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Underestimation of the authigenic fraction of Cu and Ni in organic-rich sediments

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ABSTRACT

There are two possible techniques to estimate the degree of authigenic (or non-lithogenic) metal enrichment in sediments. First, the authigenic metal fraction can be calculated according to $M_{auth} = M_{total} - (M/Al_{background} \cdot Al_{total})$ while M is the metal of interest and Al is aluminum. Second, a metal enrichment factor (EF) is calculated according to $EF = M/Al_{total}/M/Al_{background}$. Both techniques rely on the appropriate use of the M/Al ratio of the lithogenic background. For the latter, the M/Al ratio of average shale or crust is widely applied as lithogenic background in marine geochemistry. However, as we show here, the lithogenic background based on average shale or crust is too high for Cu and Ni. As a consequence, the authigenic fraction of Cu and Ni in sediments and suspended particulate matter (SPM) is significantly underestimated as shown for examples from various environments (upwelling areas of Peru, Chile and the Gulf of California, the Norwegian Kyllaren fjord and the German Wadden Sea). By correlating Cu/Al and Ni/Al with TOC in the samples the apparent M/Al ratio of the background can be estimated. A prerequisite for this technique is high linearity and high quality of correlation ($r^2 \geq 0.8$) otherwise the lithogenic background cannot be exactly determined. The resulting higher authigenic level of Cu and Ni may promote their use as productivity indicators while the status of Cu and Ni may shift from moderately to highly enriched when the enrichment is assessed via EFs.

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1. Introduction

Copper and Ni exhibit typical dissolved nutrient profiles in the open ocean and relatively high concentrations in plankton indicating their involvement in biological cycling (see compilation in Bruland and Lohan, 2003). Both metals are enriched in reducing organic-rich sediments where they are significantly correlated with the amount of total organic carbon (TOC). Further, studies from modern and ancient settings suggested that Cu and Ni are brought to the marine sediment with settling biodetritus from surface waters, either adsorbed onto biodetrital surfaces or incorporated into soft tissue of plankton (e.g. Calvert and Price, 1983; Brumsack, 1989; Algeo and Maynard, 2004; Van der Weijden et al., 2006).

However, in contrast to metals with a low lithogenic fraction (like Cd, Mo, Re and U) Cu and Ni are less used for environmental reconstructions. Either their modes of enrichment in the sediment are less clear or their lithogenic fraction was interpreted to be too high masking an enrichment of these metals (e.g. Nameroff et al., 2002; Böning et al., 2009). The latter may notably be the case in reducing sediments with rather low organic matter (OM) contents. An example for this is the sediments of south-central Chile at 36°S (Böning et al., 2009). These authors found that the measured metal/Al ratio of river SPM was much lower than that of average shale, crust or

the major local rock type (andesite) used as proxy for the lithogenic metal fraction. Hence, the calculation of the authigenic metal fraction did no longer yield negative values, which was oceanographically more consistent. The problem of negative authigenic metal fractions was already discussed, e.g. for sediments off West Mexico (Nameroff et al., 2002). Further, the interpretation of Cu and Ni data for sediments off West India (Agnihotri et al., 2008) would also benefit from precise knowledge of the lithogenic background.

Here a simple approach is shown to better extract information on the "true" lithogenic metal background, based on the correlation between the M/Al ratio and TOC. A similar approach was done to determine enrichment modes of several metals in black shales (Algeo and Maynard, 2004). However, in this study a variety of recent materials with even rather low OM is used (TOC values from 0.5 to 11 wt.%). It becomes apparent that the use of average shale or crust as proxy for the lithogenic background of Cu and Ni is inappropriate, and that the authigenic fractions of Cu and Ni may indeed be much higher.

2. Material and methods

The sediment material chosen is a typical continental margin sediment (i.e. fine-grained diatom-bearing silty clays with TOC contents below 15 wt.% and carbonate and opal contents less than 20 wt.%). The normalization of components to Al has two advantages: (i) dilution issues are eliminated given the problem that variable amounts of (metal-free) carbonate or opal may control metal variability, and

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(ii) enrichment (or depletion) can be assessed by comparing the M/Al ratio of the samples with the M/Al ratio of the lithogenic background.

The Peru–Chile system and the Gulf of California (GoC) exhibit considerable preservation of organic-rich detritus and metals in the underlying sediments (e.g. Brumsack, 1989; Böning et al., 2004, 2005; Niggemann et al., 2007). Off Peru, data are from six short cores (published in Böning et al., 2004) and from one long core (Table 1) distributed along the shelf from 10° to 12°S at the upper edge of the oxygen minimum zone (OMZ) to cover the full spatial influence of the hinterland lithology. The six short cores cover the last ~100 years (Böning et al., 2004) while the long core comprises pre-industrial sediments (shale-like Pb/Al ratios of $\sim 2.5 \cdot 10^{-4}$). Off south-central Chile, data are from three short cores in part within the OMZ (published in Böning et al., 2009) also covering the last 100 years (Niggemann et al., 2007) (Table 1). For the GoC, unpublished data are from several surface sediments above and within the OMZ, the latter of which is in 400–800 m water depth (Table 1). The age of these sediments is unknown however, assumed to be recent at sampling time.

