguish between restricted basins and upwelling settings.

Keywords

Trace-metals, organic-rich sediments, productivity, preservation, upwelling, restricted basin

1. Introduction

Intervals of widespread organic-rich sediment deposition have been associated with perturbations in the global carbon cycle, rapid global warming and severe biotic crises including mass extinctions (e.g. Jenkyns, 2010, 2003). Understanding the forcing mechanisms behind organic-rich sediment deposition can therefore provide insights in the global carbon cycle and the environmental and climatic changes related to these events. Organic-rich sediments are also of economic interest as they are the source rocks for hydrocarbons that are generated from the precursor organic matter upon burial and heating. Since the quantity, quality and distribution of organic matter in these source rocks are strongly controlled by environmental processes, the ability to predict presence and extent of source rocks in time and space strongly depends on accurate reconstructions of the palaeo-environmental setting.

Trace metals have been recognized as powerful proxies for (palaeo-)environmental reconstructions as they are typically enriched in organic-rich deposits due to their physiochemical properties. To date, most studies have focused on the redox sensitivity of trace metals and their application as palaeo-redox proxies (e.g. Algeo and Maynard, 2004; Calvert and Pedersen 1993; Crusius et al., 1996; Emerson and Huested, 1991; Morford et al., 2001). Moreover, many trace metal studies have focused on restricted basinal settings where shallow sills hamper the renewal of deep waters and result in the formation of anoxic to euxinic bottom waters (e.g. Lyons et al., 2003; Nijenhuis et al., 1999; Russel and Morford, 2001; Skei et al., 1988; Tribovillard et al., 2008). Although primary productivity in the water column has been recognized to influence trace metal enrichments in sediments (e.g. Brumsack, 2006; Little et al., 2015; Piper and Calvert, 2009; Tribovillard et al., 2006), metal-based proxies that allow this to be assessed are not as well established in the literature.

In this study a comprehensive trace metal database from published data sources is presented that covers a wide range of well-characterised modern marine environments where organic matter deposition occurs. The principal aim is to compare and contrast trace metal data systematically between hydrographically distinct settings and to establish trace metal-based proxies that allow these settings to be distinguished in the sediment record. The settings included in this study differ in, amongst others, geographic location, climate, level of primary productivity in the water column and degree of hydrographic restriction, which all affect the (chemical) composition of the sediments. To a first approximation, however, the settings can be subdivided into two broad end-members: (1) continental margin upwelling systems, and (2) hydrographically restricted basins. It is shown that Cd/Mo ratios and the levels of Mn and Co enrichments can be used to distinguish between these different hydrographic regimes as the result of changes in the relative importance of biological, physical and chemical processes that control trace metal enrichment patterns.

2. Background

2.1. *Hydrographically restricted basins versus open marine upwelling settings*

The presence of oxygen depleted waters in hydrographically restricted basins and upwelling settings is related to fundamentally different processes. In restricted basins a sill limits deep-water circulation and the exchange with oxygenated waters from the open ocean, which typically results in de-oxygenated deeper water masses because the rate of oxygen consumption through degradation of organic matter exceeds its re-supply by vertical mixing and deep-water ventilation. Circulation patterns in hydrographically restricted basins can also impact primary productivity rates because of its control on the basinal nutrient budget.

Continental margin upwelling settings are characterized by high rates of primary productivity as the result of enhanced nutrient supply to the photic zone through the upwelling of deep and nutrient-rich ocean waters. An Oxygen Minimum Zone (OMZ) is a typical feature of these upwelling settings and develops below the photic zone where oxygen demand is high as the result of high export productivity and if advected waters are sufficiently low in oxygen (e.g. Paulmier and Ruiz-Pino, 2009 and references therein). Organic-rich sediments are generally deposited where the

OMZ impinges on the shelf, whereas in restricted basins organic-rich sediment deposition typically occurs throughout the area that underlies the chemocline.

2.2 Trace metal characteristics

The focus in this study is on the elements Mn, Co, Cd and Mo as they have been observed to show large differences in their water column behaviour and/or removal pathways to the sediment (for general characteristics and distribution of these metals in the Earth's reservoirs see Table 1). The typical depletion of dissolved Mn and Co with depth in the oceans (Figure 1) is the result of active scavenging from the water column (Knauer et al., 1982; Landing and Bruland, 1980; Statham and Burton, 1986), while the distribution of dissolved Cd in the modern ocean is dominated by uptake and release of Cd by phytoplankton (Bruland, 1980; Conway and John, 2015). In contrast, dissolved Mo concentrations vary little with depth, which reflects its more conservative behaviour in the oxygenated water column (Emerson and Husteded, 1991; Nakagawa et al., 2012).

The behaviour of all four elements changes with different redox conditions, which affects their removal pathways to the sediment. Under more reducing conditions Mn is more soluble while Co, Cd and Mo are more effectively removed to the sediment (Erickson and Helz, 2000; Huerta-Diaz and Morse, 1992; Little et al., 2015; Tribovillard et al., 2006; Vorlicek et al., 2004 and references therein). The removal behaviour of Mo into sediments underlying euxinic waters is particularly well established, which in combination with its low detrital abundance makes it a powerful (palaeo)redox proxy (e.g. Algeo and Lyons, 2006; Algeo and Tribovillard, 2009; Crusius et al., 1996; Scott and Lyons, 2012). For a more comprehensive discussion on the characteristics of these elements see e.g. Algeo and Maynard (2004), Brumsack (2006), Little et al. (2015) and Tribovillard et al. (2006).

Table 1. Overview of trace metal characteristics and concentrations in the Earth's main reservoirs. Sources: (a) Sarmiento and Gruber (2004), (b) Morford and Emerson (1999) (c) McLennan (2001), (d) Wedepohl (1971) and references therein.

	Unit	Mn	Co	Mo	Cd
Atomic number		25	27	42	48
Ocean dissolved concentration (a,b)	nmol/kg	0.182	0.034	105	0.6
River dissolved concentration (a,b)	nmol/kg	149	3	5	0.1-0.4
Residence time (a,b)	kyr	0.04	0.35	800	30-150
Average upper continental crust (c)	mg/kg	600	17	1.5	0.098
Average shale (d)	mg/kg	850	19	2.6	0.8

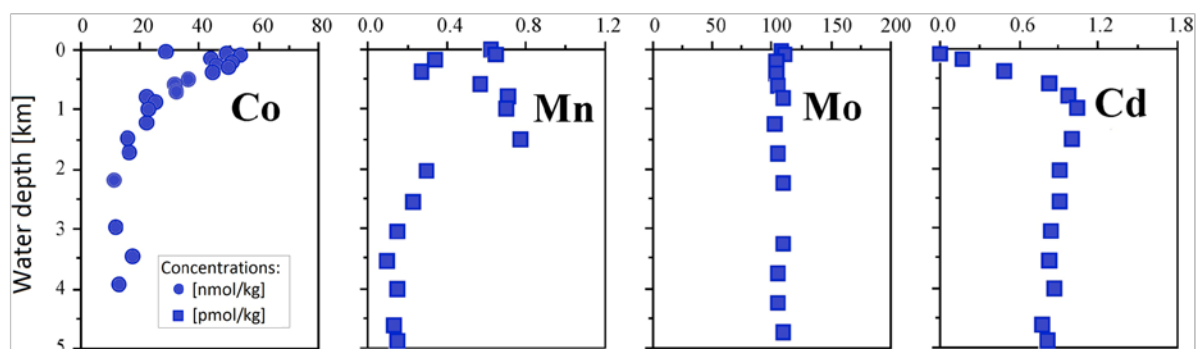


Figure 1. Depth profiles of dissolved trace metals concentrations in the North Pacific Ocean. Modified from a compilation by Nozaki (1997).

3. Materials, data and methods

A comprehensive literature survey was undertaken with the aim to collect trace metal data from a range of modern/recent marine settings that are associated with deposition and burial of organic-rich sediments (Figure 2; Table 4).

