Copper isotope signatures in modern marine sediments

Journal Article**Author(s):**

Little, Susan H.; Vance, Derek; McManus, James; Severmann, Silke; Lyons, Timothy W.

Publication date:

2017-09-01

Permanent link:

<https://doi.org/10.3929/ethz-b-000191704>

Rights / license:

[Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International](#)

Originally published in:

Geochimica et Cosmochimica Acta 212, <https://doi.org/10.1016/j.gca.2017.06.019>

Funding acknowledgement:

153087 - Understanding the oceanic cycling of trace metal micronutrients (SNF)

Copper isotope signatures in modern marine sediments

Susan H. Little^{a*}, Derek Vance^b, James McManus^c, Silke Severmann^d, Timothy W. Lyons^e

*corresponding author: s.little@imperial.ac.uk
+44 (0) 20 759 47358

^a Department of Earth Science and Engineering, Royal School of Mines, Imperial College London, London SW7 2BP, U.K.

^b Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, Clausiusstrasse 25, 8092 Zürich, Switzerland.

^c Bigelow Laboratory for Ocean Sciences, 60 Bigelow Drive, P.O. Box 380, East Boothbay, Maine 04544, USA.

^d Department of Marine and Coastal Science, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08901-8521, USA.

^e Department of Earth Sciences, University of California, Riverside, USA.

timothy.lyons@ucr.edu

Abstract

The development of metal stable isotopes as tools in paleoceanography requires a thorough understanding of their modern marine cycling. To date, no Cu isotope data has been published for modern sediments deposited under low oxygen conditions. We present data encompassing a broad spectrum of hydrographic and redox regimes, including continental margin and euxinic (sulphide-containing) settings. Taken together with previously published data from oxic settings, these data indicate that the modern oceanic sink for Cu has a surprisingly homogeneous isotopic composition of about +0.3‰ ($\delta^{65}\text{Cu}$, relative to NIST SRM 976). We suggest that this signature reflects one of two specific water-column processes: (1) an equilibrium isotope fractionation between soluble, isotopically heavy, Cu complexed to strong organic ligands and an isotopically light pool sorbed to particles that deliver Cu to the sediment, or (2) an equilibrium isotope fractionation between the same isotopically heavy ligand-bound pool and the particle reactive free Cu^{2+} species, with the latter being scavenged by particulates and thereby delivered to the sediment. An output flux of about +0.3‰ into sediments is isotopically light relative to the known inputs to the ocean (at around +0.6‰) and the seawater value of +0.6 to +0.9‰, suggesting the presence of an as yet unidentified isotopically light source of Cu to the oceans. We hypothesize that this source may be hydrothermal, or may result from the partial dissolution of continentally derived particles.

1. Introduction

Copper (Cu) is biologically essential, but the free Cu^{2+} form is also toxic, even at extremely low concentrations (e.g., Moffett and Brand, 1996). Aqueous Cu speciation is, however, almost universally dictated by complexation to strong organic ligands (e.g., Elderfield, 1981; Coale and Bruland, 1988; Gordon et al., 1996; Skrabal et al., 1997; 2000; Wells et al., 1998; Muller et al., 2001; Laglera and van den Berg, 2003; Shank et al., 2004a; 2004b; Bruland and Lohan, 2003; Moffett and Dupont, 2007). In addition to its biological function, Cu is particle reactive, and its speciation and solubility are sensitive to changes in redox conditions. Understanding the balance of these competing processes in controlling the oceanic distribution of Cu and its isotopes has been the subject of a large number of studies (e.g., Boyle et al., 1977; Bruland, 1980; Saager et al., 1992; Bermin et al., 2006; Vance et al., 2008; Thompson et al., 2014; Takano et al., 2014; Little et al., 2014a,b).

Isotopes provide insight into the mechanisms of metal cycling, with specific isotope signatures attributable to particular processes (e.g., Welch et al., 2003; Barling and Anbar, 2004; Severmann et al., 2008; Wasylenki et al., 2011; Peacock and Moon, 2012; Xue et al., 2013; Little et al., 2014b; Vance et al., 2016a). Isotopic measurements are also a useful way to place constraints on oceanic mass balance (e.g., Zhu and Macdougall, 1998; Schmitt et al., 2003; Tipper et al., 2006; 2010; Nielsen et al., 2006; Archer and Vance, 2008; Conway and John, 2014; Little et al., 2014a). Based on an analysis of the known inputs and outputs of Cu and its isotopes to the modern ocean, Little et al. (2014a) highlighted an imbalance in the oceanic budget of Cu. Assuming that the cycle is in steady state, these authors suggested the presence of an as yet unidentified isotopically heavy Cu sink (Little et al., 2014a).

No Cu isotope data exist to date for reducing sedimentary settings, making them a prime candidate for the missing Cu sink. Reducing depositional environments include locations where the water column is euxinic (sulphide-containing), such as the Black Sea and Cariaco Basin, and those in which dissolved oxygen concentrations are negligible but sulphide is either absent or restricted to pore-waters. The latter are typical of oxygen minimum zones (OMZs) along productive continental margins. Copper is insoluble under

reducing conditions. Consequently, water column removal of Cu is nearly quantitative below the redoxcline of the euxinic Black Sea and Cariaco Basin (Jacobs et al., 1987; Haraldsson and Westerlund, 1988; Tankéré et al., 2001), and variable Cu enrichments have previously been observed in reducing sediments (e.g., Francois, 1988; Calvert and Perderson, 1993; Algeo and Maynard, 2004; Brumsack, 2006; Little et al., 2015). An iron-rich (ferruginous) pore water profile from the oxygen-poor Santa Monica basin (California) shows evidence of Cu diffusion into sediments and no detectable Cu in pore waters within a few centimetres of the sediment-water interface, suggesting diagenetic removal of Cu into sedimentary sulphide phases (Shaw et al., 1990). Generally, however, there is a lack of similar pore water studies from sediment underlying anoxic ocean waters.

Reduction of Cu(II) to Cu(I) is likely to be associated with a light isotope fractionation into the reduced phase (e.g., Zhu et al., 2002; Ehrlich et al., 2004; Fujii et al., 2013, Sherman, 2013), i.e., fractionation in the opposite direction to that required for an isotopically heavy Cu sink. However, quantitative removal from the water column implies that the authigenic Cu isotope values of sediments deposited under euxinic conditions should reflect the Cu isotope composition of the dissolved pool of the oceans, as observed previously for similar metal isotope systems (e.g., Mo, Zn, Cr; Barling et al., 2001; Nägler et al., 2011; Reinhard et al., 2014; Vance et al., 2016a). The dissolved Cu pool in seawater is, indeed, isotopically heavy, at +0.6 to +0.9‰ (Vance et al., 2008; Thompson et al., 2014; Takano et al., 2014).

Euxinic sites play a relatively minor role as a global sink for trace metals in the modern ocean, however, due to the restricted areal extent of such conditions (e.g., Emerson and Huested, 1991; Morford and Emerson, 1999; Poulson Brucker et al., 2009; Little et al., 2015). Today, upwelling margins with prominent OMZs are likely a much more important sink for trace metals (e.g., Morford and Emerson, 1999; Böning et al., 2004; 2009; McManus et al., 2006; Poulson Brucker et al., 2009; Little et al., 2015; 2016), and forecasts suggest their expansion in a warming world (Stramma et al., 2008; Keeling et al., 2010). To date, only one estimate has been made of the role of upwelling margin sediments in the oceanic mass balance of Cu (Little et al., 2015), and the isotope composition of the flux of Cu into margin sediments is unknown. In this study, we present Cu isotope data for a wide range of reducing environments, including the euxinic Black Sea and Cariaco Basin, and multiple continental margin sites. This dataset provides considerably improved constraints on the reducing sedimentary sink for Cu.

2. Study sites

2.1 The Black Sea

Open ocean euxinia is thought to have been more prevalent at times during Earth's history, particularly along productive margins (Canfield, 1998; Li et al., 2010a; Lyons et al., 2014). Today, however, euxinia is largely restricted to marginal basins, with the Black Sea as the world's largest permanently euxinic basin. The Black Sea is thus frequently cited as an analogue of the Precambrian oceans and for periods of widespread anoxia during the Phanerozoic. Euxinia below ~100 m water depth in the Black Sea is the result of a positive water balance, moderate primary production, and restricted circulation, with limited inflow and outflow to the Mediterranean Sea via the narrow (0.76 – 3.6 km wide) and shallow (<110 m deep) Bosphorus Strait. Total sulphide concentrations increase to 380 μM at 2200 m water depth and are associated with near quantitative removal of Cu from the dissolved phase (Haraldsson and Westerlund, 1991; Tankéré et al., 2001). The samples analysed in this study have been described previously (Lyons, 1991; Little et al., 2015). Two deep sites underlie the euxinic water column (stations 9 and 14; Fig. 1), while two others are from the shallow shelf and underlie oxic water (stations 16 and 16B; Fig. 1). Station 16B was recovered from a depth close to the modern day chemocline. A broad array of sedimentological observations (Lyons, 1991) and complementary geochemical analyses has been made on these sediments. These include C-S-Fe systematics (Lyons and Berner, 1992; Lyons et al., 1993), S-isotope trends (Lyons, 1997), Fe speciation and isotope patterns (Lyons and Severmann, 2006; Severmann et al., 2008), Mo abundance and isotope compositions (Arnold et al., 2004; Algeo and Lyons, 2006), trace metal concentrations (Little et al., 2015) and Zn and Ni isotope analyses (Vance et al., 2016a). We present bulk sediment Cu isotope data for a total of 31 samples from the four locations, all of which are confined to the upper ~25 cm of the sediment pile at each locality (Fig. 1; see also Little et al., 2015).

2.2 The Cariaco Basin

The Cariaco Basin is the world's second largest anoxic basin (Fig. 1, Table 1). It is located on the northern continental shelf off Venezuela and contrasts with the Black Sea in that it has a less restricted hydrographic setting, higher productivity, and higher sedimentation rate. The Cariaco Basin has been euxinic since the last deglaciation (Haug et al., 1998;

Dean et al., 1999; Peterson et al., 2000), but euxinia in the water column is less extreme than that in the Black Sea, with peak total sulphide concentrations of ~65 μM (Li et al., 2010b; 2011). Again, Cu removal from the water column is observed due to the presence of sulphide (Jacobs et al., 1987). The 22 drill core samples (20 cm to 8 m depth) included in this study from ODP Site 1002 span the oxic-euxinic transition at 14.5 ka and the associated redox-related geochemical changes in the core have previously been studied in detail (Lyons et al., 2003; Werne et al., 2003; Lyons and Severmann, 2006; Reinhard et al., 2014; Little et al., 2015).

2.3 Continental Margin sites

2.3.1 California Borderland basins

The Southern California Bight is a region of elevated primary production, primarily due to coastal upwelling (e.g., Eppley, 1992; Macías et al., 2012). The resultant carbon flux to depth, in combination with related ocean circulation patterns, generates oxygen-deficient waters at depths of 200 m to 1000 m along the margin. The Southern California Borderland basins exhibit even lower oxygen contents than equivalent depths along the open margin because the silled topography restricts mixing of basin waters with surrounding seawater (e.g. Emery, 1954; Berelson, 1991). The samples used in this study come from four of the Borderland basins: Santa Barbara, Santa Monica, San Nicolas, and Tanner Basin (Fig. 1). These settings have been characterised geochemically, and samples for this study were taken from expeditions described previously (e.g., McManus et al., 1997; McManus et al., 1998; McManus et al., 2006; Poulson-Brucker et al., 2009; Little et al., 2016).

The Santa Barbara and Santa Monica basins are near shore and have sill depths within the region's OMZ. The Santa Barbara basin is the most reducing of the four Borderland basins included for study, though the core studied was sampled just below the sill (sill: 475 m, core site: 493 m; Poulson-Brucker et al., 2009). Dissolved sulphide is present to varying degrees within the shallow sediment package and has been observed at low (<15 nM) levels in the water column (e.g., Kuwabara et al., 1999; Zheng et al., 2000). These observations, coupled with the fact that the shallow pore fluids (upper 3–8 cm, with sulphide appearing below) are ferruginous (e.g., Kuwabara et al., 1999; Zheng et al., 2000), imply that iron reduction and sulphate reduction are dominant electron transfer pathways within the shallow sediment package. The mass accumulation rate in Santa

Barbara is the highest of all the sites studied (Table 1), which is largely the result of high fluxes of lithogenic material (Thunell et al., 1995).

The Santa Monica sill is at 740 m, the basin floor is at 910 m, and the sediment core was collected at 905 m. Bottom-water oxygen concentrations vary within the basin but are generally 2 - 10 μM (Berelson, 1991; Stott et al., 2000; Berelson et al., 2005; McManus et al., 2006). Like Santa Barbara basin, shallow pore fluids in Santa Monica are ferruginous (e.g., Shaw et al., 1990; McManus et al., 1997; 1998). Although Shaw et al. (1990) report a thin (~ 1 cm) layer of extractable Fe at the sediment-water boundary, transfer of dissolved Fe occurs across this boundary (McManus et al., 1997; Elrod et al., 1991; Severmann et al., 2010). To our knowledge there are no reports of shallow sediment-column or bottom-water accumulation of dissolved sulphide; net sulphate reduction is nevertheless an important pathway for electron transport, as manifest in iron sulphide minerals that form within the sediments (Berelson et al., 1996).