The Jade Bay is a large tidal inlet in the seasonally productive German Wadden Sea where water masses from the southern North Sea prevail during high tide over local water masses (Götschenberg and Kahlfeld, 2008; Böning and Schnetger, 2011). In general, the particles from the sampled surface waters from the Jade Bay are dominated by the fine fraction. Sediment analyses from traps deployed in different water depths of the Jade Bay point to fine material likely imported from the southern North Sea (Gerd Liebezeit, ICBM, unpublished data). Metal and TOC data (unpublished) are from water column particles taken during low and high tide in July 2010 at a fixed station close to tidal flats in the southern Jade Bay (Böning and Schnetger, 2011; Table 1).

The 29 m deep Kyllaren fjord is located on the west coast of Norway, connected with the Norwegian Sea by a narrow channel, and is sulfidic below 4 m (see Fig. 1 in Smittenberg et al., 2004). Data are presented from two cores taken in 2009 in 10 and 29 m water depth (Table 1).

Freeze-dried and ground sediment was mixed with Li-tetraborate to produce glass beads measured with a Philips X-ray spectrometer PW 2400 for Al, Ni, Cu (and Pb) (Böning et al., 2004). Particulate contents of Al, Ni, Cu (and Pb) were determined by filtering Jade Bay water samples through 0.45 μm polycarbonate filters, total digestion of the filters with concentrated HNO_3–HF–$HClO_4$ (Dellwig et al., 2007) and measurement of the resulting solutions using a Thermo iCap 5000 ICP-OES. To determine TOC on particles water samples were filtered through 0.7 μm glass filters. TOC in sediments and on particles was determined according to Böning et al. (2004) and Dellwig et al. (2007), respectively, using Eltra and UIC elemental analyzers. Overall analytical precision and accuracy were ascertained using internationally certified reference and in-house materials, and were typically better than 3% for Al and TOC and better than 8% for Cu and Ni. All data were corrected for pore water salt contribution. TOC contents were not determined for the cores from the Kyllaren fjord, however, typically increase from 7 to 11 wt.% downcore in sediments close to those of this study (e.g. Station 2 in Smittenberg et al., 2004). According to these authors the upper 50 cm corresponds to ~400 years.

All data presented here can be made available upon request.

3. Results and discussion

3.1. Low lithogenic background in Cu and Ni

The correlation between the M/Al ratio and TOC helps to extract information on the "true" lithogenic metal background. As we show for the sediments and water column particles of this study, Al-normalized Cu and Ni are significantly correlated with TOC ($r^2 \geq 0.8$; Fig. 1). Variations in the slope of the regression line suggest different proportions of lithogenic and authigenic metals in addition to possible (but rather low) dilution effects on TOC (see sections below). High linearity of each of the correlations suggests that the depositional processes and diagenetic overprints affect OM and metals in a similar way. The y-axis intercept of the regression line indicates the M/Al ratio of the apparent lithogenic background (Fig. 1, Table 2). The latter should have zero TOC contents assuming negligible contribution of terrestrial OM. This is indeed the case since $\delta^{13}C$ and C/N ratios suggest that OM is essentially of marine origin off Peru and Chile (Niggemann and Schubert, 2006; Niggemann et al., 2007), in the GoC (Garcia-Parmenes et al., 2011) and the Jade Bay (A. Klugkist, ICBM, pers. comm.). By contrast, OM in Kyllaren fjord sediments contains considerable amounts of refractory terrestrial origin (Smittenberg et al., 2004), which neither directly nor indirectly, lead to metal enrichments.

Table 1
Summary of sampling sites.

Site	Latitude	Longitude	Material	Water depth (m)	Sampling technique
Peru					
126MC	13°30.86 S	76°16.97	Sediment	85	Multi-corer[a]
2MC	11°34.97 S	77°33.08	Sediment	86	Multi-corer[a]
5MC	11°56.95 S	77°18.04	Sediment	96	Multi-corer[a]
29MC	10°03.28 S	78°17.10	Sediment	102	Multi-corer[a]
120MC	12°50.77 S	76°42.06	Sediment	115	Multi-corer[a]
96SL	11°01.52 S	77°52.41	Sediment	127	Gravity core[b]
Chile					
GeoB 7161	36°25.51 S	73°23.32	Sediment	126	Multi-corer[a]
GeoB 7160	36°02.33 S	73°04.39	Sediment	376	Multi-corer[a]
GeoB 7163	36°25.55 S	73°35.71	Sediment	536	Multi-corer[a]
Gulf of Calif.					
E series[c]	28°10.9 N	111°22.5	Sediment	220–630	Grab sampler[a]
F series[c]	26°10.0 N	109°41.0	Sediment	320–433	Grab sampler[a]
H	25°33.5 N	110°40.6	Sediment	835	Grab sampler[a]
I series[c]	25°47.4 N	111°00.0	Sediment	720–760	Grab sampler[a]
Kyllaren					
Kyll09-1	61°22.0 N	5°6.37	Sediment	10	Single shortcorer[a]
Kyll09-3	61°22.2 N	5°6.23	Sediment	29	Single shortcorer[a]
Wadden Sea					
Jade2010-V12	53°28.2 N	8°13.3	SPM	Surface	PE bucket

[a] 0–50 cm sediment depth.
[b] 0–350 cm sediment depth.
[c] Collection of surface samples centered around given geographical position.