3.1 Hydrographically restricted basins

Data from five different sites with variably restricted water masses have been included in this study: (1) Black Sea, (2) Cariaco Basin, (3) Saanich Inlet, (4) Baltic Sea (Bornholm and Arkona Basin) and (5) Mediterranean Sea (sapropels). The characteristics of these basins in terms of hydrographic restriction and primary productivity vary considerably (Table 2). The Black Sea has the most strongly restricted water column as exemplified by a deep-water age of 500-4000 years (Algeo and Lyons, 2006 and references therein). In comparison, deep-water renewal in the Baltic Sea (Bornholm basin) occurs on timescales of only a few years (Meier et al., 2006). Primary productivity rates in the strongly restricted Black Sea are relatively low, especially when compared to the Saanich Inlet and Cariaco Basin (Algeo and Lyons, 2006; Lyons et al., 2003; Morford et al., 2001; Piper and Dean, 2002; Russel and Morford, 2001). Mediterranean sapropels are discrete layers of organic-rich sediments that record recent periods of elevated primary production in the eastern Mediterranean Sea (e.g. Calvert et al., 1992; Kemp et al., 1999), and are preserved because of restricted bottom water ventilation (e.g. Menzel et al., 2002; Passier et al., 1999). Although not strictly speaking modern sediments, the Mediterranean sapropels were included because of their well-studied nature and trace metal data availability.

Table 2. Main characteristics of the different restricted basins included in this study. Sources: (a) Algeo and Lyons (2006) and references therein, (b) Gingele et al. (1997), (c) Rheinheimer et al. (1989), (d) Meier et al. (2006), (e) Yunev (2011), (f) Muller-Karger et al. (2000), (g) Rydberg et al. (2006), (h) Timothy and Soon (2001). No quantitative present-day information is reported here for the Mediterranean Sea as sapropel formation took place in the recent past.

	Black Sea	Cariaco Basin	Baltic Sea	Saanich Inlet
Volume [km ³]	541,000 ^a	8,000 ^a	-	5.4 ^a
Total depth [m]	2240 ^a	1425 ^a	46-77 ^b	238 (120) ^a
Sill depth [m]	33 ^a	146 ^a	-	70 ^a
Chemo-cline depth [m]	50-150 ^a	250-375 ^a	~30-60 ^c	150-238 ^a
Sill Depth /Total Depth [m]	0.015 ^a	0.1 ^a	n.a.	0.29 ^a
Chemocline Depth/Total Depth	0.02-0.06 ^a	0.18-0.26 ^a	n.a.	0.63-1.0 ^a
Deepwater Age (year)	500-4000 ^a	50-100 ^a	~1 ^d	~1.5 ^a
Bulk sediment accumulation [g m ⁻² yr ⁻¹]	10-200 ^a	80 – 250 ^a	n.a.	420-4800 ^a
Primary productivity [g C m ⁻² yr ⁻¹]	63-135 ^e	> 500 ^f	50-500 ^g	490 ^h
Organic carbon accumulation [g m ⁻² yr ⁻¹]	1-10 ^a	10-60 ^a	n.a.	20-110 ^a

3.2 Continental margin upwelling settings

Sediments from four prominent upwelling regions in the modern ocean have been included: (1) Namibian Margin, (2) Peruvian Margin, (3) Gulf of California and (4) Arabian Sea. The characteristics of the Namibian and Peruvian Margin are very similar as they both feature perennial upwelling, high primary productivity and sedimentation rates, a pronounced OMZ and strong organic carbon enrichment in the sediments (up to 20% TOC) (Table 2, Böning et al., 2004; Brongersma-Sanders, 1980; Robinson et al., 2002; Scholz et al., 2011). The Arabian Sea and Gulf of California feature only seasonal upwelling and have a less pronounced OMZ and lower organic carbon enrichments (up to 5 % TOC) (Table 2; Böning et al., 2004; Brumsack, 1989; Pattan and Pearce, 2009; Van der Weijden et al., 2006). The Gulf of California differs from the other upwelling sites in the sense that the Lower California Peninsula shields it from the open ocean. It can thus be considered as an intermediate

between fully open marine upwelling sites and hydrographically enclosed basins, which is exemplified by relatively low primary productivity rates.

Table 3. Main characteristics of the different upwelling systems included in this study (Böning et al., 2004 and references therein). Other sources: (a) Nixon and Thomas (2001), (b) Barlow et al. (2009).

	Upwelling type	Water depth OMZ (m)	Average primary productivity (g C m ⁻² yr ⁻¹)	Average sedimentation rate (cm kyr ⁻¹)
Peruvian Margin	perennial	50-650	350 (-1200 ^a)	150
Namibian Margin	perennial	50-700	300 (-600 ^b)	100
Oman Margin	seasonal	150-1200	300	14
Gulf of California	seasonal	400-800	100	180

3.3 Dataset filtering

Surface sediment data from some of the settings included in this study come from multiple coring locations and may therefore incorporate some spatial variability in environmental conditions and possibly metal enrichments. In other settings trace metal data were measured down core in near surface sediments and may therefore incorporate a degree of temporal variability. In an attempt to reduce the artefacts associated with spatial and/or temporal variability in the dataset, a data filtering approach was applied (see Table 4). Temporal data was filtered to include only samples representing Holocene age (or top 2m of the sediment cores if no age constraints were available, i.e. <10.000 years assuming sedimentation rates of >0.2 mm/year). Accounting for spatial variations is more difficult and often arbitrary, but an attempt was made to include only samples from areas where the OMZ impinges on the shelf in upwelling settings and from areas below the chemocline in hydrographically restricted basins. The results of this filtering exercise are discussed below.

Table 4. Overview of literature sources of the various datasets. Numbers refer to the amount of data points included, letters to the following data sources: (a) Arnaboldi et al., 2007, (b) Baturin et al., 2011, (c) Böning et al., 2004, (d) Brongersma-Sanders et al., 1980, (e) Brumsack et al., 1989, (f) Morford et al., 2001, (g) Nijenhuis et al., 1999, (h) Piper and Dean 2002, (i) Russel and Morford 2001, (j) Gingele et al., 1997, (k) Hirst et al., 1974, (l) Presley et al., 1972, (m) Van der Weijden et al., 2006.

	Cd and Mo data (Figure 3, 4)	Co and Mn data (Figure 3, 6)	Cd, Mo, Co and Mn data (Figure 7a)	Filtered data (Figure 7b)
Black Sea	5b + 22e	5b + 27k + 22e	5b + 22e	12e
Cariaco Basin	191h	199h	191h	37h
Saanich Inlet	59f + 28i	8l		
Mediterranean Sea	84a + 12g			
Baltic Sea		253j		
Arabian Sea	201m	200m	200m	
Gulf of California	59e	59e	59e	29e
Peruvian Margin	11c	11c	11c	4c
Namibian Margin	152d	247d	152d	61d



Figure 2. Map with approximate geographic location of the basins and continental margins from which data are included in this study.

4. Results

The data are summarised in Figure 3 as percentile plots that provide an overview of the variability in trace metal concentrations in the different settings. With the exception of the Cariaco basin, there is a clear difference in the Co and Mn content between restricted basins and upwelling settings. Cobalt and Mn concentrations are generally near (or above) reported crustal abundances in restricted basins (McLennan, 2001), whilst sediments from upwelling settings and the Cariaco Basin are depleted in Co and Mn.

In contrast to Co and Mn, virtually all samples are enriched in Cd and Mo relative to background values with Cd generally being most enriched in sediments from upwelling settings, and specifically those featuring perennial upwelling (i.e. Namibian and Peruvian margin). Sediments from the Arabian Sea and Gulf of California are notable for the lack of strong Mo enrichments.