The offshore basins, San Nicolas and Tanner, have sill depths at 1100 m and 1160 m, respectively, below the depth of the most intense oxygen deficiency. Tanner Basin is further offshore than San Nicolas (Emery, 1960). Maximum water depths in the San Nicolas basin are 1832 m (core collected at 1750 m), with bottom-water oxygen contents of ~ 30 μM (Shaw et al., 1990). Pore fluids from the upper 10 cm are rich in dissolved Mn, with strong increases in Mn appearing just below the sediment-water interface (Shaw et al., 1990). Dissolved Fe concentrations increase below ~ 2 cm, with much lower Fe concentrations in the upper sediment package compared to those in the basins nearer to shore (Shaw et al., 1990). The Tanner Basin reaches a maximum depth of 1550 m, and the core was collected at 1514 m. Bottom water oxygen contents are ~ 30 μM . Sediments in this basin also exhibit pore fluid Fe and Mn enrichments, but the concentrations of both are lower than those in San Nicolas Basin sediments (c.f., Shaw et al., 1990; McManus et al., 1997; 1998). Despite differences in dissolved metal concentrations, these two basins are quite similar diagenetically, with Tanner having an estimated sediment depth of oxygen penetration that is slightly shallower than in San Nicolas (e.g., 0.4 vs. 0.5 cm, Berelson et al., 1996) and slightly higher total organic carbon contents (~ 6 wt% vs. ~ 4.5 wt%; Little et al., 2016).

2.3.2 Mexican Margin

Oxygen deficiency is more pronounced along the Mexican margin compared to the California margin, with oxygen concentrations of $< 1 \mu\text{M}$ at our study sites (Chong et al., 2012). This OMZ extends more than 1500 km off the coast of Mexico (Sansone et al., 2004), and anaerobic diagenetic processes dominate in sediments where the OMZ intercepts the seafloor (Berelson et al., 2005). Of the three sites included in this study, two are from the open ocean margin off Baja California (Magdalena and the Soledad Basin), and the other is from the Pescadero Slope, which is at the eastern edge of the mouth of the Gulf of California (Chong et al., 2012) (Fig. 1).

The Magdalena site is situated on the western margin of Baja California at 692 m water depth. The upper 1 - 2 cm of the sediment core is bioturbated, and organic carbon contents are particularly high ($\sim 11\%$). Dissolved sulphide appears in pore waters at 3 cm depth ($2 \mu\text{M}$) and increases rapidly at depths greater than 20 cm (Chong et al., 2012). The Soledad Basin is also on the western side of Baja California and has an effective sill depth of ~ 250 m (Silverberg et al., 2004). The core studied here was collected at 544 m water depth, close to the deepest point of the basin (545 m). Sediments at this site are laminated (including extensive traceable coccolith laminae; van Geen et al., 2003), with sulphide ($\sim 10 \mu\text{M}$) in pore waters close to the sediment-water interface and increasing below 8 cm (to $> 40 \mu\text{M}$) (Chong et al., 2012). Because of the high sulphide concentrations, dissolved iron is titrated from the pore fluids at relatively shallow depths (Chong et al., 2012). Clastic input on the open ocean side of Baja California is low, but sediment accumulation rates are high, particularly in the Soledad Basin, due to elevated productivity (Sansone et al., 2004; Table 1). Clastic input is high along the Pescadero slope, due to the location of this coring site on the eastern edge of the mouth of the Gulf of California, where it receives continental drainage from the Sierra Madre Occidental Mountains (e.g., Berelson et al., 2005; Chong et al., 2012). The laminated sediment core discussed in this study was taken at 616 m, close to the centre of the OMZ (at ~ 600 m). High concentrations of dissolved Fe have been reported from the pore waters of this site, rising from near zero to $260 \mu\text{M}$ within the first 2 cm (Chong et al., 2012), compared to peaks of $\sim 10 \mu\text{M}$ at 3 cm for the Magdalena site and a $\sim 65 \mu\text{M}$ peak in the upper 1 cm of the Soledad sediment core. Chong et al. (2012) classified the Pescadero site as Fe-rich, Magdalena as Fe-rich/sulphidic, and Soledad Basin as sulphidic.

2.3.3 Peru Margin

The Peru margin is an open ocean margin setting with high upwelling-driven productivity and an associated intense OMZ at depths of ~100 to 700 m (Emeis et al., 1991; Lückge and Reinhardt, 2000). The core used in our study (Fig. 1, see also McManus et al., 2006; Little et al., 2015; 2016) was collected at 264 m, with bottom-water oxygen concentrations of <10 μM . Bulk sediments contain ~15% organic carbon and >1% total sulphur (McManus et al., 2006; Little et al., 2016). This combination of high organic carbon and low oxygen results in intense anaerobic diagenesis, with prior work demonstrating the potential for reduced iron fluxes across the sediment water interface (Noffke et al., 2012; Scholz et al., 2014). Episodic efflux of sulphide has also been reported further south along the Peruvian margin (Schunck et al., 2013).

Figure 1. Locations of sites included for study. The Peru margin site (site MC82; Table 1; McManus et al., 2006) is from the core of the Peruvian OMZ. The California Borderland Basins (N Pacific Margin Sites inset) comprise: Barb – Santa Barbara Basin, Mon – Santa Monica Basin, Nic – San Nicolas Basin and Tan – Tanner Basin. The Mexican margin sites (N Pacific Margin Sites inset) comprise: Sol – Soledad Basin, Mag – Magdalena margin and Pesc – Pescadero Slope. The Cariaco Basin samples are from spliced cores A and B at Site 1002 of Leg 165 of the Ocean Drilling Program (see inset). Samples from four Black Sea stations were analysed: two underly the deep euxinic water column (Stations 9 and 14) and two are from the shallow oxic shelf region (Stations 16 and 16B). Maps were made using Ocean Data View software (odv.awi.de; Schlitzer, 2015).

3. Methods

3.1 Elemental concentrations and Cu isotope data

All work was carried out under trace metal clean conditions, with MilliQ water (18.2Ω) and Savillex PFA labware. Acids and reagents used were either ultrapure (HF, H₂O₂) or double distilled (HNO₃, HCl). Sample digestion and analytical methods have been described previously (Little et al., 2014a; 2015). In brief, dilute nitric acid was added dropwise to 50-500 mg of powdered sediment until effervescence ceased (signalling complete dissolution of carbonate). The sediment was then digested in a 3:1 mix of concentrated HF and concentrated HNO₃ for 48 hours. Digestion was followed by triple treatment with concentrated HNO₃ to remove fluoride salts before dissolution in 7M HCl. An aliquot of these solutions was analysed for multi-element concentrations on a ThermoFinnigan Element 2 at the University of Bristol or a ThermoFinnigan Element XR at ETH Zürich.

After elemental analysis, an aliquot of the total digest solution was taken for Cu isotope purification using a two-stage anion exchange procedure (Bio-Rad AG MP-1M resin) modified from Maréchal et al. (1999) and detailed previously (Archer and Vance, 2004; Vance et al., 2008; Little et al., 2014a). Final Cu concentrations for analysis were ~100 ppb, dissolved in ~1 ml 2% HNO₃. Isotopic analyses were carried out on a ThermoFinnigan Neptune MC-ICP-MS at the University of Bristol or a Neptune Plus at ETH Zürich, in low-resolution mode with introduction via a CPI PFA nebuliser (50 µl/min) or a Savillex C-Flow PFA nebuliser (50 µl/min) attached to a glass spray chamber. Copper isotope ratios for samples were calculated using a standard bracketing approach by comparison to pure untreated NIST SRM 976 and are reported relative to this standard in delta-notation:

$$\delta^{65}\text{Cu} = 1000 \left[\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{SRM976}}} - 1 \right]$$

The long-term reproducibility of a secondary pure Cu standard was $\delta^{65}\text{Cu} = +0.11 \pm 0.11\text{‰}$ ($n = 102$) and $+0.11 \pm 0.06\text{‰}$ ($n = 112$) at Bristol and ETH Zürich respectively, compared to $+0.10 \pm 0.06\text{‰}$ measured at the Hebrew University (Asael et al., 2007). The

USGS reference materials BHVO-2, BIR-1A, BCR-2, and Nod P1 were analysed to assess accuracy. All uncertainties are given as 2 SD, unless stated otherwise.

4. Results

Accuracy and reproducibility of measured Cu and Al concentrations for two secondary standards – the commercially available SLRS-5 river standard from the National Research Council Canada and USGS Green River Shale SGR-1 – are reported in Table 2. Note that all Cu/Al ratios are given by mass, in ppm Cu/wt % Al (i.e., $\times 10^{-4}$). Copper isotope data for USGS reference materials are reported in Table 3. Values for BHVO-2, BIR-1A and BCR-2 fall within the ranges recommended in Moynier et al. (2017). Values obtained for Nod-P1 are consistent with that reported by Bigalke et al. (2010), and with the published mean for global Fe-Mn crusts and nodules $+0.31 \pm 0.12\text{‰}$ (1SD, $n=31$; Data sources: Albarède, 2004; Little et al., 2014a).

4.1 Cu/Al ratios and Cu isotope data

Down-core Cu/Al and $\delta^{65}\text{Cu}_{\text{bulk}}$ data are presented graphically in Figures 2 – 5 and tabulated in full in the electronic supplementary material (ESM Table 1) and summarised in Table 4 (site-by-site averages). Where available, plotted isotope data are compared to mean values for proximal oxic sediments (Black Sea: oxic Station 16, Cariaco Basin: oxic section of core). In other locations, comparisons are made to the published average lithogenic Cu isotope composition ($\delta^{65}\text{Cu}_{\text{lith}} = +0.08 \pm 0.17\text{‰}$, 1 SD, $n = 334$; Moynier et al., 2017).

Aluminium is assumed to be immobile during diagenesis and is used as a tracer of the lithogenic component of the sediment. To accurately define the non-lithogenic sedimentary Cu component, measured Cu/Al ratios should ideally be compared to the Cu/Al ratio of local lithogenic background material (e.g., Böning et al., 2012; Little et al., 2015). In this study, the local background is taken as the minimum measured Cu/Al ratio from proximal oxic sediments where available (Black Sea, Cariaco Basin), following Böning et al. (2012). In the absence of an estimate for the local lithogenic background sedimentation in the California Borderland Basins, we compare Cu/Al ratios in Figure 4 with the most recent upper continental crust (UCC) estimate of 3.5×10^{-4} (Rudnick and Gao, 2003). The lithogenic background for sediments deposited close to Peru has previously been

approximated to that of a Peruvian andesite (Böning et al., 2004; Scholz et al., 2011; Little et al., 2015). A Cu/Al ratio of 4.5×10^{-4} can be calculated for average andesite from the Central Volcanic Zone of Peru (values derived from the GEOROC database of the Max-Planck Institute for Chemistry, Mainz, Germany; Sarbas and Nohl, 2009). A similar value of 4.0×10^{-4} can be calculated for a compilation of Trans Mexican Volcanic Belt samples (also derived from the GEOROC database). It is to this range of values ($4.0 - 4.5 \times 10^{-4}$) that samples from the Mexican and Peru margins are compared in Figure 5.

Elevated Cu/Al ratios compared to the (local) lithogenic background (Figures 2 – 5) are indicative of the presence of authigenic (chemically precipitated or scavenged) and/or biogenic (cellular and/or skeletal) Cu, which together are termed the ‘bioauthigenic’ fraction (after Little et al., 2016). Note that the biogenic (or uptake-derived) component of Cu in the sediment is predicted to be small (<20%; Little et al., 2015), but that scavenging of Cu by particulate organic carbon is likely an important route by which Cu is delivered to the sediment.

4.1.1 Black Sea

Cu/Al and $\delta^{65}\text{Cu}$ data for the four Black Sea sites are presented in Figure 2. Sediments from oxic Station 16 are assumed to represent the local lithogenic background sedimentation (mean Cu/Al = $5.3 \pm 0.5 \times 10^{-4}$, minimum Cu/Al = 4.8×10^{-4}). In support of this assumption, these sediments have a lithogenic Cu isotope composition with an average $\delta^{65}\text{Cu}$ of $+0.04 \pm 0.07\text{‰}$. Chemocline Station 16B shows Cu/Al ratios (mean Cu/Al = $5.7 \pm 0.9 \times 10^{-4}$) very close to those of oxic Station 16, suggesting no significant bioauthigenic enrichment, except for the two surface-most samples (Cu/Al = 6.5 and 6.1×10^{-4} at 0 – 2 cm and 2 – 4 cm respectively). However, despite dominantly lithogenic Cu/Al ratios, samples from Station 16B exhibit heavier and more variable $\delta^{65}\text{Cu}$, with an average of $+0.14 \pm 0.15\text{‰}$. The two upper-most samples (both at $+0.25\text{‰}$) again exhibit the greatest deviation from lithogenic values. The two euxinic stations 9 and 14 are indistinguishable and isotopically heavy compared to lithogenic Cu (Station 9: $+0.30 \pm 0.12\text{‰}$, Station 14: $+0.32 \pm 0.05\text{‰}$), despite slightly more elevated Cu/Al ratios at Station 9 compared to Station 14 (mean Cu/Al at Station 9 = $26.9 \pm 9.2 \times 10^{-4}$ compared to $17.6 \pm 5.5 \times 10^{-4}$ for Station 14). The mean $\delta^{65}\text{Cu}$ for all Black Sea euxinic samples is $+0.31 \pm 0.10\text{‰}$.

Figure 2. Down-core Cu/Al and bulk $\delta^{65}\text{Cu}$ data for the four Black Sea sites. Ox – Station 16, Chem – Station 16B, Eux-9 – Station 9, Eux-14 – Station 14. The local lithogenic background, which is taken as the minimum Cu/Al and mean $\delta^{65}\text{Cu}$ at oxic Station 16, is given as a dashed black line. The error bar represents 2 SD external reproducibility on Cu isotope measurements from Bristol MC-ICP-MS (0.11‰).

4.1.2 Cariaco Basin

Cu/Al and $\delta^{65}\text{Cu}$ data for the Cariaco Basin drill-core samples are presented in Figure 3. The lowermost four samples represent deposition under oxic conditions linked to the sea-level low stand of the last glacial period (Lyons et al., 2003). These four oxic samples have a lithogenic $\delta^{65}\text{Cu}$ of $+0.08 \pm 0.06\text{‰}$ and an average Cu/Al ratio of $5.2 \pm 1.0 \times 10^{-4}$, which is elevated compared to average UCC (at $3.1 - 3.5 \times 10^{-4}$). The euxinic (interglacial) sediments have a lower average Cu/Al ratio ($4.5 \pm 0.8 \times 10^{-4}$) and significantly heavier Cu isotope values compared to those deposited under oxic conditions, with a mean $\delta^{65}\text{Cu} = +0.20 \pm 0.06\text{‰}$. If the four oxic samples are assumed to represent the local lithogenic input, euxinic sediments in the Cariaco Basin show no bioauthigenic enrichment in Cu over the lithogenic background value (Fig. 3).