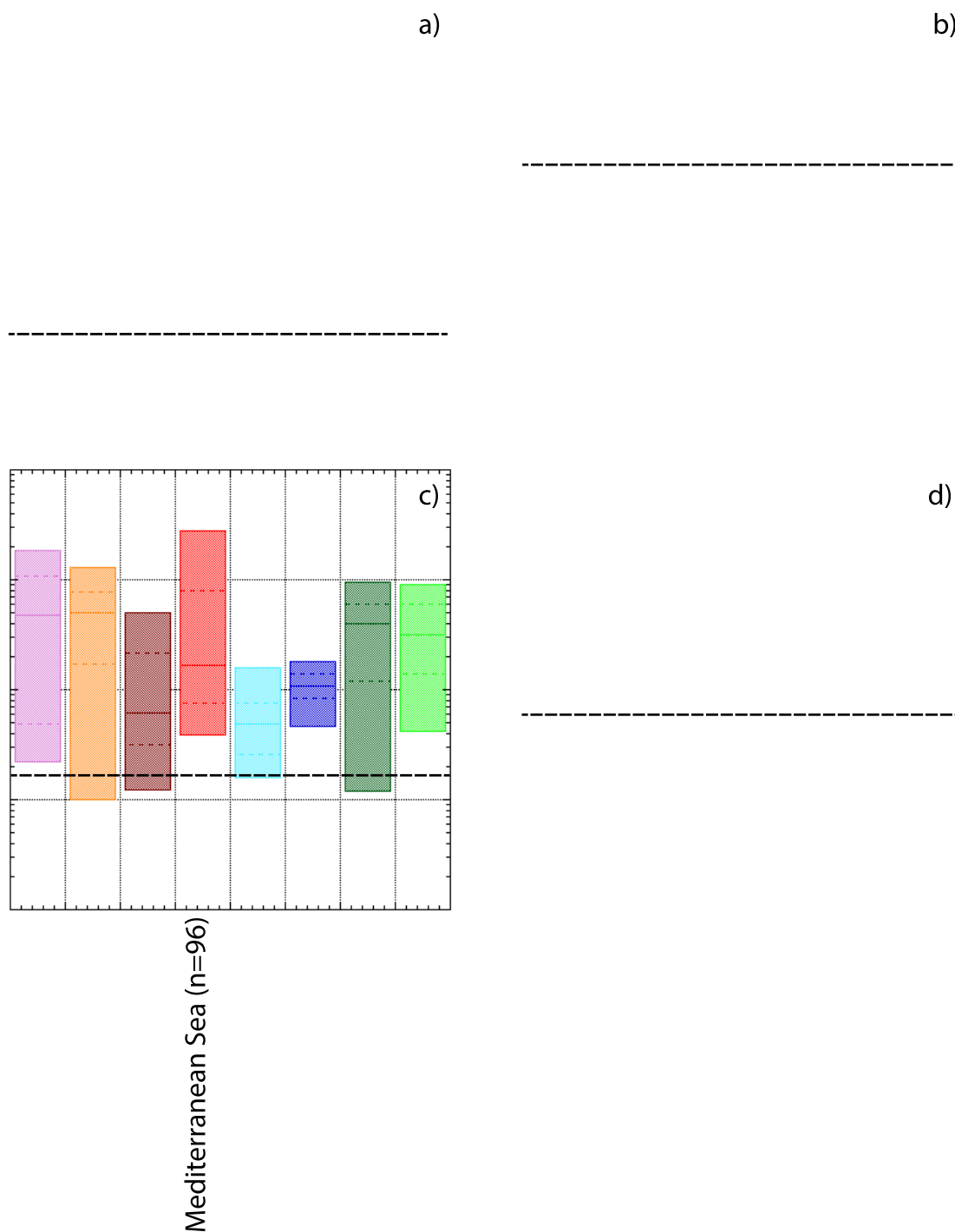


Figure 3. Percentile plots with boxes covering 90% of the data (bottom and top representing 5% and 95%, respectively). Median values are indicated by solid coloured lines, and 25% and 75% of the data with coloured dashed lines, respectively. Bold dashed black lines reflect average upper continental crust concentrations as reported by McLennan (2001).

5. Discussion

5.1 Cadmium and Molybdenum

Cadmium and Mo enrichment patterns in sediments from upwelling settings are clearly distinct from those from hydrographically restricted basins (see Figure 4). The difference is most pronounced for settings that feature high metal enrichments (e.g. Namibian and Peruvian margin sediments versus Cariaco Basin and Black Sea sediments) and is illustrated in Figure 4 by sharply contrasting Cd/Mo ratios. Although the contrast is less pronounced for settings with relatively modest metal

enrichments (e.g. Arabian Sea and Gulf of California versus Saanich inlet), differences do exist with Cd/Mo ratios above 0.1 being characteristic for upwelling settings and values below 0.1 for hydrographically restricted settings. Importantly, there is no clear co-variation between the Cd/Mo ratio and TOC content of the sediments, which suggests that the proxy is valid regardless of the amount of TOC enrichment. There is, however, increased scatter in the data for samples with relatively low organic matter (TOC < ~3%) and metal contents, which may be attributed to a relatively higher proportion of metals from detrital phases (Figure 5).

Besides the clear overall difference in Cd/Mo ratios between the two end-member settings, there appear to be more subtle but systematic differences between individual restricted and upwelling settings (Figure 4). Linear regressions through the datasets of settings with strong perennial upwelling (i.e. Peruvian and Namibian margin) show very similar slopes with much higher Cd/Mo ratios than those from systems that feature only seasonal upwelling (e.g. Arabian Sea and Gulf of California). The latter are generally characterized by less pronounced OMZs and lower OM enrichments. Similarly, the strongly restricted Black Sea with its relatively long deep water residence time and low rates of primary productivity can be differentiated from the Cariaco Basin, Mediterranean Sea and Saanich Inlet based on Cd/Mo ratios.

The low Cd/Mo ratios that are observed in sediments from hydrographically restricted settings are close to the average dissolved Cd/Mo ratio of seawater (Tribovillard et al., 2006 and references therein), while the much higher Cd/Mo ratios in sediments from upwelling settings approach values that have been measured in planktonic material (Brumsack, 1986 and references therein; Figure 4). This is significant as Cd is closely linked to primary productivity and has a strong nutrient-like profile in the water column (Bruland, 1980; Conway and John, 2015). Hence, the strong Cd enrichments in upwelling sediments are likely to be the result of the large flux of Cd-rich plankton material that reaches sediments underlying upwelling-induced high productivity settings. Molybdenum, on the other hand, shows conservative behaviour in the water column, which illustrates that its distribution is not significantly affected by biological uptake (Nakagawa et al., 2012). This is in marked contrast to restricted settings where strong Mo enrichments are attributed to dominantly anoxic to euxinic conditions and, as a result, enhanced preservation of organic matter (e.g. Algeo and Lyons, 2006). This difference in the behaviour of Cd and Mo can thus explain why Cd/Mo ratios are high in upwelling induced high productivity settings and low in strongly oxygen deficient basins that are characterized by hydrographic restriction.

The difference in behaviour of Cd and Mo and the relative importance of primary productivity in the water column also provides a likely explanation for the more subtle differences in Cd/Mo gradients between the individual restricted settings. In anoxic/euxinic waters both Cd and Mo are thought to be effectively removed to the sediment through the formation of sulphides and the formation of particle reactive thiomolybdates, respectively (Emerson and Huested, 1991; Erickson and Helz, 2000; Little et al., 2015; Vorlicek et al., 2004). Since all hydrographically restricted settings included in this study experience strongly reducing bottom water conditions, Cd and Mo are expected to be removed at similar rates and thus result in sedimentary Cd/Mo ratios close to seawater. This is the case in the Black Sea where primary productivity and the associated rate of organic matter accumulation is low so enhanced transport of Cd to the sediment water interface by sinking planktonic biomass is limited and sedimentary Cd/Mo ratios approach seawater values. Relatively higher levels of primary productivity in the other basins are likely to result in more effective transport of Cd to the deeper waters and sediments when compared to Mo, which may thus explain the observed slight enrichments in Cd. Additional factors that may play a role are the substitution of Cd for Ca in hydroxyapatite (Tribovillard et al., 2006 and references therein) and more efficient trapping (and removal) of Cd relative to Mo under suboxic (non-sulphidic) conditions (see discussion in Little et al., 2015).

In summary, the data presented here clearly demonstrate that organic-rich sediments from productivity driven upwelling settings and preservation driven restricted basins can be distinguished based on Cd/Mo ratios, with an empirically defined cut-off value of ~0.1 (Figures 4 and 5).