Figure 3. Down-core Cu/Al and bulk $\delta^{65}\text{Cu}$ data for the Cariaco Basin core. Lowermost four samples (filled stars, ‘Ox’) were deposited during the last glacial period, under oxic conditions. The remainder of the sediment core was deposited during the present interglacial, when the water column was euxinic (crosses, ‘Eux’). The grey bar represents a range of possible lithogenic Cu/Al ratios (including UCC and the local oxic minimum from the glacial period samples). The dashed line represents global mean lithogenic $\delta^{65}\text{Cu}$ (Moynier et al., 2017). The error bar represents 2 SD external reproducibility on Cu isotope measurements from ETH MC-ICP-MS (0.06‰).

4.1.3 California Borderland Basins

The most reducing of the four California Borderland sites, Santa Barbara, exhibits little or no bioauthigenic enrichment of Cu (mean Cu/Al = $4.5 \pm 0.8 \times 10^{-4}$) with $\delta^{65}\text{Cu}$ values ($\delta^{65}\text{Cu} = +0.04 \pm 0.09\text{‰}$) that are unfractionated from lithogenic values. Santa Monica Basin, which has ferruginous porewaters, exhibits higher Cu/Al ratios and slightly isotopically heavy Cu, particularly the surface-most sample (Cu/Al at 1.5 cm = 11.4×10^{-4} cf. mean Cu/Al at depths >1.5 cm = $6.5 \pm 0.3 \times 10^{-4}$; $\delta^{65}\text{Cu}$ at 1.5 cm = $+0.18\text{‰}$ cf. mean $\delta^{65}\text{Cu}$ >1.5 cm = $+0.11 \pm 0.05\text{‰}$; Fig. 4). Note that an anthropogenic source of metals has been identified at this site, and this may contribute to the enrichment observed in the surface 1 – 2 cm (Finney and Huh, 1989; Bruland et al., 1994). San Nicolas, where porewaters can be defined as manganoous, also has a surface-most sample that is isotopically heavier than the remainder of the sediment core (at $+0.31\text{‰}$ versus $+0.12 \pm 0.04\text{‰}$; Fig. 4). Copper throughout this core is significantly enriched (mean Cu/Al = $10.9 \pm 4.8 \times 10^{-4}$) relative to UCC. The most Cu enriched of the California Borderland Basin sites is Tanner Basin. Mean Cu/Al ratios at this site are $18.1 \pm 6.5 \times 10^{-4}$ and Cu is isotopically heavy compared to lithogenic Cu at $+0.24 \pm 0.06\text{‰}$.

Figure 4. Down-core Cu/Al and bulk $\delta^{65}\text{Cu}$ data for the California Borderland basins. Barb – Santa Barbara basin, Mon – Santa Monica basin, Nic – San Nicolas basin, Tan – Tanner basin. Estimates of the lithogenic background (UCC Cu/Al: Rudnick and Gao, 2003; global mean lithogenic $\delta^{65}\text{Cu}$; Moynier et al., 2017) are given as a dashed black line. Error bar represents 2 SD external reproducibility on Cu isotope measurements from ETH MC-ICP-MS (0.06‰).

4.1.4 Mexican and Peru Margins

The Peru margin exhibits the highest absolute Cu concentrations of any of the sites analysed here (up to 75 ppm). Enrichment is greatest close to the sediment surface and declines with depth (Fig. 5; mean Cu/Al = $22.6 \pm 4.2 \times 10^{-4}$). Copper isotope values at this site are homogeneous with depth and isotopically heavy compared to the lithogenic baseline ($\delta^{65}\text{Cu} = +0.32 \pm 0.07\text{‰}$; Fig. 5).

The Magdalena and Peru margin sites are similar in their Cu geochemistry. The Magdalena margin also exhibits high Cu/Al ratios ($22.1 \pm 4.4 \times 10^{-4}$) and isotopically heavy $\delta^{65}\text{Cu}$ ($+0.20 \pm 0.12\text{‰}$). By contrast, the sites of Soledad Basin (Cu/Al = $7.3 \pm 0.6 \times 10^{-4}$) and Pescadero Slope (Cu/Al = $3.0 \pm 0.2 \times 10^{-4}$) are only moderately elevated or not enriched (or even slightly depleted), respectively. These two sites are isotopically indistinguishable and exhibit slightly heavier Cu isotope values compared to typical lithogenic signatures (Soledad: $+0.15 \pm 0.06\text{‰}$; Pescadero: $+0.14 \pm 0.10\text{‰}$).

Figure 5. Down-core Cu/Al and bulk $\delta^{65}\text{Cu}$ data for the Mexican and Peru margin sites. Pesc – Pescadero slope, Sol – Soledad basin, Mag – Magdalena margin, Peru – Peru margin. Grey bar gives range of Peruvian andesite-Mexican volcanic zone Cu/Al ratios, see text in section 4.1 for details. Dashed black line represents global mean lithogenic $\delta^{65}\text{Cu}$ (Moynier et al., 2017). Error bar represents 2 SD external reproducibility on Cu isotope measurements from ETH MC-ICP-MS (0.06‰).

5. Discussion

5.1 Covariation of $\delta^{65}\text{Cu}$ and Al/Cu in marine sediments

As a whole, the dataset presented here shows limited variability in $\delta^{65}\text{Cu}$ values, from –0.02‰ to +0.37‰. For comparison, the measured range in $\delta^{65}\text{Cu}$ found for typical Earth surface materials spans approximately –1.5‰ to +2‰ (e.g., Moynier et al., 2017), though this range is extended considerably with the inclusion of Cu-bearing ore minerals (–16.5‰ to +10.0‰; Mathur et al., 2009).

All samples from this study are isotopically lighter than data for the dissolved phase in seawater (at +0.6 to +0.9‰, Fig. 6; Vance et al., 2008; Thompson et al., 2014; Takano et al., 2014). A negative correlation (Fig. 6; $R^2_{\text{all data}} = 0.40$, $p < 0.001$) is observed between $\delta^{65}\text{Cu}$ values and Al/Cu ratios. This relationship can be explained, to a first order, by mixing of two distinct end-member sources of Cu. The first is a lithogenic source, with a high Al/Cu ratio and a lithogenic Cu isotope composition of ~0 to +0.1‰ (grey box, Fig. 6). The second mixing component can be termed the bioauthigenic Cu end member. It has a low Al/Cu ratio and an isotope composition of about +0.3‰. While the presence of a lithogenic end member is intuitive, the fact that just one other component can explain a

significant fraction of the variability in the remainder of the dataset is unexpected and merits further discussion.

Figure 6. Covariation of $\delta^{65}\text{Cu}$ with Al/Cu in marine sediments. Each site is represented by its mean $\delta^{65}\text{Cu}$ and Al/Cu values ± 2 SD error bars. Symbols for each site are the same as in Figures 2 – 5. The range of estimated bulk seawater isotopic compositions (+0.6 to +0.9‰) is shown as a shaded blue bar. The range and mean of lithogenic Al/Cu values and $\delta^{65}\text{Cu}$ ratios are shown as a grey box. For comparison, the mean and 1 SD of the surface layers of global Fe-Mn oxide sediments is shown as an orange star.

The isotope composition of the bioauthigenic Cu component of the sediment can be calculated for individual samples by mass balance, assuming a Cu/Al ratio and $\delta^{65}\text{Cu}$ value of the lithogenic background material ($\text{Cu}/\text{Al}_{\text{lith}}$ and $\delta^{65}\text{Cu}_{\text{lith}}$). First, the lithogenic fraction (X_{lith}) of the total Cu is calculated:

$$X_{\text{lith}} = \frac{\frac{\text{Cu}}{\text{Al}_{\text{lith}}} \times \text{Al}_{\text{sample}}}{\text{Cu}_{\text{sample}}},$$

where $\text{Al}_{\text{sample}}$ and $\text{Cu}_{\text{sample}}$ are the measured bulk Al and Cu concentrations of the sample.

The bioauthigenic $\delta^{65}\text{Cu}_{\text{auth}}$ value can then be calculated:

$$\delta^{65}\text{Cu}_{\text{auth}} = \frac{(\delta^{65}\text{Cu}_{\text{bulk}} - \delta^{65}\text{Cu}_{\text{lith}} \cdot X_{\text{lith}})}{X_{\text{auth}}},$$

where $\delta^{65}\text{Cu}_{\text{bulk}}$ is the measured $\delta^{65}\text{Cu}$ ratio of the sample, and X_{auth} is the fraction of bioauthigenic Cu (i.e., $X_{\text{auth}} = 1 - X_{\text{lith}}$). This calculation is straightforward but gives unreasonable values when the lithogenic fraction is very large (>90%). This situation

applies to the Cariaco Basin, the Santa Barbara Basin, and the Pescadero Slope sites, which all show little or no bioauthigenic enrichment. Excluding these three sites, and assuming lithogenic $\text{Cu}/\text{Al}_{\text{lith}}$ and $\delta^{65}\text{Cu}_{\text{lith}}$ values for the remaining sites as detailed in section 4.1, the calculated bioauthigenic end member has a Cu isotope composition of $+0.31 \pm 0.11\text{‰}$ (1 SD, $n = 43$; see ESM Table 1 for sample-by-sample calculated $\delta^{65}\text{Cu}_{\text{auth}}$ values). Exclusion of the Black Sea data yields a margin-only $\delta^{65}\text{Cu}_{\text{auth}}$ of $+0.28 \pm 0.11\text{‰}$ (1 SD, $n = 29$). Note that using a single $\text{Cu}/\text{Al}_{\text{lith}}$ value for all sites and varying this ratio between 3.0 and 4.5×10^{-4} alters the calculated $\delta^{65}\text{Cu}_{\text{auth}}$ by less than $\pm 0.02\text{‰}$. The calculation is somewhat more sensitive to the assumed $\delta^{65}\text{Cu}_{\text{lith}}$ value. Taking the published mean $\delta^{65}\text{Cu}_{\text{lith}} \pm 1$ SD (where $\delta^{65}\text{Cu}_{\text{lith}} = 0.08 \pm 0.17\text{‰}$; Moynier et al., 2017) – i.e. using a range for $\delta^{65}\text{Cu}_{\text{lith}}$ of -0.09 to $+0.25\text{‰}$ – gives a range in the calculated mean $\delta^{65}\text{Cu}_{\text{auth}}$ of $+0.39$ to $+0.23\text{‰}$.

The calculated bioauthigenic end member isotope composition of about $+0.3\text{‰}$ closely corresponds to observed values for the surface layers of Fe-Mn crusts and nodules (orange star in Fig. 6; mean $\delta^{65}\text{Cu}_{\text{Fe-Mn oxides}} = +0.31 \pm 0.12\text{‰}$, 1SD, $n = 31$, data sources: Albarède, 2004; Little et al., 2014a). Fe-Mn crusts have previously been used as an analogue for the dispersed Fe-Mn oxide phases found throughout deep-sea pelagic sediments that are thought to be responsible for Cu removal from the ocean under normal ‘oxic’ marine conditions (Little et al., 2014a). Somewhat surprisingly, therefore, the data presented here suggest that Cu is removed from the ocean with a homogeneous isotopic composition (of about $+0.3\text{‰}$) in all oceanic settings. Particularly surprising is the observation that, despite near quantitative removal of Cu from the sulphidic water columns of the Black Sea and Cariaco Basin (Jacobs et al., 1987; Haraldsson and Westerlund, 1991; Tankéré et al., 2001), bioauthigenic Cu isotope values from these two basins do not appear to record the $\delta^{65}\text{Cu}$ of global mean seawater (at $+0.6$ to $+0.9\text{‰}$; Vance et al., 2008; Thompson et al., 2014; Takano et al., 2014). We return to this observation in section 5.3.

5.2 Bioauthigenic Cu in sediments: the isotopic counterpart to strong organic ligand-bound Cu in the dissolved pool?

The vast majority of dissolved copper in all aqueous environments, from rivers and their estuaries (e.g., Dryden et al., 2004; Laglera and Van den Berg, 2003) to the open ocean (e.g., Coale and Bruland, 1988, 1990; Moffett et al., 1990; Lucia et al., 1994; Leal and Van den Berg, 1998; Moffett and Dupont, 2007; Jacquot and Moffett, 2015), is complexed to

strong organic ‘L1-type’ ligands, which have binding constants (log K) in the range of about 12–16. Both *ab initio* calculations (Sherman, 2013) and experiments (Bigalke et al., 2010; Ryan et al., 2014) indicate that strong organic ligands preferentially complex the heavy Cu isotope. Isotopically heavy Cu in the dissolved pool of rivers and the ocean has thus previously been hypothesised to result from preferential complexation of heavy Cu isotopes by these strong organic ligands (Vance et al., 2008; Thompson et al., 2014; Little et al., 2014b). Specifically, Vance et al. (2008) proposed that an equilibrium fractionation occurs directly between an organically complexed dissolved pool and the surface of scavenging particles (Vance et al., 2008). This scenario could also be invoked to explain the homogenous composition of the bioauthigenic Cu output flux observed here. The homogeneous composition of the oceanic Cu sink would, in this case, require open system steady-state fractionation with a fractionation factor ($\Delta = \delta^{65}\text{Cu}_{\text{seawater}} - \delta^{65}\text{Cu}_{\text{sinks}}$) of ~0.4‰ between the aqueous and particulate phase.