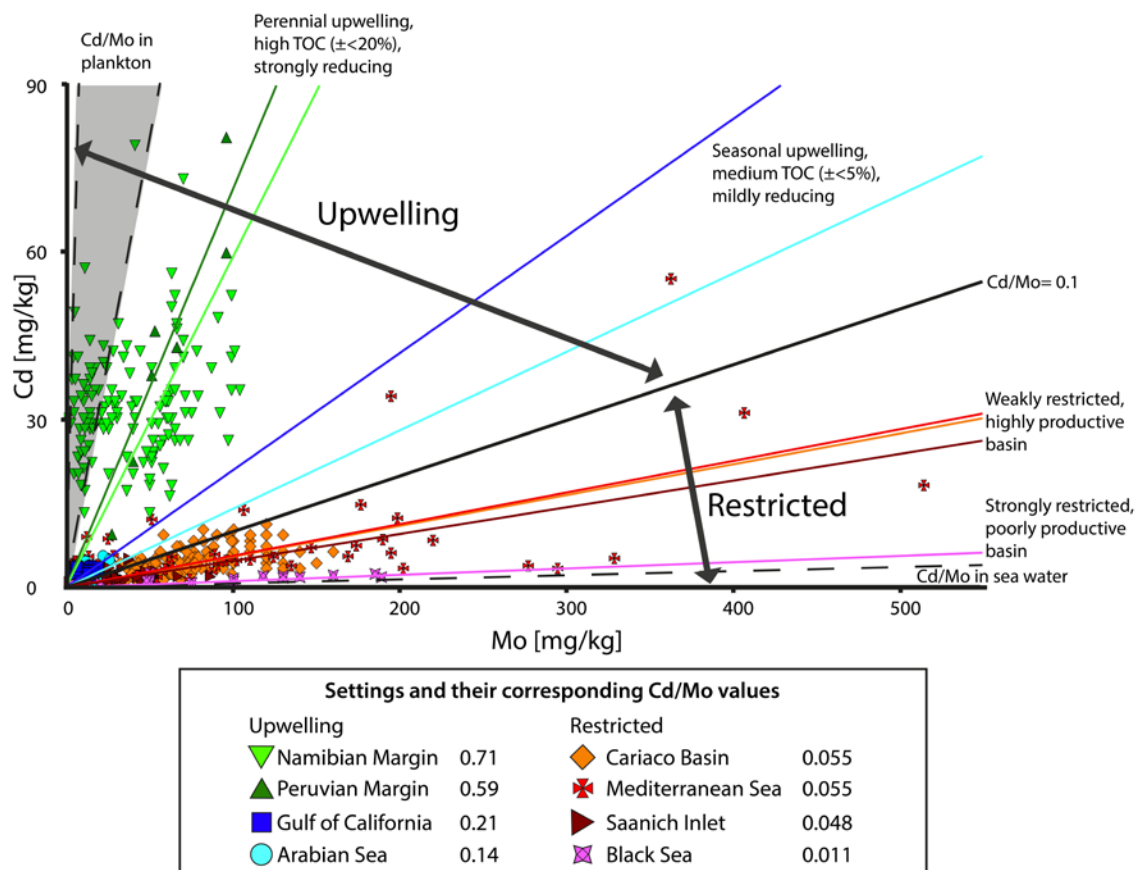


Figure 4. Mo versus Cd plot showing linear regressions forced through the origin for the dataset of each individual setting (see table 4 for literature sources). Cd/Mo ratios for plankton (Brumsack, 1986) and average seawater (Tribouillard et al., 2006) are included for comparison.

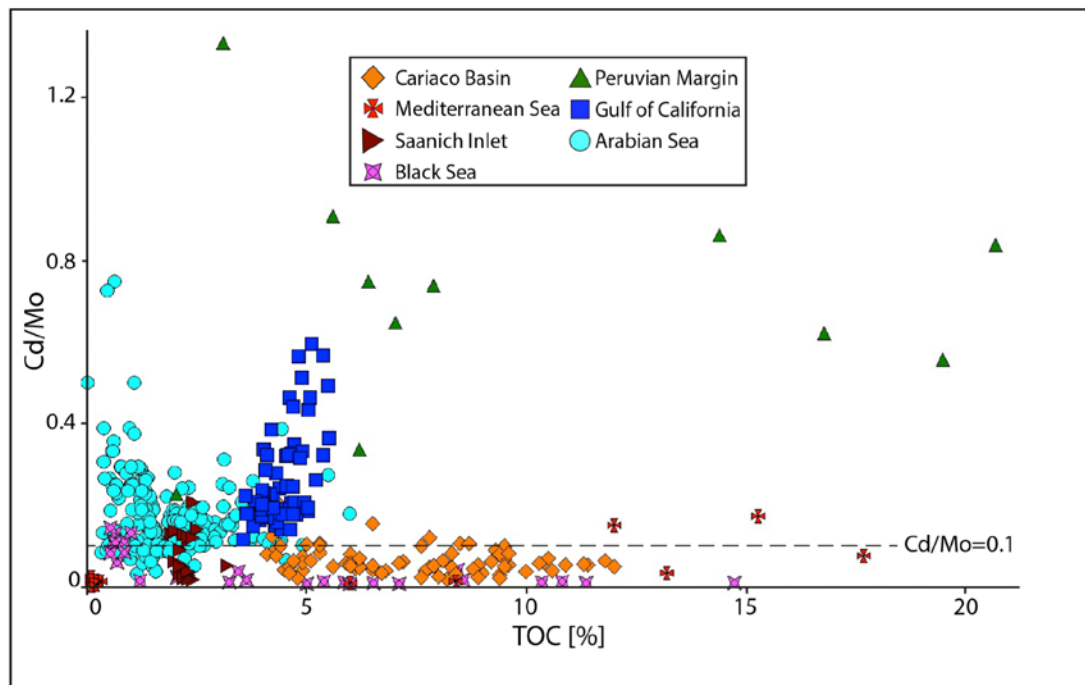


Figure 5. Cd/Mo ratios versus TOC content (wt%). A cut-off value of $Cd/Mo \sim 0.1$ is proposed for the distinction between upwelling settings (>0.1) and hydrographically restricted settings (<0.1). Caution needs to be exercised with applying this cut-off value to sediments with low TOC, Cd and/or Mo enrichments (see text for explanation). Note that Cariaco Basin samples with Mo concentrations <5 mg/kg were excluded from this figure because precision of the reported data (rounded to mg/kg) is deemed insufficient for the use in ratios. Namibian margin sediments are not shown because TOC data was not reported. Literature sources are given in table 4.

5.2 Cobalt and Manganese

Cobalt and Mn show similar distribution patterns but with strong contrasts between the studied settings (Figure 3). This similarity in behaviour suggests that the enrichment/depletion of these elements in accumulating sediments is governed by similar processes. The absence of strong Co and Mn enrichments and the relatively good co-variation between Al and Co x Mn (Figure 6a) in the Cariaco Basin, Peruvian Margin and Gulf of California suggests that the Co and Mn contents in these samples are largely controlled by the presence of detrital minerals; Aluminium is used in this context as a tracer for the input of detrital minerals. In contrast, samples from the Black Sea and Baltic Sea have higher Co and Mn abundances that do not show a systematic relationship with Al, which points to authigenic enrichments of Co and/or Mn above detrital background values.

It is postulated here that the observed differences in the Co and Mn content between restricted and upwelling settings are primarily related to systematic differences in the supply of these metals to the water column. In upwelling systems the supply of nutrients including many metals is, by definition, largely driven by upwelling of deeper oceanic waters that are typically depleted in Co and Mn (Figure 1). As a result, the authigenic enrichment of Co and Mn in sediments underlying upwelling zones is limited due to insufficient (re-)supply of Co and Mn. In hydrographically restricted basins, on the other hand, the supply of Co and Mn is dominated by the influx of Co- and Mn-rich (Table 1) river waters and these settings are thus less likely to develop to a stage where authigenic enrichments are limited by supply. The remarkably low Co and Mn contents of the Cariaco Basin sediments when compared to e.g. the Black Sea may be attributed to similar processes as dissolved Mn contents are relatively low in the Cariaco Basin (Little et al., 2015 and references therein). Strong seasonal upwelling and sub-thermocline inflow of what are likely to be relatively Co and Mn depleted waters from the Caribbean Sea into the Cariaco Basin (Lyons et al., 2003), are believed to play a role in keeping dissolved Mn and Co concentrations low and thereby limit authigenic enrichments.