Another plausible explanation for the homogeneous isotopic composition of the bioauthigenic Cu output flux, regardless of *sedimentary* redox state, is that an equilibrium isotopic fractionation exists between two species in the oxygenated *aqueous* phase. First, the organically complexed pool is highly soluble and enriched in heavy isotopes due to the strong binding environment provided by the strong organic ligands. Second, a particle reactive free Cu^{2+} pool, which is ~0.4‰ lighter than the organic ligand-bound pool, is scavenged to particulates. Consistent with this scenario, Ryan et al. (2014) measured an isotopic fractionation factor $\Delta_{\text{ligand-free}} = 0.44 \pm 0.40 \text{ ‰}$ (n = 3, 2SD) for a synthetic ligand (NTA) with a similar log K to natural L1-type ligands (log $K_{\text{NTA}} = 14.4$). In this case, where fractionation occurs between two Cu species in the aqueous phase, the nature of the particulate material to which Cu is scavenged is not relevant to the isotopic fractionation expressed. In the alternative scenario, where an equilibrium fractionation exists between the aqueous and particulate pools, there would need to be a near constant fractionation factor between aqueous Cu and all potential scavenging surfaces.

In either scenario, we hypothesise that scavenging by particulate organic matter plays a key role in the water column. If this scavenging is a reversible process (e.g., Little et al., 2013), and exchange continues with the dissolved pool as particles sink, then bottom water isotope compositions will determine the isotope composition of particles when they reach the sediment. In turn, this process may contribute to the homogeneity of the output flux,

because deep waters exhibit less isotopic variability than the upper water column (Vance et al., 2008; Takano et al., 2014, Thompson et al., 2014). Scavenging associated with Fe-Mn cycling either in the water column or within the sediment is also likely to be important, dependent on the setting. For example, active Fe-Mn oxide cycling close to the sediment-water interface (e.g., San Nicolas, Santa Monica; Fig. 4) appears to enhance fixation of Cu with the bioauthigenic $\delta^{65}\text{Cu}$ signature. Detailed spectroscopic and experimental work at the mineral-organic-water interface increasingly supports the suggestion that organic and oxide-bound phases are often inextricably linked (Lalonde et al., 2012; Johnson et al., 2015; Tribovillard et al., 2015). In the case of an equilibrium isotope fractionation between the dissolved phase and scavenging particles, this organic-oxide linkage may also contribute to the isotopic homogeneity of the sedimentary sink.

5.3 Cu in euxinic settings

5.3.1 The Cariaco Basin

Near quantitative removal of Cu is observed from the euxinic water columns of both the Black Sea and Cariaco Basin (Haraldsson and Westerlund, 1991; Tankéré et al., 2001; Jacobs et al., 1987). Despite this removal from the water column, we do not observe significantly elevated Cu/Al in Cariaco Basin sediments (Fig. 3). There is, however, a shift in $\delta^{65}\text{Cu}$ ratios across the oxic-anoxic transition of the sediment core, from about +0.08 in the oxic interval to +0.20‰ in the euxinic interval (Fig. 3). Given the absence of appreciable Cu enrichment, one possible explanation of this isotopic shift is a change in the isotope composition of the local lithogenic background material. A change in the source of lithogenic material to the Cariaco Basin on glacial-interglacial timescales has previously been proposed based on Al/Ti ratios. This change is hypothesised to reflect an increased supply of Ti-rich dust from the Sahara during glacial periods, due to the more southerly position of the ITCZ (Yarincik et al., 2000; Martinez et al., 2010). Alternatively, the data and their uncertainties do permit the presence of a small amount of bioauthigenic Cu in the euxinic interval. For example, assuming an UCC Cu/Al ratio of 3.5×10^{-4} (Note: this ratio is lower than that observed in the oxic interval), and $\delta^{65}\text{Cu}_{\text{lith}}$ of +0.08‰, the mean calculated $\delta^{65}\text{Cu}_{\text{auth}}$ for the euxinic portion of the sediment pile is $+0.66 \pm 0.25\text{‰}$, similar to that of modern open ocean seawater $\delta^{65}\text{Cu}$ (at approximately +0.7‰). There is an indication, therefore, that bioauthigenic Cu deposited in sediments under Cariaco Basin-type hydrographic conditions, where euxinia is primarily driven by productivity without

strong basin restriction, may indeed record open ocean $\delta^{65}\text{Cu}$. However, due to the very low Cu enrichment observed (see also section 5.4), the local lithogenic background must be carefully characterised and corresponding calculated $\delta^{65}\text{Cu}_{\text{auth}}$ values should be interpreted with caution.

5.3.2 The Black Sea

Copper is enriched by a factor of 3 to 7 in sediments from the Black Sea euxinic stations compared to those from the oxic stations (Fig. 2), such that the assumed composition of the local lithogenic background has very little impact on calculated $\delta^{65}\text{Cu}_{\text{auth}}$ values (unlike in the Cariaco Basin). The Black Sea Cu isotope data therefore present us with a puzzle: given near quantitative removal from the water column, why are the $\delta^{65}\text{Cu}$ values of euxinic Black Sea sediments not more similar to the isotopic composition of mean global seawater (at approximately +0.7‰)? Instead we find that the Black Sea bioauthigenic Cu has an isotope composition that is similar to the remainder of the reducing sedimentary dataset presented here (i.e., at around +0.3‰).

One possibility is that the Cu isotope composition of the upper water column of the Mediterranean, which supplies the Black Sea through the shallow Bosphorus Strait between 13 and 110 m water depth, is isotopically lighter than that of mean global seawater. Although Cu isotope data for seawater remains relatively sparse, the data that exist show limited variability in deep waters (at +0.6 to 0.9‰: Vance et al., 2008; Takano et al., 2014; Thompson et al., 2014), but frequent small deviations towards lighter $\delta^{65}\text{Cu}$ values in the upper water column (down to +0.4 to 0.5‰: Takano et al., 2014). These relatively light surface values are most easily explained as the result of the deposition of aerosol dust, and the Mediterranean does receive a high mineral dust flux from the Sahara (Prospero, 1996). However, assuming modern inflow through the Bosphorus Strait of $305 \text{ km}^3 \text{ yr}^{-1}$ (Özsoy and Ünlüata, 1997), and a surface water Cu concentration in the Mediterranean of 2.5 nM (Saager et al., 1993), the magnitude of the Mediterranean Cu source is about $7 \times 10^7 \text{ g yr}^{-1}$. The mean calculated authigenic Cu content of euxinic Black Sea sediments is ~35 ppm (ESM Table 1, range: 28 – 48 ppm). Given this value, and assuming a sediment density of 2.3 g cm^{-3} , porosity of 80%, anoxic basin area of $318,582 \text{ km}^2$ and a sedimentation rate of $0.0155 \text{ cm yr}^{-1}$, we calculate a Cu output flux to Black Sea euxinic sediments of $8 \times 10^8 \text{ g yr}^{-1}$. This estimate is an order of magnitude higher than the estimated Mediterranean input flux. This imbalance is exacerbated by the fact that there is

also a return flux to the Mediterranean from the surface Black Sea, representing a further substantial output of Cu from the basin. Hence, input of Cu from the Mediterranean alone can explain neither the enrichment nor the isotope signature of Cu observed in Black Sea sediments.

Rivers are the other likely key input of Cu to the Black Sea. The previously measured range of $\delta^{65}\text{Cu}$ in a subset of relatively pristine global rivers is +0.02 to +1.45 ‰, with a discharge-weighted average of +0.68 ‰ (Vance et al., 2008). A measurement of Black Sea surface water of +0.92 ‰ (Table 5; for sample collection and pre-concentration techniques, see Vance et al., 2016a) is within this riverine range and the range of published open ocean values. Though the isotope composition of the Black Sea surface ocean may be anthropogenically perturbed (e.g., Vance et al., 2016a), it seems unlikely – though we cannot definitively rule it out – that the relatively light isotopic composition of Black Sea sediments is a direct result of supply of isotopically light Cu from rivers.

A plausible explanation for the coherent isotopic composition of Black Sea sediments versus those from other marine settings is that the source of Cu to the restricted deep basin has, in fact, been subject to biogeochemical cycling similar to that envisaged in section 5.2. In this view, rivers supply isotopically heavy Cu to the oxic Black Sea surface layer. The transfer of this Cu to the deep euxinic portion of the basin is then mediated by the cycling of Fe and Mn and is associated with an isotopic fractionation between the aqueous and particulate phase similar to that which is proposed for the open ocean. Copper is complexed by organic ligands in Black Sea surface waters (Muller et al., 2001), and significant cycling of trace metals across the redoxcline has been hypothesised associated with the cycling of nanoparticulate Fe and Mn oxides at this depth (e.g., Lyons and Severmann, 2006; Little et al., 2015; Vance et al., 2016a). Specifically, nanoparticulate Fe and Mn oxides may form following their efflux from shelf sediments. These nanoparticulate phases can then be transported to the basin interior, where they are re-reduced and dissolve: this is a version of the *benthic redox shuttle* (Severmann et al., 2008; Scholz et al., 2013; 2014). These Fe-Mn nanoparticles sorb other trace metals, forming a fine particle layer at the redoxcline that is rich in Cu, Ni, Zn, and other metals (Tankéré et al., 2001). The scavenged Cu, which need not be shelf-sediment sourced (as invoked for Fe and Mn), is then released to the euxinic portion of the basin on reduction of the host Fe-Mn nanoparticles. Once there, sulphide minerals quantitatively re-scavenge the supplied Cu. In

this view, the ‘shuttled’ Cu would have an isotope composition of the bioauthigenic end member at +0.3‰, i.e., approximately +0.6‰ lighter than organically complexed, isotopically heavy, residual Cu in modern Black Sea surface waters.

Some support for this hypothesis comes from chemocline site 16B. Here, the upper two data points (upper 4 cm of core) are slightly enriched in Cu and are distinctly isotopically heavy at +0.25‰ – similar to the bioauthigenic end member – compared to lithogenic-like $\delta^{65}\text{Cu}$ values observed deeper in the core (Fig. 2). The sediments at Station 16B were deposited close to the position of the redoxcline at the time of coring, with dissolved oxygen at trace levels (Lyons, 1991). Enrichments in AVS (acid volatile sulphur) were evident in the black-grey, banded upper 2-4 cm of the core, compared to the increasingly bioturbated grey layers below. These observations have been interpreted to reflect an evolution from a more to a less oxygenated environment at this site (Lyons, 1991), i.e., a shoaling of the redoxcline, an assertion that is supported by the $\delta^{65}\text{Cu}$ data presented here.

5.4 The lithogenic dilution effect on Cu enrichment in marine sediments

Cu/Al data from the Cariaco Basin highlight that anoxia, and even euxinia, is not by itself sufficient to produce strong authigenic Cu enrichments in sediments. Other data presented here also illustrate this point clearly: the most reducing sedimentary environment of the California Borderland basins is the Santa Barbara basin, which shows no authigenic Cu enrichment and a lithogenic isotope composition. In Figure 7 we highlight one key reason for this, the control on Cu enrichment by sediment accumulation rate.

To isolate the role of lithogenic dilution of Cu contents in marine sediments, Al accumulation rates (S_{Al}) were calculated using estimates of sediment accumulation rates from the literature, summarised in Table 1, and measured Al concentrations from this study. Significant Cu enrichment is observed only at sites with an S_{Al} of considerably less than $0.1 \text{ mg cm}^{-2} \text{ yr}^{-1}$ (Fig. 7). Plotting the S_{Al} – Al/Cu relationship in this way allows a quantitative assessment of the lithogenic dilution effect on Cu enrichment, via a box model approach outlined by Jacobs et al. (1985; 1987). Full details of the box model are given in the ESM. In brief, it is assumed that the flux of Cu (or any metal) to the sediment is comprised of two components, the relative magnitude of which will determine metal enrichment in the sediment: (1) a detrital (or lithogenic) flux defined by the Cu/Al ratio of

upper continental crust $(\text{Cu}/\text{Al})_{\text{lith}}$ and the accumulation rate of Al (S_{Al}) and (2) a bioauthigenic flux derived from removal of dissolved Cu from the water column. We assume that the latter may reflect either sulphidisation or uptake/scavenging by particulate organic carbon and/or Fe-Mn oxides. The model is made up of an oxic surface ocean box (Box 1) and an anoxic deep water box (Box 2), each of which are well mixed and exchange on a timescale, T , in m yr^{-1} (ESM Fig. 1). The authigenic enrichment of a metal, S_{enrich} , then depends on three parameters: (1) S_{Al} ; (2) the concentration difference between oxic box 1 and anoxic box 2, $C_1 - C_2$; and (3) the timescale of mixing, T . We apply this model to the Cariaco Basin (directly following Jacobs et al., 1987) and to the Black Sea. Parameters used are given in Table 6. Note that T is related to the residence time of water in the deep box, τ_2 , by the thickness of this box, z_2 : $T = z_2 \tau_2^{-1}$. This mixing timescale is somewhat slower in the Black Sea ($\sim 5 \text{ m yr}^{-1}$) than in the Cariaco Basin ($\sim 11 \text{ m yr}^{-1}$), due to the longer residence time of Black Sea deep waters (Table 6). In addition, the parameter $C_1 - C_2$ in the Black Sea (6.5 nM; Tankéré et al., 2001) is quadruple that of the Cariaco Basin (1.1 nM, Jacobs et al., 1987), due to the relatively low Cu concentration of the South Atlantic source waters that flow into the Cariaco Basin. The results of the model are plotted as dashed (Black Sea model parameters) and solid (Cariaco Basin model parameters) black lines in Figure 7 for the full range of S_{Al} values observed for sites in this study. Agreement between the model and site-averaged Cu/Al values is observed for the two euxinic sites.

This simple 2-box model is not directly applicable to open margin sites, like the Peru and Magdalena margin regions, and we have insufficient data to perform a detailed analysis for the other basinal sites included here. We can, however, find parameters that give reasonable results, even for the exceptional Peru margin site (dotted black line, Fig. 7). For this model we assume a removal term of Cu into particulate organic matter of 2 nM, over a depth range of 100 m, and with a very short water residence time (1 year). This result should be considered illustrative only, nevertheless, the model gives clear mechanistic insight into lithogenic dilution of the bioauthigenic flux of Cu.