Another process that probably plays an important role in preventing Mn enrichments in upwelling settings is the so-called Mn conveyor belt (Brumsack, 2006). This “Mn-conveyor belt” is driven by changes in the redox state of Mn, which forms insoluble Mn(IV) compounds in the presence of oxygen but is soluble and mobile under oxygen deficient conditions (e.g. Calvert and Pedersen, 1993; Tribovillard et al., 2006 and references therein). As a result, Mn (oxyhydr)oxide particles that form in oxic surface waters or that are delivered to surface waters by dust particles from wind and/or river activity, are dissolved when they settle through the OMZ. This remobilized Mn is then transported away to the open ocean. In the stratified and anoxic/euxinic waters of restricted basins Mn will predominantly exist in its soluble reduced form, and high dissolved Mn concentrations typically exist below the chemocline (Tribovillard et al., 2006 and references therein). Since restricted settings have sensu-stricto limited exchange with the open ocean, this dissolved load of Mn is trapped within the basin waters. Without a significant efflux of Mn, the concentrations can build up in the anoxic water mass and eventually lead to authigenic enrichment when the saturation threshold for Mn incorporating minerals is reached. Although the fundamentals of Co cycling in the water column are much less well understood, the observed similarities between Co and Mn suggest that similar processes control Co incorporation into the sediments. This can explain low enrichments of Co in upwelling settings even if surface waters are fed by intermediate waters with relatively high dissolved Co loads (Böning et al., 2004; Dulaquais et al., 2014).

The combined effects of the conveyor belt principle and differences in supply are believed to cause the observed differences in Co and Mn contents between the two end-member settings. Additional factors that may play a role and amplify or obscure the observed trends are incorporation of these metals into pyrite and/or the formation of sulphides and oxides. However, these processes are not believed to exert the dominant control over the observed abundance variations. For example, the Cariaco Basin features similarly reducing conditions as the other restricted basins but yet displays much lower Co and Mn abundances. The relative enrichments of Co and Mn in the Arabian Sea when compared to the other upwelling settings may be related to (seasonally driven)

enrichments of Mn (oxyhydr)oxides due to a less pronounced OMZ. A final cautionary note is warranted for settings with detrital input from (ultra)mafic rocks that are exposed in the hinterland, given considerable enrichments of Co (and other trace metals) in these rocks (e.g. Zhou et al., 2004).

Although the use of trace metal ratios is preferred over absolute concentrations because it removes possible dilution effects, no metal ratios including Co or Mn could be established that allowed a distinction between the settings that was as clear as with the Co*Mn parameter. The cut-off value that distinguishes between the two end-member settings is not as clearly defined as for the Cd/Mo proxy, but restricted settings typically show Co*Mn values in excess of 0.4 and upwelling settings below 0.4 (Figure 3 and 6a). Enrichment factors have the benefit of removing the effects of both detrital contributions and dilution, but Al data (used for normalization) is not available for all settings. Nevertheless, comparison between the enrichment factors and concentrations with different Al-abundances (Figure 6) suggests that the contribution from detrital minerals and dilution is not the primary driver for the observed differences between the end-member settings. This justifies the use of the non-normalised values further on in this study, which allows the inclusion of more data. However, it is stressed that the use of enrichment factors or (Al-)normalised values is generally preferred, to correct for any dilution effects that may explain smaller scale variations within the end-member settings, with $EF(Mn)*EF(Co) > 2$ being characteristic for restricted basins and <0.5 for upwelling settings (Figure 6b).

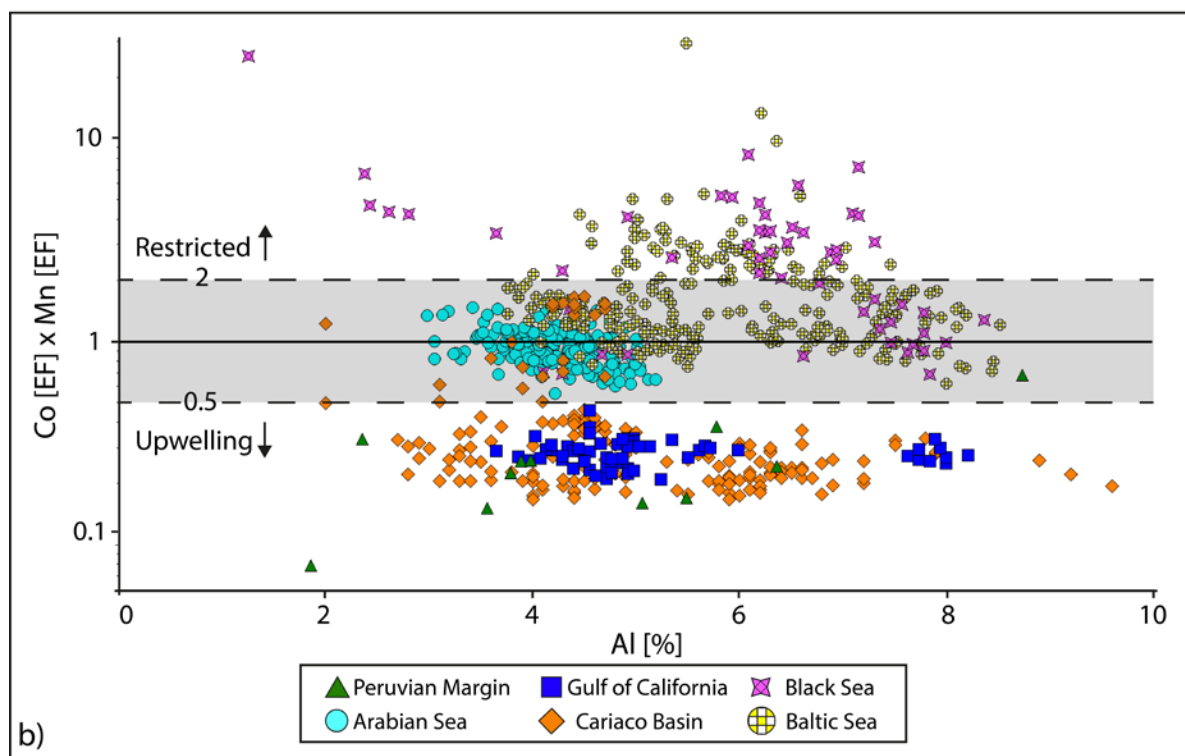
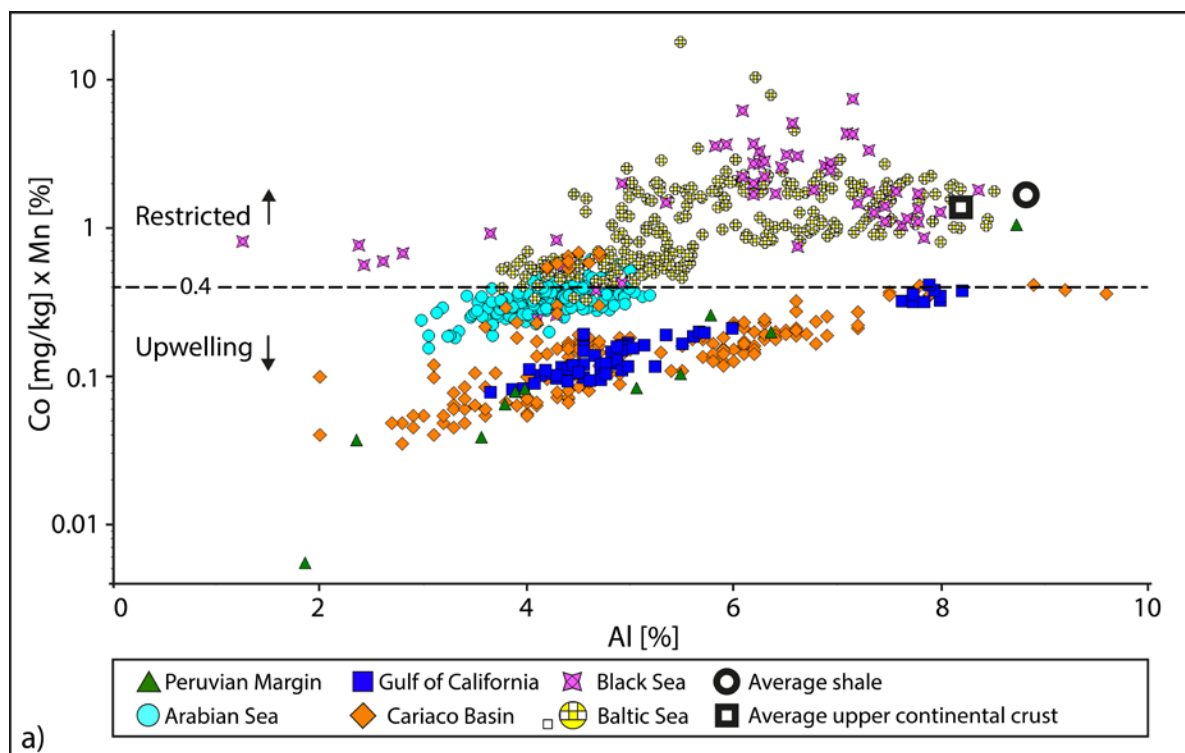


Figure 6. (a) Co x Mn versus Al. A cut-off value of ~ 0.4 is proposed for the distinction between upwelling (<0.4) and restricted settings (>0.4). (b) Co [EF] x Mn [EF] versus Al. References are given in table 4. Note that data from the Namibian Margin cannot be shown because no Al concentrations were reported.

*5.3 The combined use of the Cd/Mo and Co*Mn proxy*

The combined use of the Cd/Mo and Co*Mn proxy is proposed here as a novel and highly effective way to distinguish different marine environments that are prone to organic-rich sediment formation (Figure 7a). The Black Sea represents the most strongly restricted and euxinic basin on the modern earth and organic-rich sediments from this basin plot consistently in the bottom right corner of the Cd/Mo versus Co*Mn diagram. The high Co*Mn values are consistent with the restricted nature of the basin and the associated long deep-water renewal times. The enrichments suggest a relatively high supply of Co and Mn from river waters, whereas the supply of metal-depleted deep oceanic waters is subordinate. The strongly stratified water column and slow bottom water renewal rates lead to the formation of euxinic bottom waters that, together with relatively low bulk sediment and organic carbon accumulation rates, classify the Black Sea as the type example of a system that is driven by preservation rather than productivity, which is consistent with the low Cd/Mo values.

On the other end of the spectrum are the Peruvian and Namibian Margin sediments that serve as end-members for highly productive upwelling settings. These settings are both characterized by perennial upwelling and very high primary productivity rates and high sedimentary organic carbon enrichments. Samples from these settings consistently plot in the upper left corner of the Cd/Mo versus Co*Mn diagram with elevated Cd/Mo ratios caused by enhanced primary productivity and low Co*Mn values related to water column dynamics. The other settings have more intermediate Cd/Mo ratios and Co*Mn values because of their hybrid nature (e.g. Cariaco Basin featuring both upwelling and restriction) or occasional oxygenation events (e.g. Arabian Sea) that would limit the enrichments of Cd and Mo and possibly allows the precipitation of Mn-oxide complexes.

Some of the scatter in Figure 7a may be attributed to temporal and/or spatial variability in the different datasets. This is illustrated in Figure 7b where the dataset is filtered based on the spatial and temporal constraints explained in section 3.3 and which results in a much sharper distinction between the different hydrographic regimes. Alternatively, the dataset can be filtered using well-established environmental constraints. For example, Scott and Lyons (2012) proposed that sediments with Mo>25 mg/kg are at least occasionally euxinic. It is interesting to note that the scatter is again significantly reduced when the data is filtered to only include the most reducing sediments for the different settings (i.e. Mo>25 mg/kg). It shows that (short-lived) oxygenation events may partly obliterate the observed patterns and that such a filtering approach may prove useful for the identification of ancient end-member settings (see below).

5.4 Application to ancient settings

The current study is meant to provide a framework for the use of the proposed proxies as palaeo-environmental indicators, but direct application to ancient settings is beyond the scope of this study. It is recognized that diagenetic and catagenetic processes may alter or obscure primary signals and that spatial and temporal variability in climatic conditions, trace metal budget of the oceans, marine ecology and/or hydrothermal/volcanic activity could all affect to variable degrees the metal proxies and their interpretation. Variations in past seawater metal concentrations are of specific concern as it has been shown to affect authigenic enrichment (e.g. Algeo and Lyons, 2006 and 2007 for Mo) especially during periods of widespread oceanic anoxia when global trace metal inventories were reduced (e.g. Algeo, 2004). Despite these complications, it is believed that the process-based understanding put forward in this study and the notion that the same underlying processes will likely have played a role in the deposition of organic-rich sediments in the geological past, holds promise for the application of these proxies in palaeo-environmental reconstructions.

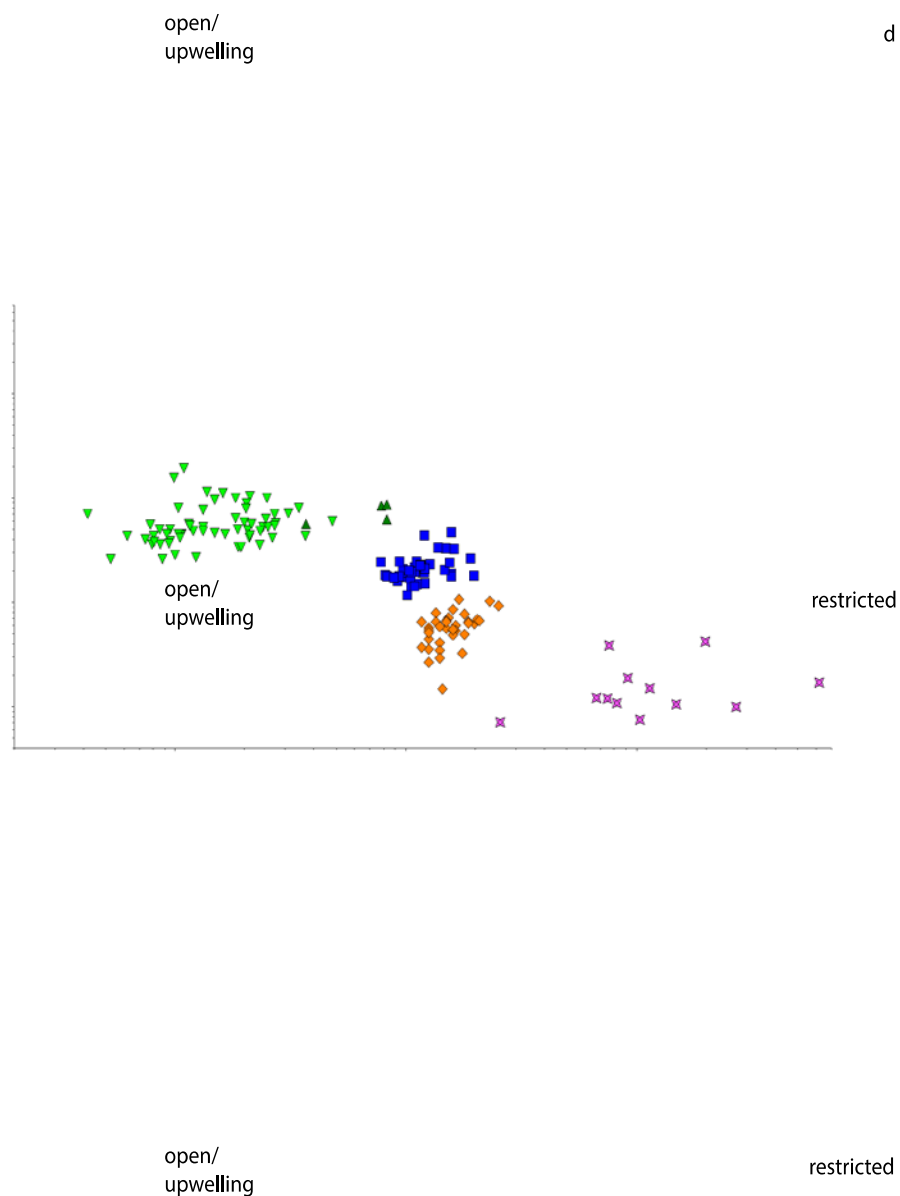


Figure 7. Distinction between end-member settings based on the proposed Cd/Mo and Co*Mn proxies. The position of the lines (productivity-preservation and deep water – river dominated) are meant to provide approximate boundaries between the different settings (see text for discussion). (a) All samples from the database included; (b) Only samples included that meet the temporal and spatial constraints outlined in section 3.3; (c) Only samples included that contain Mo >25 mg/kg, since this is thought to be indicative of at least occasionally euxinic conditions (Scott and Lyons, 2012).