Figure 7. Al accumulation rate (S_{Al}) versus site average Cu/Al. Black lines show superimposed box model results (solid – Cariaco Basin; dashed – Black Sea; dotted – Peru margin; see Table 6 for selected model parameters and ESM for additional model details). All symbols are the same as in Figs 2 – 5. Coloured dotted ranges in S_{Al} reflect published range in sediment accumulation rates for nearby sites compiled from the literature (see Table 1). Error bars on Cu/Al ratios and S_{Al} (where sediment accumulation rates for the same sediment core have been published) reflect 2 SD variability for the core.

5.5 Implications for Cu oceanic mass balance: a missing isotopically light Cu source

One of the motivations for this study was to place constraints on the modern reducing sedimentary sink for Cu and Cu isotopes. A first order approximation of the net flux of Cu into continental margin settings can be calculated using an estimate of marine organic C burial rate and the slope of the C_{org}/Al versus Cu/Al relationship for continental margin sites. This slope is 0.00041 g Cu/g C (ESM Fig. 3; data from this study and Böning et al., 2012). Smith et al. (2015) calculate a global marine C_{org} burial rate of $\sim 170 \times 10^{12}$ g C yr⁻¹. Together, this equates to an organic C associated Cu burial flux of $\sim 11 \times 10^8$ mol yr⁻¹. This value is an order of magnitude higher than an estimate for the role of continental margin sediments based on Mo as an analogue (Little et al., 2015) and slightly above the range of Cu removal estimates to oxic pelagic sedimentary settings, estimated at $1.6 - 9.7 \times 10^8$ mol/yr (Little et al., 2014a; Little et al., 2015). The calculation excludes the additional flux of Cu to euxinic sediments via the redox-shuttle mechanism proposed for the Black Sea, which is quantitatively small today ($\sim 0.5 \times 10^8$ mol/yr; Little et al., 2015), but may have been more significant in the past. Given a total ocean Cu budget of 4.2×10^{12} moles (Little et al., 2014a) and the sum of the three output fluxes (pelagic, continental margin, redox-

shuttle), we calculate a Cu oceanic residence time (where τ = total inventory of element $\div$ annual total input or output flux of element) of 2000 – 3200 years.

Together, the continental margin and pelagic Cu sinks sum to approximately twice the total estimated riverine and dust input flux of Little et al. (2014a) ($6.5 - 9.2 \times 10^8$ mol/yr). In addition, all sedimentary sinks for Cu are isotopically light (at about +0.3‰) compared to the isotope composition of the combined riverine and dust flux (at approximately +0.6‰, Little et al., 2014a). If the Cu oceanic budget is at steady state, these observations require either an additional sink that is isotopically heavy or (a) further source(s) that is/are isotopically light. Given the flux imbalance (i.e., known output fluxes $\gg$ known input fluxes) and the fact that the major output fluxes have now been characterised, a missing input flux appears more probable. Mass balance implies this missing source be $\sim 9 \times 10^8$ mol/yr and have an isotope composition of ~ 0 ‰, illustrated schematically in Figure 8.

Figure 8. Schematic illustrating the updated oceanic budget of Cu and Cu isotopes (after Little et al., 2014a; 2015; this study). Arrows are scaled by flux magnitude and labelled and coloured by isotope composition (yellow represents the isotopically light components, blue the isotopically heavier components, and green is intermediate). The projected missing source size and isotope composition is shown as a dashed arrow to the left of the figure (see text for details). For reference to colours, please see online version of this figure.

The main input of Cu to the modern ocean has typically been assumed to be the dissolved phase in rivers (e.g., Little et al., 2014a). Two independent estimates put this riverine

dissolved flux at $6 - 9 \times 10^8$ mol/yr (Gaillardet et al., 2003; Vance et al., 2008). This dissolved riverine flux is isotopically heavy, with a discharge-weighted riverine average $\delta^{65}\text{Cu}$ of +0.68‰ (Vance et al., 2008). These estimates assume conservative behaviour of Cu during estuarine mixing, as observed, for example, for two major river systems: the Chiang Jiang and the Amazon (Boyle et al., 1982; Edmond et al., 1985). However, non-conservative behaviour of Cu has also been observed in a spectrum of estuarine systems (e.g., Morris et al., 1978; Windom et al., 1983; Ackroyd et al., 1986). Furthermore, the dissolved flux of Cu accounts for only ~20% of the total riverine flux of Cu to the ocean, with the remainder delivered in particulate form (e.g., Martin and Meybeck, 1979). The partial dissolution of riverine particulates has recently been suggested as a significant oceanic source of several metals (e.g., Oelkers et al., 2012; Jones et al., 2012; 2014). Vance et al. (2008) report isotopically light Cu in the particulate phase of one small river system in the U.K, which is complementary to the heavy dissolved pool. Partial remobilisation of isotopically light riverine particulates, whether lithogenic or other (e.g. terrestrial organic matter) particles, may therefore provide one possible isotopically light flux of Cu to the ocean. Release could be envisaged in, e.g., anoxic estuarine environments, or further out in continental margin or open ocean settings. By analogy, release of neodymium (Nd) from the lithogenic phase has been hypothesised in continental margin settings (e.g., Jeandel et al., 2007; Pearce et al., 2013; Abbott et al., 2015; Abbott et al., 2016).

The natural (non-anthropogenic) dust flux of Cu to the ocean appears to be isotopically unfractionated from the lithogenic Cu source (at ~0‰), based on analysis of the water-leachable fraction of aerosols and loess particles (Little et al., 2014a; Dong et al., 2013). The magnitude of this natural dust flux has been calculated by two studies, one data-driven (Little et al., 2014a) and one model-based (Takano et al., 2014). In the data-driven approach, the flux is calculated based on a model of global dust deposition (Jickells et al., 2005), an estimate of the Cu concentration in UCC (35ppm; Rudnick and Gao, 2003), and an estimate of mineral dust solubility (27%; Desboeufs et al., 2005), yielding a Cu flux of 0.5×10^8 mol/yr (Little et al., 2014a). In the model-derived approach, Takano et al. (2014) invoked a much larger dust flux, at $\sim 10 \times 10^8$ mol/yr, in order to balance their steady state model-derived output flux of 17×10^8 mol/yr. The latter value is, itself, in line with the sum of the pelagic and continental margin sinks proposed here. Assuming a lithogenic isotope composition (0‰) for their postulated dust flux, Takano et al. (2014) further

calculate that the Cu isotope composition of the output flux should be +0.3‰ (Takano et al., 2014), also consistent with results in this study. Nevertheless, we consider a very large dust flux to be rather unlikely, due in part to the low solubility of Cu in dust (e.g., Desboeufs et al., 2005; Sholkovitz et al., 2010). Even if mineral dust were completely soluble – for example, if solubility is enhanced by the presence of organic ligands (as suggested for Fe; Fishwick et al., 2014) – the maximum Cu input flux possible based on an estimate of global mineral dust deposition and the Cu concentration in UCC is five times lower than that required by Takano et al. (2014), at 2.0×10^8 mol/yr.

Of other possible inputs, a hydrothermal Cu source has to date been assumed to be globally insignificant due its to efficient removal close to the vent (e.g., Trocine and Trefry, 1988; German et al., 1991; 2002). Scavenging within the Atlantic TAG hydrothermal plume indicates that hydrothermal activity may in fact be a net sink of Cu, at least in certain environments (Jacquot and Moffett, 2015; Roshan and Wu, 2015). However, recent water column data for a range of trace elements and their isotopes, collected as part of the international GEOTRACES program, has highlighted significant basin scale heterogeneity in the iron (Fe) and zinc (Zn) hydrothermal flux, indicating that this potential source should be re-evaluated (Resing et al., 2015; Roshan et al., 2016). Sander and Koschinsky (2011) suggest that organic complexation may be one means to stabilise metals from hydrothermal vent sources in the dissolved phase. Primary hydrothermal fluxes are likely to have a lithogenic Cu isotope composition (at ~0‰), though these may be subject to considerable secondary isotope fractionation effects resulting from sulphide precipitation, organic complexation, and/or scavenging to oxide phases.

Benthic fluxes have long been considered to play a role in the water column distribution of dissolved Cu (e.g., Boyle et al., 1977). In terms of oceanic mass balance, there are two ways in which such a benthic flux can be envisaged, which differ according to the solid phase from which the Cu is released to bottom waters. The first requires that Cu be released from external sources, either via rivers (as discussed above), or hydrothermal particulates. This possibility would then represent a true new source of Cu to the ocean and might be expected to be isotopically light if lithogenic or hydrothermal material is the source. The second type of benthic flux involves re-release to bottom waters of bioauthigenic Cu (i.e., Cu from the water column). This process may occur in porewaters of suboxic sediments, where suboxic denotes negligible dissolved oxygen and sulphide.

Under these conditions, Cu carrier phases (Fe-Mn oxides, organic matter) are reduced, and Cu could diffuse into bottom water (Shaw et al., 1990; Elderfield et al., 1981; Heggie et al., 1987; Klinkhammer, 1980; Sawlan and Murray, 1983). This process may be aided by complexation to strong organic ligands in porewaters (Skrabal et al., 1997; 2000; Shank et al., 2004a; 2004b). In itself, this process does not constitute a true new source of Cu to the oceans, because the Cu that is returned to the water column came from the water column – i.e., the Cu is recycled. Note that any such recycling is implicit in the calculation of the organic C burial-associated Cu flux (i.e., this is a net flux). This recycling could, however, be accompanied by an isotopic effect, if isotope fractionation occurs in the sediment pile. An isotopically light signature for such a source would require preferential retention of heavy Cu isotopes in the solid phase. This direction of fractionation would not be consistent, however, with what would be predicted based on organic complexation of Cu in pore waters. This process is likely to favour retention of heavy Cu isotopes in the soluble phase, with the removal of light Cu isotopes to particles.

Ultimately, we suggest that better resolution of the Cu isotope budget requires future studies focussing on: (1) an improved evaluation of the diagenetic processing of Cu and its isotopes, (2) the fate and isotopic signature of hydrothermally sourced Cu, and (3) the behaviour of continent-derived particulate Cu in the marine environment, both in estuaries and more distally.

6. Conclusions and Outlook

This study presents a Cu isotope dataset for recent organic rich sediments from a range of low oxygen and reducing sedimentary environments. The data indicate that the modern bioauthigenic (i.e., non-lithogenic) oceanic Cu output flux is isotopically homogeneous across many sedimentary environments – at about +0.3‰. This value is significantly lighter than the isotope composition of the open oceans, at +0.6 to +0.9‰. We suggest that the homogeneous isotopic composition of the Cu output flux reflects either (1) an equilibrium isotope fractionation between two species in the dissolved phase, with an isotopically heavy dissolved pool complexed by strong organic ligands and a particle reactive, isotopically light free Cu²⁺ pool, or (2) an equilibrium isotope fractionation directly between the organically complexed dissolved pool and the particulate phase. In the

latter scenario all particulates would be required to exhibit the same fractionation from the dissolved pool. In either case, continuous reversible exchange between sinking particulates and the dissolved pool, all the way down through the water column, may contribute to the homogeneity of the output flux.

Unexpectedly, highly Cu enriched euxinic Black Sea sediments (with $\delta^{65}\text{Cu}_{\text{auth}}$ of +0.3‰) do not record the Cu isotope signature of the open ocean (at around +0.6 to +0.9‰), despite near quantitative removal of Cu from the water column. We hypothesize that this signature reflects active Fe-Mn cycling at the Black Sea redoxcline, with shuttling of isotopically ‘bioauthigenic’ Cu (i.e., at +0.3‰) to the restricted deep basin where it is removed to sediment via sulphide precipitation. A similar process, albeit on a smaller length-scale, likely also occurs at the sediment-water interface of suboxic to anoxic continental margin sediments (e.g., San Nicolas Basin) and is also evident in the modern-day near-chemocline station of the Black Sea (Station 16B). In all cases, we envisage that an isotopically heavy pool of Cu is retained in the dissolved phase via complexation to strong organic ligands.

Low oxygen conditions alone are not sufficient to generate strong enrichment of Cu in marine sediments. Variability in the dataset presented here can be explained to first order in terms of dilution of the bioauthigenic signature (at about +0.3‰) with lithogenic material (at ~0‰), and the lithogenic sedimentary accumulation rate is a strong control on the presence or absence of the bioauthigenic $\delta^{65}\text{Cu}$ signature in sediments.

We note that all characterised sinks for Cu in the modern ocean are isotopically light (at about +0.3‰) relative to the current best estimate for the input flux (at about +0.6‰; Little et al., 2014a). This disparity indicates the presence of an as yet unidentified isotopically light source, of approximately lithogenic composition (~0‰; Fig. 8). Dust is one such possible light source, as previously suggested by Takano et al. (2014). We suggest two other possible light sources of Cu: (1) hydrothermal input, (2) partial dissolution of continentally derived particulates. Distinguishing among these three possible input fluxes requires future detailed research.

Finally, our findings, along with those of several previous studies, indicate that strong organic ligands play a key role in the modern biogeochemical cycle of Cu and Cu isotopes.

This role must be fully considered in future studies seeking to apply Cu isotopes in the rock record as a paleoceanographic tracer.

Acknowledgments

The authors would like to thank three anonymous reviewers and the associate editor R. James for comments that significantly improved the manuscript. Little is supported by a Leverhulme early career fellowship at Imperial. Isotopic measurements at Bristol were supported by a NERC-funded PhD studentship NE/H525111/1 to Little. The ETH Zürich project work was supported by Swiss National Science Foundation Project 200021_153087 to Vance. Continental margin sediment sample collection was supported by multiple US NSF grants to McManus including OCE-0624777 and OCE-0219651. McManus was also supported by U.S. National Science Foundation grant OCE-1657832. Lyons is grateful for support from the NASA Astrobiology Institute and the NSF FESD and ELT programs. We thank William Berelson and Gary Klinkhammer for their contributions to cruises where some of these samples were collected, and Chris Coath and Corey Archer for facilitating the smooth running of clean labs and mass spectrometers in Bristol and Zürich.