6. Conclusion

This study presents a comprehensive database of trace metal concentrations in organic-rich sediments from modern/recent marine environments. It demonstrates that sedimentary Cd/Mo ratios show conspicuous differences between continental margin upwelling settings and hydrographically restricted basins. These empirical observations are attributed to the relative enrichment of Cd in upwelling settings through enhanced primary productivity and the associated biological uptake and transport of Cd to the sediment. In contrast, in basins with hydrographically restricted water masses and/or lower primary productivity rates, sedimentary Cd/Mo compositions approach the seawater composition due to effective removal of both Cd and Mo under strongly reducing conditions. The Cd/Mo proxy is thus believed to track the relative importance of organic carbon production in the water column through primary productivity versus organic matter preservation in the sediment through restricted deep-water ventilation.

A second parameter that was observed to show pronounced differences between sediments from upwelling and restricted settings is the Co*Mn proxy, with elevated values being characteristic of sediments from restricted basins. Although Mn is considered to be mobile under anoxic conditions, the limited exchange between restricted water masses and the open ocean in combination with the continuous influx of Mn and Co through rivers and/or dust particles allows concentrations to build up in the water column, which will ultimately lead to authigenic enrichment. Conversely, the main source of metals in open marine continental margin is the upwelling of deep oceanic waters that are relatively depleted in Mn and Co. In addition, more hydrographically exposed locations allow and facilitate the transportation of remobilized Mn (and Co) to the open ocean through the so-called “conveyor belt” principle, which prevents enrichments in the organic-rich sediments.

The combination of the Cd/Mo and Co*Mn elemental proxies has the potential to be a valuable tool for reconstructing environmental conditions that prevailed during deposition of organic-rich sediments in the past. The results presented here are based on modern/recent settings and the empirically defined cut-off values may need adjustment for the study of ancient settings as the result of diagenetic/catagenetic modifications and/or temporal changes in the trace metal budget of the oceans. However, because the proxies are rooted in the distinct geochemical behaviour of the different elements under differing environmental conditions, it is likely that relative differences will allow similar deconvolution exercises of palaeo-environmental settings.

Acknowledgements

We thank Olaf Podlaha for helpful discussions and Nicolas Tribovillard, Thomas Algeo and an anonymous reviewer for their useful comments. Financial support was provided by Shell.

References

- Algeo, T. J. (2004). "Can marine anoxic events draw down the trace element inventory of seawater?" *Geology* 32(12): 1057-1060.
- Algeo, T. J. and T. W. Lyons (2006). "Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions." *Paleoceanography* 21(1).
- Algeo, T. J., T. W. Lyons, R. C. Blakey and D. J. Over (2007). "Hydrographic conditions of the Devonian–Carboniferous North American Seaway inferred from sedimentary Mo–TOC relationships." *Palaeogeography, Palaeoclimatology, Palaeoecology* 256(3): 204-230.
- Algeo, T. J. and J. B. Maynard (2004). "Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems." *Chemical geology* 206(3): 289-318.
- Algeo, T. J. and N. Tribovillard (2009). "Environmental analysis of paleoceanographic systems based on molybdenum–uranium covariation." *Chemical Geology* 268(3): 211-225.
- Arnaboldi, M. and P. A. Meyers (2007). "Trace element indicators of increased primary production and decreased water-column ventilation during deposition of latest Pliocene sapropels at five locations across the Mediterranean Sea." *Palaeogeography, Palaeoclimatology, Palaeoecology* 249(3): 425-443.
- Barlow, R., T. Lamont, B. Mitchell-Innes, M. Lucas and S. Thomalla (2009). "Primary production in the Benguela ecosystem, 1999–2002." *African Journal of Marine Science* 31(1): 97-101.
- Baturin, G. (2011). "Geochemistry of sapropel in the Black Sea." *Geochemistry International* 49(5): 531-535.
- Böning, P., H.-J. Brumsack, M. E. Böttcher, B. Schmetger, C. Kriete, J. Kallmeyer and S. L. Borchers (2004). "Geochemistry of Peruvian near-surface sediments." *Geochimica et Cosmochimica Acta* 68(21): 4429-4451.
- Brongersma-Sanders, M., K. Stephan, T. Kwee and M. De Bruin (1980). "Distribution of minor elements in cores from the Southwest Africa shelf with notes on plankton and fish mortality." *Marine Geology* 37(1): 91-132.
- Bruland, K. W. (1980). "Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific." *Earth and Planetary Science Letters* 47(2): 176-198.
- Brumsack, H. J. (1986). "The inorganic geochemistry of Cretaceous black shales (DSDP Leg 41) in comparison to modern upwelling sediments from the Gulf of California." *Geological Society, London, Special Publications* 21(1): 447-462.
- Brumsack, H.-J. (1989). "Geochemistry of recent TOC-rich sediments from the Gulf of California and the Black Sea." *Geologische Rundschau* 78(3): 851-882.
- Brumsack, H.-J. (2006). "The trace metal content of recent organic carbon-rich sediments: implications for Cretaceous black shale formation." *Palaeogeography, Palaeoclimatology, Palaeoecology* 232(2): 344-361.

Calvert, S., B. Nielsen and M. Fontugne (1992). "Evidence from nitrogen isotope ratios for enhanced productivity during formation of eastern Mediterranean sapropels."

Calvert, S. and T. Pedersen (1993). "Geochemistry of recent oxic and anoxic marine sediments: implications for the geological record." *Marine geology* 113(1): 67-88.

Conway, T. M. and S. G. John (2015). "Biogeochemical cycling of cadmium isotopes along a high-resolution section through the North Atlantic Ocean." *Geochimica et Cosmochimica Acta* 148: 269-283.

Crusius, J., S. Calvert, T. Pedersen and D. Sage (1996). "Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition." *Earth and Planetary Science Letters* 145(1): 65-78.

Dulaquais, G., Boye, M., Rijkenberg, M. J. A., & Carton, X. J. (2014). "Physical and remineralization processes govern the cobalt distribution in the deep western Atlantic Ocean." *Biogeosciences*, 11(6), 1561-1580.

Emerson, S. R. and S. S. Husted (1991). "Ocean anoxia and the concentrations of molybdenum and vanadium in seawater." *Marine Chemistry* 34(3): 177-196.

Erickson, B. E. and G. R. Helz (2000). "Molybdenum (VI) speciation in sulfidic waters: stability and lability of thiomolybdates." *Geochimica et Cosmochimica Acta* 64(7): 1149-1158.

Gingele, F. X. and T. Leipe (1997). "Clay mineral assemblages in the western Baltic Sea: recent distribution and relation to sedimentary units." *Marine Geology* 140(1): 97-115.

Hirst, D. (1974). "Geochemistry of sediments from eleven Black Sea cores." In: *The Black Sea – Geology, Chemistry, and Biology*.

Huerta-Diaz, M. A. and J. W. Morse (1992). "Pyritization of trace metals in anoxic marine sediments." *Geochimica et Cosmochimica Acta* 56(7): 2681-2702.

Jenkyns, H. C. (2003). "Evidence for rapid climate change in the Mesozoic–Palaeogene greenhouse world." *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* 361(1810): 1885-1916.

Jenkyns, H. C. (2010). "Geochemistry of oceanic anoxic events." *Geochemistry, Geophysics, Geosystems* 11(3).