References

- Abbott, A. N., Haley, B. A., and McManus, J. (2015). Bottoms up: Sedimentary control of the deep North Pacific Ocean's ϵNd signature. *Geology* **43**(11), 1035–1035.
- Abbott, A. N., Haley, B. A., and McManus, J. (2016). The impact of sedimentary coatings on the diagenetic Nd flux. *Earth Planet. Sci. Lett.* **449**, 217–227.
- Ackroyd, D. R., Bale, A. J., Howland, R. J. M., Knox, S., Millward, G. E., and Morris, A. W. (1986). Distributions and behaviour of dissolved Cu, Zn and Mn in the Tamar Estuary. *Estuar. Coast. Shelf S.* **23**(5), 621–640.
- Albarède, F. (2004) The stable isotope geochemistry of copper and zinc. *Rev. Mineral. Geochem.* **55**(1), 409–427.
- Algeo, T., and Lyons, T. (2006) Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions. *Paleoceanography* **21**(1), PA1016.
- Algeo, T. J., and Maynard, J. B. (2004) Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem. Geol.* **206**(3–4), 289–318.

908 Archer C. and Vance D. (2004) Mass discrimination correction in multiple-collector
 909 plasma source mass spectrometry: an example using Cu and Zn isotopes. *J. Anal. At.*
 910 *Spectrom.* **19**(5), 656–665.

911 Arnold, G. L., Anbar, A. D., Barling, J., and Lyons, T. W. (2004) Molybdenum isotope
 912 evidence for widespread anoxia in mid-Proterozoic oceans. *Science* **304**(5667), 87–90.

913 Asael, D., Matthews, A., Bar-Matthews, M., and Halicz, L. (2007). Copper isotope
 914 fractionation in sedimentary copper mineralization (Timna Valley, Israel). *Chem.*
 915 *Geol.* **243**(3), 238–254.

916 Barling, J., and Anbar, A. D. (2004). Molybdenum isotope fractionation during adsorption
 917 by manganese oxides. *Earth Planet. Sci. Lett.* **217**(3), 315–329.

918 Barling, J., Arnold, G. L., and Anbar, A. D. (2001). Natural mass-dependent variations in
 919 the isotopic composition of molybdenum. *Earth Planet. Sci. Lett.* **193**(3), 447–457.

920 Berelson, W. M. (1991). The flushing of two deep-sea basins, southern California
 921 borderland. *Limnol. Oceanogr.* **36**(6), 1150–1166.

922 Berelson, W. M., Hammond, D. E., and Johnson, K. S. (1987). Benthic fluxes and the
 923 cycling of biogenic silica and carbon in two southern California borderland basins.
 924 *Geochim. Cosmochim. Acta* **51**(6), 1345–1363.

925 Berelson, W. M., McManus, J., Coale, K. H., Johnson, K. S., Kilgore, T., Burdige, D., and
 926 Pilskaln, C. (1996). Biogenic matter diagenesis on the sea floor: A comparison
 927 between two continental margin transects. *J. Mar Res.* **54**(4), 731–762.

928 Berelson, W. M., Prokopenko, M., Sansone, F. J., Graham, A. W., McManus, J., and
 929 Bernhard, J. M. (2005). Anaerobic diagenesis of silica and carbon in continental
 930 margin sediments: discrete zones of TCO₂ production. *Geochim. Cosmochim. Acta*
 931 **69**(19), 4611–4629.

932 Bermin J., Vance D., Archer C. and Statham P. J. (2006) The determination of the isotopic
 933 composition of Cu and Zn in seawater. *Chem. Geol.* **226**(3–4), 280–297.

934 Bigalke, M., Weyer, S., and Wilcke, W. (2010). Copper isotope fractionation during
 935 complexation with insolubilized humic acid. *Environ. Sci. Technol.* **44**(14), 5496–
 936 5502.

937 Böning, P., Brumsack, H., Böttcher, M. E., Schnetger, B., Kriete, C., Kallmeyer, J., and
 938 Borchers, S. L. (2004) Geochemistry of Peruvian near-surface sediments. *Geochim.*
 939 *Cosmochim. Acta* **68**(21), 4429–4451.

940 Böning, P., Cuypers, S., Grunwald, M., Schnetger, B., and Brumsack, H. J. (2005).
 941 Geochemical characteristics of Chilean upwelling sediments at ~ 36 S. *Mar. Geol.*
 942 **220**(1), 1–21.

943 Böning, P., Fröllje, H., Beck, M., Schnetger, B., and Brumsack, H. J. (2012).
 944 Underestimation of the authigenic fraction of Cu and Ni in organic-rich sediments.
 945 *Mar. Geol.* **323**, 24–28.

946 Boyle, E. A., Sclater, F. R., and Edmond, J. M. (1977). The distribution of dissolved
 947 copper in the Pacific. *Earth Planet. Sci. Lett.* **37**(1), 38–54.

948 Bruland, K. W. (1980). Oceanographic distributions of cadmium, zinc, nickel, and copper
 949 in the North Pacific. *Earth Planet. Sci. Lett.* **47**(2), 176–198.

950 Bruland K. W. and Lohan M. C. (2003) Controls of Trace Metals in Seawater. Pergamon,
951 Oxford, 23–47.

952 Bruland K. W., Orians K. J. and Cowen J. P. (1994) Reactive trace metals in the stratified
953 central North Pacific. *Geochim. Cosmochim. Acta* **58**(15), 3171–3182.

954 Bruland, K. W., Koide, M., and Goldberg, E. D. (1974). The comparative marine
955 geochemistries of lead 210 and radium 226. *J. Geophys. Res.* **79**(21), 3083–3086.

956 Bruland, K. W., Franks, R. P., Landing, W. M., and Soutar, A. (1981). Southern California
957 inner basin sediment trap calibration. *Earth Planet. Sci. Lett.* **53**(3), 400–408.

958 Brumsack H. (2006) The trace metal content of recent organic carbon-rich sediments:
959 implications for cretaceous black shale formation. *Palaeogeogr. Palaeoclimatol.*
960 *Palaeoecol.* **232**(2), 344–361.

961 Buesseler, K. O., and Benitez, C. R. (1994). Determination of mass accumulation rates and
962 sediment radionuclide inventories in the deep Black Sea. *Deep Sea Res. Pt I* **41**(11),
963 1605–1615.

964 Calvert S. and Pedersen T. (1993) Geochemistry of recent oxic and anoxic marine
965 sediments: implications for the geological record. *Mar. Geol.* **113**(1), 67–88.

966 Canfield, D. E. (1998). A new model for Proterozoic ocean chemistry. *Nature* **396**(6710),
967 450–453.

968 Chong, L. S., Prokopenko, M. G., Berelson, W. M., Townsend-Small, A., and McManus, J.
969 (2012). Nitrogen cycling within suboxic and anoxic sediments from the continental
970 margin of Western North America. *Mar. Chem.* **128**, 13–25.

971 Coale K. H. and Bruland K. W. (1988) Copper complexation in the Northeast Pacific.
972 *Limnol. Oceanogr.* **33**(5), 1084–1101.

973 Coale, K. H., and Bruland, K. W. (1990). Spatial and temporal variability in copper
974 complexation in the North Pacific. *Deep Sea Res.* **37**(2), 317–336.

975 Conway, T. M., and John, S. G. (2014). Quantification of dissolved iron sources to the
976 North Atlantic Ocean. *Nature* **511**(7508), 212–215.

977 Dean, W. E., Piper, D. Z., and Peterson, L. C. (1999) Molybdenum accumulation in
978 Cariaco Basin sediment over the past 24 k.y.: A record of water-column anoxia and
979 climate. *Geology* **27**(6), 507–510.

980 Desboeufs K., Sofikitis A., Losno R., Colin J. and Ausset P. (2005) Dissolution and
981 solubility of trace metals from natural and anthropogenic aerosol particulate matter.
982 *Chemosphere* **58**(2), 195–203.

983 Deutsch, C., Berelson, W., Thunell, R., Weber, T., Tems, C., McManus, J., Crusius, J., Ito,
984 T., Baumgartner, T., Ferreira, V., Mey, J., and van Geen, A. (2014). Centennial
985 changes in North Pacific anoxia linked to tropical trade winds. *Science* **345**(6197),
986 665–668.

987 Dong, S., Weiss, D. J., Strekopytov, S., Kreissig, K., Sun, Y., Baker, A. R., and Formenti,
988 P. (2013). Stable isotope ratio measurements of Cu and Zn in mineral dust (bulk and
989 size fractions) from the Taklimakan Desert and the Sahel and in aerosols from the
990 eastern tropical North Atlantic Ocean. *Talanta* **114**, 103–109.

991 Douville, E., Charlou, J.-L., Oelkers, E.H., Bienvenu, P., Jove Colan, C.F., Donval, J.P.,
992 Fouquet, Y., Prieur, D. and Appriou, P. (2002). The Rainbow vent fluids (36°14'N,

993 MAR): the influence of ultramafic rocks and phase separation on trace metal content
 994 in Mid-Atlantic Ridge hydrothermal fluids. *Chem. Geol.* **184**, 37–48.

995 Dryden, C. L., Gordon, A. S., and Donat, J. R. (2004). Interactive regulation of dissolved
 996 copper toxicity by an estuarine microbial community. *Limnol. Oceanogr.* **49**(4), 1115–
 997 1122.

998 Ehrlich, S., Butler, I., Halicz, L., Rickard, D., Oldroyd, A., and Matthews, A. (2004).
 999 Experimental study of the copper isotope fractionation between aqueous Cu (II) and
 1000 covellite, CuS. *Chemical Geology* **209**(3), 259–269.

1001 Elderfield, H. (1981). Metal-organic associations in interstitial waters of Narragansett Bay
 1002 sediments. *Am. J. Sci.* **281**(9), 1184–1196.

1003 Elderfield, H., Luedtke, N., McCaffrey, R. J., and Bender, M. (1981) Benthic flux studies
 1004 in Narragansett Bay. *Am. J. Sci.* **281**(6), 768–787.

1005 Elrod, V. A., Johnson, K. S., and Coale, K. H. (1991). Determination of subnanomolar
 1006 levels of iron (II) and total dissolved iron in seawater by flow injection and analysis
 1007 with chemiluminescence detection. *Anal. Chem.* **63**(9), 893–898.

1008 Emerson, S. R., and Huested, S. S. (1991). Ocean anoxia and the concentrations of
 1009 molybdenum and vanadium in seawater. *Mar. Chem.* **34**(3–4), 177–196.

1010 Emery, K. O. (1954). General geology of the offshore area, southern California. *Bull.*
 1011 *Calif. Div. Mines Geol.* **170**, 107–111.

1012 Emery, K. O. (1960). Basin plains and aprons off southern California. *J. Geology*, 464–
 1013 479.

1014 Emeis, K. C., Whelan, J. K., and Tarafa, M. (1991) Sedimentary and geochemical
 1015 expressions of oxic and anoxic conditions on the Peru shelf. Geological Society,
 1016 London, Special Publications **58**(1), 155–170.

1017 Eppley, R. W. (1992). Chlorophyll, photosynthesis and new production in the Southern
 1018 California Bight. *Prog. Oceanogr.* **30**(1-4), 117–150.

1019 Finney, B., and Huh, C. A. (1989). High resolution sedimentary records of heavy metals
 1020 from the Santa Monica and San Pedro Basins, California. *Marine Poll. Bull.* **20**(4),
 1021 181–187.

1022 Fishwick, M. P., P. N. Sedwick, M. C. Lohan, P. J. Worsfold, K. N. Buck, T. M. Church,
 1023 and S. J. Ussher (2014), The impact of changing surface ocean conditions on the
 1024 dissolution of aerosol iron, *Global Biogeochem. Cycles* **28**, 1235–1250.

1025 Francois R. (1988) A study on the regulation of the concentrations of some trace metals
 1026 (Rb, Sr, Zn, Pb, Cu, V, Cr, Ni, Mn and Mo) in Saanich Inlet Sediments, British
 1027 Columbia, Canada. *Mar. Geol.* **83**(1), 285–308.

1028 Fujii, T., Moynier, F., Abe, M., Nemoto, K., and Albarède, F. (2013). Copper isotope
 1029 fractionation between aqueous compounds relevant to low temperature geochemistry
 1030 and biology. *Geochim. Cosmochim. Acta* **110**, 29–44.

1031 Gaillardet J., Viers J. and Dupré B. (2003) Trace elements in river waters. *Treatise*
 1032 *Geochem.* **5**, 225–272.

1033 German C. R., Campbell A. C. and Edmond J. M. (1991) Hydrothermal scavenging at the
 1034 mid-Atlantic ridge: modification of trace element dissolved fluxes. *Earth Planet. Sci.*
 1035 *Lett.* **107**(1), 101–114.

- 1036 German C. R., Colley S., Palmer M. R., Khripounoff A. and Klinkhammer G. P. (2002)
1037 Hydrothermal plume-particle fluxes at 13 N on the East Pacific Rise. *Deep Sea Res.*
1038 **49**(11), 1921–1940.
- 1039 Goni, M. A., Aceves, H. L., Thunell, R. C., Tappa, E., Black, D., Astor, Y., ... and Muller-
1040 Karger, F. (2003). Biogenic fluxes in the Cariaco Basin: a combined study of sinking
1041 particulates and underlying sediments. *Deep Sea Res. Pt I.* **50**(6), 781–807.
- 1042 Gordon, A. S., Dyer, B. J., Kango, R. A., and Donat, J. R. (1996). Copper ligands isolated
1043 from estuarine water by immobilized metal affinity chromatography: temporal
1044 variability and partial characterization. *Mar. Chem.* **53**(3), 163–172.
- 1045 Haraldsson, C., and Westerlund, S. (1991). Total and suspended cadmium, cobalt, copper,
1046 iron, lead, manganese, nickel, and zinc in the water column of the Black Sea. In *Black*
1047 *Sea Oceanography* (pp. 161–172). Springer Netherlands.
- 1048 Hartnett, H. E., Keil, R. G., Hedges, J. I., and Devol, A. H. (1998). Influence of oxygen
1049 exposure time on organic carbon preservation in continental margin sediments. *Nature*
1050 **391**(6667), 572–575.
- 1051 Haug, G. H., Pedesen, T. F., Sigman, D. M., Calvert, S. E., Nielsen, B., and Peterson, L. C.
1052 (1998) Glacial/interglacial variations in production and nitrogen fixation in the
1053 Cariaco Basin during the last 580 kyr. *Paleoceanography* **13**(5), 427–432.
- 1054 Heggie, D., Klinkhammer, G., and Cullen, D. (1987). Manganese and copper fluxes from
1055 continental margin sediments. *Geochim. Cosmochim. Acta* **51**(5), 1059–1070.
- 1056 Huh, C. A., Small, L. F., Niemi, S., Finney, B. P., Hickey, B. M., Kachel, N. B., ... and
1057 Williams, P. M. (1990). Sedimentation dynamics in the Santa Monica-San Pedro
1058 Basin off Los Angeles: radiochemical, sediment trap and transmissometer studies.
1059 *Cont. Shelf Res.* **10**(2), 137–164.
- 1060 Jacobs L., Emerson S. and Huested S. (1987) Trace metal geochemistry in the Cariaco
1061 Trench. *Deep Sea Res.* **34**(5), 965–981.
- 1062 Jacobs L., Emerson S. and Skei J. (1985) Partitioning and transport of metals across the O₂
1063 H₂S interface in a permanently anoxic basin: Framvaren Fjord, Norway. *Geochim.*
1064 *Cosmochim. Acta* **49**(6), 1433–1444.
- 1065 Jacquot, J. E., and Moffett, J. W. (2015). Copper distribution and speciation across the
1066 International GEOTRACES Section GA03. *Deep Sea Res. Pt II* **116**, 187–207.
- 1067 Jeandel, C., Arsouze, T., Lacan, F., Techine, P., and Dutay, J. C. (2007). Isotopic Nd
1068 compositions and concentrations of the lithogenic inputs into the ocean: A
1069 compilation, with an emphasis on the margins. *Chem. Geol.* **239**(1), 156–164.
- 1070 Jickells T., An Z., Andersen K. K., Baker A., Bergametti G., Brooks N., Cao J., Boyd P.,
1071 Duce R. and Hunter K., et al. (2005) Global iron connections between desert dust,
1072 ocean biogeochemistry, and climate. *Science* **308**(5718), 67–71.
- 1073 Johnson, K., Purvis, G., Lopez-Capel, E., Peacock, C., Gray, N., Wagner, T., ... and
1074 Robertson, S. (2015). Towards a mechanistic understanding of carbon stabilization in
1075 manganese oxides. *Nat. Commun.* **6**, 7628.
- 1076 Jones, M. T., Pearce, C. R., Jeandel, C., Gislason, S. R., Eiriksdottir, E. S., Mavromatis,
1077 V., and Oelkers, E. H. (2012). Riverine particulate material dissolution as a significant
1078 flux of strontium to the oceans. *Earth Planet. Sci. Lett.* **355**, 51–59.

- 1079 Jones, M. T., Gislason, S. R., Burton, K. W., Pearce, C. R., Mavromatis, V., von
1080 Strandmann, P. A. P., and Oelkers, E. H. (2014). Quantifying the impact of riverine
1081 particulate dissolution in seawater on ocean chemistry. *Earth Planet. Sci. Lett.* **395**,
1082 91–100.
- 1083 Keeling, R. F., Körtzinger, A., and Gruber, N. (2010). Ocean deoxygenation in a warming
1084 world. *Marine Science* **2**.
- 1085 Klinkhammer, G. P. (1980). Early diagenesis in sediments from the eastern equatorial
1086 Pacific, II. Pore water metal results. *Earth Planet. Sci. Lett.* **49**(1), 81–101.
- 1087 Kuwabara, J. S., Topping, B. R., Coale, K. H., and Berelson, W. M. (1999). Processes
1088 affecting the benthic flux of trace metals into the water column of San Francisco Bay.
1089 In *US Geological Survey Toxic Substances Hydrology Program--Proceedings of the*
1090 *Technical Meeting, Charleston, South Carolina* **2**, 115–119.
- 1091 Laglera, L. M., and van den Berg, C. M. (2003). Copper complexation by thiol compounds
1092 in estuarine waters. *Mar. Chem.* **82**(1), 71–89.
- 1093 Lalonde, K., Mucci, A., Ouellet, A., and Gélinas, Y. (2012). Preservation of organic matter
1094 in sediments promoted by iron. *Nature* **483**(7388), 198–200.
- 1095 Leal, M. F. C., and Van Den Berg, C. M. (1998). Evidence for strong copper (I)
1096 complexation by organic ligands in seawater. *Aquat. Geochem.* **4**(1), 49–75.
- 1097 Li, C., Love, G. D., Lyons, T. W., Fike, D. A., Sessions, A. L., and Chu, X. (2010a). A
1098 stratified redox model for the Ediacaran ocean. *Science* **328**(5974), 80–83.
- 1099 Li, X., Gilhooly, W. P., III, Zerkle, A. L., Lyons, T. W., Farquhar, J., Werne, J. P., Varela,
1100 R., and Scranton, M. L. (2010b) Stable sulfur isotopes in the water column of the
1101 Cariaco Basin. *Geochim. Cosmochim. Acta* **74**(23), 6764–6778.
- 1102 Li, X., Cutter, G. A., Thunell, R. C., Tappa, E., Gilhooly, W. P., III, Lyons, T. W., Astor,
1103 Y., and Scranton, M. I. (2011) Particulate sulfur species in the water column of the
1104 Cariaco Basin. *Geochim. Cosmochim. Acta* **75**(1), 148–163.
- 1105 Little, S. H., Vance, D., Walker-Brown, C., and Landing, W. M. (2014a) The oceanic mass
1106 balance of copper and zinc isotopes, investigated by analysis of their inputs, and
1107 outputs to ferromanganese oxide sediments. *Geochim. Cosmochim. Acta* **125**, 673–
1108 693.
- 1109 Little, S. H., Sherman, D. M., Vance, D., and Hein, J. R. (2014b). Molecular controls on
1110 Cu and Zn isotopic fractionation in Fe–Mn crusts. *Earth Planet. Sci. Lett.* **396**, 213–
1111 222.
- 1112 Little, S. H., Vance, D., Lyons, T. W., and McManus, J. (2015). Controls on trace metal
1113 authigenic enrichment in reducing sediments: Insights from modern oxygen-deficient
1114 settings. *Am. J. Sci.* **315**(2), 77–119.
- 1115 Little, S. H., Vance, D., McManus, J., and Severmann, S. (2016). Key role of continental
1116 margin sediments in the oceanic mass balance of Zn and Zn isotopes. *Geology* **44**(3),
1117 207–210.
- 1118 Lucia, M., Campos, A. M., and van den Berg, C. M. (1994). Determination of copper
1119 complexation in sea water by cathodic stripping voltammetry and ligand competition
1120 with salicylaldoxime. *Anal. Chim. Acta* **284**(3), 481–496.

- 1121 Lückge, A., and Reinhardt, L. (2000) CTD measurements in the water column off Peru, in
1122 Kudrass, H. R., editor, Cruise report SO147 Peru Upwelling: Valparaiso-Callao,
1123 29.05-03.07, 35–37.
- 1124 Lyons, T. W. (1991) Upper Holocene sediments of the Black Sea: Summary of Leg 4 box
1125 cores (1988 Black Sea oceanographic expedition), in Izdar, E., and Murray, J. W.,
1126 editors, Black Sea Oceanography. NATO ASI Series **351**, 401–441.
- 1127 Lyons, T. W. (1997) Sulfur isotopic trends and pathways of iron sulfide formation in upper
1128 Holocene sediments of the anoxic Black Sea. *Geochim. Cosmochim. Acta* **61**(16),
1129 3367–3382.
- 1130 Lyons, T. W., and Berner, R. A. (1992) Carbon-sulfur-iron systematics of the uppermost
1131 deep-water sediments of the Black Sea. *Chem. Geol.* **99**(1–3), 1–27.
- 1132 Lyons, T. W., and Severmann, S. (2006) A critical look at iron paleoredox proxies: New
1133 insights from modern euxinic marine basins. *Geochim. Cosmochim. Acta* **70**(23),
1134 5698–5722.
- 1135 Lyons, T. W., Berner, R. A., and Anderson, R. F. (1993) Evidence for large pre-industrial
1136 perturbations of the Black Sea chemocline. *Nature* **365**, p. 538–540,
- 1137 Lyons, T. W., Werne, J. P., Hollander, D. J., and Murray, R. W. (2003) Contrasting sulfur
1138 geochemistry and Fe/Al and Mo/Al ratios across the last oxic-to-anoxic transition in
1139 the Cariaco Basin, Venezuela. *Chem. Geol.* **195**(1–4), 131–157.
- 1140 Lyons, T. W., Reinhard, C., and Planavsky, N. (2014) The rise of oxygen in Earth’s early
1141 ocean and atmosphere. *Nature* **506**, 307–315.
- 1142 Macías, D., Franks, P. J., Ohman, M. D., and Landry, M. R. (2012). Modeling the effects
1143 of coastal wind-and wind–stress curl-driven upwellings on plankton dynamics in the
1144 Southern California current system. *J. Marine Sys.* **94**, 107–119.
- 1145 Malouta, D. N., Gorsline, D. S., and Thornton, S. E. (1981). Processes and rates of recent
1146 (Holocene) basin filling in an active transform margin: Santa Monica Basin, California
1147 Continental Borderland. *J. Sed. Res.* **51**(4).
- 1148 Maréchal C. N., Telouk P. and Albarède F. (1999) Precise analysis of copper and zinc
1149 isotopic compositions by plasma-source mass spectrometry. *Chem. Geol.* **156**(1–4),
1150 251–273.
- 1151 Martinez, N. C., Murray, R. W., Thunell, R. C., Peterson, L. C., Muller-Karger, F.,
1152 Lorenzoni, L., ... and Varela, R. (2010). Local and regional geochemical signatures of
1153 surface sediments from the Cariaco Basin and Orinoco Delta, Venezuela. *Geology*
1154 **38**(2), 159–162.
- 1155 Mathur, R., Titley, S., Barra, F., Brantley, S., Wilson, M., Phillips, A., ... and Hart, G.
1156 (2009). Exploration potential of Cu isotope fractionation in porphyry copper
1157 deposits. *J. Geochem. Explor.* **102**(1), 1–6.
- 1158 Martin, J. M., and Meybeck, M. (1979). Elemental mass-balance of material carried by
1159 major world rivers. *Mar. Chem.* **7**(3), 173–206.
- 1160 McManus, J., Berelson, W. M., Coale, K. H., Johnson, K. S., and Kilgore, T. E. (1997).
1161 Phosphorus regeneration in continental margin sediments. *Geochim. Cosmochim. Acta*
1162 **61**(14), 2891–2907.
- 1163 McManus, J., Berelson, W. M., Klinkhammer, G. P., Johnson, K. S., Coale, K. H.,
1164 Anderson, R. F., ... and McCorkle, D. C. (1998). Geochemistry of barium in marine

- 1165 sediments: Implications for its use as a paleoproxy. *Geochim. Cosmochim. Acta*
1166 **62**(21), 3453–3473.
- 1167 McManus J., Berelson W., Severmann S., Poulson R., Hammond D., Klinkhammer G. and
1168 Holm C. (2006) Molybdenum and uranium geochemistry in continental margin
1169 sediments: paleoproxy potential. *Geochim. Cosmochim. Acta* **70**(18), 4643–4662.
- 1170 Moffett J. W. and Brand L. E. (1996) Production of strong, extracellular Cu chelators by
1171 marine cyanobacteria in response to Cu stress. *Limnol. Oceanogr.* **41**(3), 388–395.
- 1172 Moffett J. W. and Dupont C. (2007) Cu complexation by organic ligands in the sub-arctic
1173 NW Pacific and Bering Sea. *Deep Sea Res. Pt I* **54**(4), 586–595.
- 1174 Moffett, J. W., Zika, R. G., and Brand, L. E. (1990). Distribution and potential sources and
1175 sinks of copper chelators in the Sargasso Sea. *Deep Sea Res.* **37**(1), 27–36.
- 1176 Morford, J. L., and Emerson, S. (1999). The geochemistry of redox sensitive trace metals
1177 in sediments. *Geochim. Cosmochim. Acta* **63**(11), 1735–1750.
- 1178 Morris, A. W., Mantoura, R. F. C., Bale, A. J., and Howland, R. J. M. (1978). Very low
1179 salinity regions of estuaries: important sites for chemical and biological
1180 reactions. *Nature* **274**(5672), 678–680.
- 1181 Moynier, F., Vance, D., Fujii, T., Savage, P. (in press) The Isotope Geochemistry of Zinc
1182 and Copper. *Rev. Mineral. Geochem.* **82**.
- 1183 Muller, F. L. L., Gulin, S. B., and Kalvøy, A. (2001) Chemical speciation of copper and
1184 zinc in surface waters of the western Black Sea. *Mar. Chem.* **76**(4), 233–251.
- 1185 Muñoz, P., Lange, C. B., Gutiérrez, D., Hebbeln, D., Salamanca, M. A., Dezileau, L., ...
1186 and Benninger, L. K. (2004). Recent sedimentation and mass accumulation rates based
1187 on ²¹⁰Pb along the Peru–Chile continental margin. *Deep Sea Res. Pt II* **51**(20), 2523–
1188 2541.
- 1189 Murray, J. W., Jannasch, H. W., Honjo, S., Anderson, R. F., Reeburgh, W. S., Top, Z.,
1190 Friederich, G. E., Codispoti, L. A., and Izdar, E. (1989) Unexpected changes in the
1191 oxic/anoxic interface in the Black Sea. *Nature* **338**, 411–413
- 1192 Murray, J. W., Top, Z., and Özsoy, E. (1991). Hydrographic properties and ventilation of
1193 the Black Sea. *Deep Sea Res.* **38**, S663–S689.
- 1194 Nägler T., Neubert N., Böttcher M., Dellwig O. and Schnetger B. (2011) Molybdenum
1195 isotope fractionation in pelagic euxinia: evidence from the modern Black and Baltic
1196 Seas. *Chem. Geol.* **289**(1), 1–11.
- 1197 Neubert, N., Nägler, T. F., and Böttcher, M. E. (2008). Sulfidity controls molybdenum
1198 isotope fractionation into euxinic sediments: Evidence from the modern Black Sea.
1199 *Geology* **36**(10), 775–778.
- 1200 Nielsen, S. G., Rehkämper, M., Teagle, D. A., Butterfield, D. A., Alt, J. C., and Halliday,
1201 A. N. (2006). Hydrothermal fluid fluxes calculated from the isotopic mass balance of
1202 thallium in the ocean crust. *Earth Planet. Sci. Lett.* **251**(1), 120–133.
- 1203 Noffke, A., Hensen, C., Sommer, S., Scholz, F., Bohlen, L., Mosch, T., Graco, M., and
1204 Wallman, K. (2012) Benthic iron and phosphorus fluxes across the Peruvian oxygen
1205 minimum zone. *Limnol. Oceanogr.* **57**(3), 851–867.
- 1206 Oelkers, E. H., Jones, M. T., Pearce, C. R., Jeandel, C., Eiriksdottir, E. S., and Gislason, S.
1207 R. (2012). Riverine particulate material dissolution in seawater and its implications for
1208 the global cycles of the elements. *C. R. Geosci.* **344**(11), 646–651.