Kemp, A. E., R. B. Pearce, I. Koizumi, J. Pike and S. J. Rance (1999). "The role of mat-forming diatoms in the formation of Mediterranean sapropels." *Nature* 398(6722): 57-61.

Knauer, G., J. Martin and R. Gordon (1982). "Cobalt in north-east Pacific waters." *Nature* 297, 49-51

Landing, W. M. and K. W. Bruland (1980). "Manganese in the north Pacific." *Earth and Planetary Science Letters* 49(1): 45-56.

Little, S. H., D. Vance, T. W. Lyons and J. McManus (2015). "Controls on trace metal authigenic enrichment in reducing sediments: Insights from modern oxygen-deficient settings." *American Journal of Science* 315(2): 77-119.

Lyons, T. W., J. P. Werne, D. J. Hollander and R. Murray (2003). "Contrasting sulfur geochemistry and Fe/Al and Mo/Al ratios across the last oxic-to-anoxic transition in the Cariaco Basin, Venezuela." *Chemical Geology* 195(1): 131-157.

McLennan, S. M. (2001). "Relationships between the trace element composition of sedimentary rocks and upper continental crust." *Geochemistry, Geophysics, Geosystems* 2(4).

Meier, H. M. (2006). "Baltic Sea climate in the late twenty-first century: a dynamical downscaling approach using two global models and two emission scenarios." *Climate dynamics* 27(1): 39-68.

Menzel, D., E. C. Hopmans, P. F. van Bergen, J. W. de Leeuw and J. S. S. Damsté (2002). "Development of photic zone euxinia in the eastern Mediterranean Basin during deposition of Pliocene sapropels." *Marine Geology* 189(3): 215-226.

Morford, J., A. Russell and S. Emerson (2001). "Trace metal evidence for changes in the redox environment associated with the transition from terrigenous clay to diatomaceous sediment, Saanich Inlet, BC." *Marine Geology* 174(1): 355-369.

Morford, J. L. and S. Emerson (1999). "The geochemistry of redox sensitive trace metals in sediments." *Geochimica et Cosmochimica Acta* 63(11): 1735-1750.

Muller - Karger, F., R. Varela, R. Thunell, M. Scranton, R. Bohrer, G. Taylor, J. Capelo, Y. Asto, E. Tappa and T. Y. Ho (2000). "Sediment record linked to surface processes in the Cariaco Basin." *Eos, Transactions American Geophysical Union* 81(45): 529-535.

Nakagawa, Y., S. Takano, M. L. Firdaus, K. Norisuye, T. Hirata, D. Vance and Y. Sohrin (2012). "The molybdenum isotopic composition of the modern ocean." *Geochemical Journal* 46(2): 131-141.

Nijenhuis, I., H.-J. Bosch, J. S. Damsté, H.-J. Brumsack and G. De Lange (1999). "Organic matter and trace element rich sapropels and black shales: a geochemical comparison." *Earth and Planetary Science Letters* 169(3): 277-290.

Nixon, S. and A. Thomas (2001). "On the size of the Peru upwelling ecosystem." *Deep Sea Research Part I: Oceanographic Research Papers* 48(11): 2521-2528.

Nozaki, Y. (1997). "A fresh look at element distribution in the North Pacific Ocean." *EOS Transactions* 78: 221-221.

Passier, H. F., H.-J. Bosch, I. A. Nijenhuis, L. J. Lourens, M. E. Böttcher, A. Leenders, J. S. S. Damsté, G. J. de Lange and J. W. Leeuw (1999). "Sulphidic Mediterranean surface waters during Pliocene sapropel formation." *Nature* 397(6715): 146-149.

Pattan, J. and N. Pearce (2009). "Bottom water oxygenation history in southeastern Arabian Sea during the past 140ka: Results from redox-sensitive elements." *Palaeogeography, Palaeoclimatology, Palaeoecology* 280(3): 396-405.

Paulmier, A. and D. Ruiz-Pino (2009). "Oxygen minimum zones (OMZs) in the modern ocean." *Progress in Oceanography* 80(3): 113-128.

Piper, D. Z. and S.E. Calvert (2009). "A marine biogeochemical perspective on black shale deposition." *Earth-Science Reviews* 95: 63-96.

Piper, D. Z. and W. E. Dean (2002). Trace-element deposition in the Cariaco Basin, Venezuela Shelf, under sulfate-reducing conditions: A history of the local hydrography and global climate, 20 ka to the present, US Geological Survey.

Presley, B., Y. Kolodny, A. Nissenbaum and I. Kaplan (1972). "Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia—II. Trace element distribution in interstitial water and sediment." *Geochimica et Cosmochimica Acta* 36(10): 1073-1090.

Rheinheimer, G., K. Gocke and H.-G. Hoppe (1989). "Vertical distribution of microbiological and hydrographic-chemical parameters in different areas of the Baltic Sea." *Marine Ecology Progress Series MESED* 52(1).

Robinson, R. S., P. A. Meyers and R. W. Murray (2002). "Geochemical evidence for variations in delivery and deposition of sediment in Pleistocene light–dark color cycles under the Benguela Current Upwelling System." *Marine Geology* 180(1): 249-270.

Russell, A. and J. Morford (2001). "The behavior of redox-sensitive metals across a laminated–massive–laminated transition in Saanich Inlet, British Columbia." *Marine Geology* 174(1): 341-354.

Rydberg, L., G. Ærtebjerg and L. Edler (2006). "Fifty years of primary production measurements in the Baltic entrance region, trends and variability in relation to land-based input of nutrients." *Journal of Sea Research* 56(1): 1-16.

Sarmiento J.L. and N. Gruber (2004). "Ocean Biogeochemical Dynamics." Princeton University Press.

Scholz, F., C. Hensen, A. Noffke, A. Rohde, V. Liebetrau and K. Wallmann (2011). "Early diagenesis of redox-sensitive trace metals in the Peru upwelling area—response to ENSO-related oxygen fluctuations in the water column." *Geochimica et Cosmochimica Acta* 75(22): 7257-7276.

Scott, C. and T. W. Lyons (2012). "Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: refining the paleoproxies." *Chemical Geology* 324: 19-27.

Skei, J., D. Loring and R. Rantala (1988). "Partitioning and enrichment of trace metals in a sediment core from Framvaren, South Norway." *Marine chemistry* 23(3): 269-281.

Statham, P. J. and J. Burton (1986). "Dissolved manganese in the North Atlantic Ocean, 0–35 N." *Earth and planetary science letters* 79(1): 55-65.

Timothy, D. A. and M. Y. Soon (2001). "Primary production and deep-water oxygen content of two British Columbian fjords." *Marine Chemistry* 73(1): 37-51.

Tribovillard, N., T. J. Algeo, T. Lyons and A. Riboulleau (2006). "Trace metals as paleoredox and paleoproductivity proxies: an update." *Chemical Geology* 232(1): 12-32.

Tribovillard, N., V. Bout-Roumazeilles, T. Algeo, T. W. Lyons, T. Sionneau, J. C. Montero-Serrano, A. Riboulleau and F. Baudin (2008). "Paleodepositional conditions in the Orca Basin as inferred from organic matter and trace metal contents." *Marine Geology* 254(1): 62-72.

Van der Weijden, C. H., G.-J. Reichert and B. J. van Os (2006). "Sedimentary trace element records over the last 200 kyr from within and below the northern Arabian Sea oxygen minimum zone." *Marine geology* 231(1): 69-88.

Vorlicek, T. P., M. D. Kahn, Y. Kasuya and G. R. Helz (2004). "Capture of molybdenum in pyrite-forming sediments: role of ligand-induced reduction by polysulfides." *Geochimica et Cosmochimica Acta* 68(3): 547-556.

Wedepohl, K. (1971). "Environmental influences on the chemical composition of shales and clays." *Physics and Chemistry of the Earth* 8: 305-333.

Yunev, O. (2011). "Eutrophication and annual primary production of phytoplankton in the deep-water part of the Black Sea." *Oceanology* 51(4): 616-625.

Zhou, J., X. Wang, J. Qiu and J. Gao (2004). "Geochemistry of Meso- and Neoproterozoic mafic-ultramafic rocks from northern Guangxi, China: Arc or plume magmatism?" *Geochemical Journal* 38(2): 139-152.