- 1209 Östlund, H.G. (1974). Expedition “Odysseus 65”: Radiocarbon age of Black Sea deep
1210 water. In *The Black Sea—Geology, chemistry, and biology* (eds. E.T. Degens and D.A.
1211 Ross). American Association of Petroleum Geologists Memoir **20**, 127–132.
- 1212 Özsoy, E., and Ünlüata, Ü. (1997). Oceanography of the Black Sea: a review of some
1213 recent results. *Earth-Sci. Rev.* **42**(4), 231–272.
- 1214 Peacock, C. L., and Moon, E. M. (2012). Oxidative scavenging of thallium by birnessite:
1215 explanation for thallium enrichment and stable isotope fractionation in marine
1216 ferromanganese precipitates. *Geochim. Cosmochim. Acta* **84**, 297–313.
- 1217 Pearce, C. R., Jones, M. T., Oelkers, E. H., Pradoux, C., and Jeandel, C. (2013). The effect
1218 of particulate dissolution on the neodymium (Nd) isotope and Rare Earth Element
1219 (REE) composition of seawater. *Earth Planet. Sci. Lett.* **369**, 138–147.
- 1220 Peterson, L. C, Haug, G. H., Murray, R. W., Yarincik, K. M., King, J. W., Bralower, T. J.,
1221 Kameo, K., Rutherford, S. D., and Pearce, R. B. (2000) Late Quaternary stratigraphy
1222 and sedimentation at Site 1002, Cariaco Basin (Venezuela). *Proc. ODP - Scientific*
1223 *Results* **165**, 85–99.
- 1224 Poulson-Brucker R., McManus J., Severmann S. and Berelson W. (2009) Molybdenum
1225 behavior during early diagenesis: insights from Mo isotopes. *Geochem. Geophys.*
1226 *Geosyst.* **10**(6), Q06010.
- 1227 Prospero, J. M. (1996). Saharan dust transport over the North Atlantic Ocean and
1228 Mediterranean: an overview. In *The impact of desert dust across the Mediterranean*
1229 (eds. S. Guerzoni and R. Chester). Springer, Netherlands. pp. 133–151.
- 1230 Reinhard, C. T., Planavsky, N. J., Wang, X., Fischer, W. W., Johnson, T. M., and Lyons,
1231 T. W. (2014) The isotopic composition of authigenic chromium in anoxic marine
1232 sediments: A case study from the Cariaco Basin. *Earth Planet. Sci. Lett.* **407**, 9–18.
- 1233 Resing, J. A., Sedwick, P. N., German, C. R., Jenkins, W. J., Moffett, J. W., Sohst, B. M.,
1234 and Tagliabue, A. (2015). Basin-scale transport of hydrothermal dissolved metals
1235 across the South Pacific Ocean. *Nature* **523**(7559), 200–203.
- 1236 Roshan, S., and Wu, J. (2015). The distribution of dissolved copper in the tropical-
1237 subtropical north Atlantic across the GEOTRACES GA03 transect. *Mar. Chem.* **176**,
1238 189–198.
- 1239 Roshan, S., Wu, J., and Jenkins, W. J. (2016). Long-range transport of hydrothermal
1240 dissolved Zn in the tropical South Pacific. *Mar. Chem.* **183**, 25–32.
- 1241 Rudnick R. and Gao S. (2003) Composition of the continental crust. *Treatise Geochem.* **3**,
1242 1–64.
- 1243 Ryan, B. M., Kirby, J. K., Degryse, F., Scheiderich, K., and McLaughlin, M. J. (2014).
1244 Copper isotope fractionation during equilibration with natural and synthetic ligands.
1245 *Environ. Sci. Technol.* **48**(15), 8620–8626.
- 1246 Saager, P. M., De Baar, H. J., & Howland, R. J. (1992). Cd, Zn, Ni and Cu in the Indian
1247 Ocean. *Deep Sea Res.* **39**(1), 9-35.
- 1248 Saager, P. M., Schijf, J., and de Baar, H. J. (1993). Trace-metal distributions in seawater
1249 and anoxic brines in the eastern Mediterranean Sea. *Geochim. Cosmochim. Acta* **57**(7),
1250 1419–1432.
- 1251 Sander, S. G., and Koschinsky, A. (2011). Metal flux from hydrothermal vents increased
1252 by organic complexation. *Nat. Geosci.* **4**(3), 145–150.

- 1253 Sansone, F. J., Graham, A. W., and Berelson, W. M. (2004). Methane along the western
1254 Mexican margin. *Limnol. Oceanogr.* **49**(6), 2242–2255.
- 1255 Sarbas, B., and Nohl, U. (2009) The GEOROC database – a decade of “online
1256 Geochemistry”. *Geochim. Cosmochim. Acta* **73**(13) Supplement, A1158.
- 1257 Sawlan, J. J., and Murray, J. W. (1983). Trace metal remobilization in the interstitial
1258 waters of red clay and hemipelagic marine sediments. *Earth Planet. Sci. Lett.* **64**(2),
1259 213–230.
- 1260 Schlitzer., R. (2015) Ocean Data View, odv.awi.de
- 1261 Schmitt, A. D., Chabaux, F., and Stille, P. (2003). The calcium riverine and hydrothermal
1262 isotopic fluxes and the oceanic calcium mass balance. *Earth Planet. Sci. Lett.* **213**(3),
1263 503–518.
- 1264 Scholz, F., Hensen, C., Noffke, A., Rohde, A., Liebetrau, V., and Wallmann, K. (2011)
1265 Early diagenesis of redox-sensitive trace metals in the Peru upwelling area – response
1266 to ENSO-related oxygen fluctuations in the water column. *Geochim. Cosmochim. Acta*
1267 **75**(22), 7257–7276.
- 1268 Scholz, F., McManus, J., and Sommer, S. (2013) The manganese and iron shuttle in a
1269 modern euxinic basin and implications for molybdenum cycling at euxinic ocean
1270 margins. *Chem. Geol.* **355**, 56–68.
- 1271 Scholz, F., Severmann, S., McManus, J., and Hensen, C. (2014) Beyond the Black Sea
1272 paradigm: The sedimentary fingerprint of an open-marine iron shuttle. *Geochim.*
1273 *Cosmochim. Acta* **127**, 368–380.
- 1274 Schunck, H., Lavik, G., Desai, D. K., Grøkopf, T., Kalvelage, T., Löscher, C. R., Paulmier,
1275 A., Contreras, S., Siegel, H., Holtappels, M., Rosenstiel, P., Schilhabel, M. B., Graco,
1276 M., Schmitz, R. A., Kuypers, M. M. M., and LaRoche, J. (2013) Giant Hydrogen
1277 Sulfide Plume in the Oxygen Minimum Zone off Peru Supports
1278 Chemolithoautotrophy. *PLoS ONE* **8**(8), e68661.
- 1279 Schwalbach, J. R., and Gorsline, D. S. (1985). Holocene sediment budgets for the basins of
1280 the California continental borderland. *J. Sed. Res.* **55**(6).
- 1281 Severmann, S., Lyons, T. W., Anbar, A., McManus, J., and Gordon, G. (2008) Modern
1282 iron isotope perspective on the benthic iron shuttle and the redox evolution of ancient
1283 oceans. *Geology* **36**(6), 487–490.
- 1284 Severmann, S., McManus, J., Berelson, W. M., and Hammond, D. E. (2010). The
1285 continental shelf benthic iron flux and its isotope composition. *Geochim. Cosmochim.*
1286 *Acta* **74**(14), 3984–4004.
- 1287 Shank, G. C., Skrabal, S. A., Whitehead, R. F., and Kieber, R. J. (2004a). Strong copper
1288 complexation in an organic-rich estuary: the importance of allochthonous dissolved
1289 organic matter. *Mar. Chem.* **88**(1), 21–39.
- 1290 Shank, G. C., Skrabal, S. A., Whitehead, R. F., Avery, G. B., and Kieber, R. J. (2004b).
1291 River discharge of strong Cu-complexing ligands to South Atlantic Bight waters. *Mar.*
1292 *Chem.* **88**(1), 41–51.
- 1293 Shaw, T. J., Gieskes, J. M., and Jahnke, R. A. (1990) Early diagenesis in differing
1294 depositional environments: The response of transition metals in pore water. *Geochim.*
1295 *Cosmochim. Acta* **54**(5), 1233–1246.

- 1296 Sherman, D. M. (2013). Equilibrium isotopic fractionation of copper during
1297 oxidation/reduction, aqueous complexation and ore-forming processes: Predictions
1298 from hybrid density functional theory. *Geochim. Cosmochim. Acta* **118**, 85–97.
- 1299 Sholkovitz, E. R., P. N. Sedwick, and T. M. Church (2010). On the fractional solubility of
1300 copper in marine aerosols: Toxicity of aeolian copper revisited, *Geophys. Res. Lett.*
1301 **37**, L20601, doi:10.1029/2010GL044817 .
- 1302 Silverberg, N., Martínez, A., Aguiñiga, S., Carriquiry, J. D., Romero, N., Shumilin, E., and
1303 Cota, S. (2004). Contrasts in sedimentation flux below the southern California Current
1304 in late 1996 and during the El Niño event of 1997–1998. *Estuar. Coast. Shelf Sci.*
1305 **59**(4), 575–587.
- 1306 Skrabal, S. A., Donat, J. R., and Burdige, D. J. (1997). Fluxes of copper-complexing
1307 ligands from estuarine sediments. *Limnol. Oceanogr.* **42**(5), 992–996.
- 1308 Skrabal, S. A., Donat, J. R., and Burdige, D. J. (2000). Pore water distributions of
1309 dissolved copper and copper-complexing ligands in estuarine and coastal marine
1310 sediments. *Geochim. Cosmochim. Acta* **64**(11), 1843–1857.
- 1311 Smith, R. W., Bianchi, T. S., Allison, M., Savage, C., and Galy, V. (2015). High rates of
1312 organic carbon burial in fjord sediments globally. *Nat. Geosci.* **8**(6), 450–453.
- 1313 Stott, L. D., Berelson, W., Douglas, R., and Gorsline, D. (2000). Increased dissolved
1314 oxygen in Pacific intermediate waters due to lower rates of carbon oxidation in
1315 sediments. *Nature* **407**(6802), 367–370.
- 1316 Stramma, L., Johnson, G. C., Sprintall, J., and Mohrholz, V. (2008). Expanding oxygen-
1317 minimum zones in the tropical oceans. *Science* **320**(5876), 655–658.
- 1318 Takano, S., Tanimizu, M., Hirata, T., and Sohrin, Y. (2014). Isotopic constraints on
1319 biogeochemical cycling of copper in the ocean. *Nat. commun.* **5**, 5663.
- 1320 Tankéré S. P. C., Muller F. L. L., Burton J. D., Statham P. J., Guieu C. and Martin J. M.
1321 (2001) Trace metal distributions in shelf waters of the northwestern black sea. *Cont.*
1322 *Shelf Res.* **21**(13–14), 1501–1532.
- 1323 Taylor S. and McLennan S. (1985). The continental crust: its composition and evolution.
- 1324 Thompson, C. M., and Ellwood, M. J. (2014). Dissolved copper isotope biogeochemistry
1325 in the Tasman Sea, SW Pacific Ocean. *Mar. Chem.* **165**, 1–9.
- 1326 Thunell, R. C., Tappa, E., and Anderson, D. M. (1995). Sediment fluxes and varve
1327 formation in Santa Barbara Basin, offshore California. *Geology* **23**(12), 1083–1086.
- 1328 Thunell, R. C., Varela, R., Llano, M., Collister, J., Karger, F. M., and Bohrer, R. (2000).
1329 Organic carbon fluxes, degradation, and accumulation in an anoxic basin: sediment
1330 trap results from the Cariaco Basin. *Limnol. Oceanogr.* **45**(2), 300–308.
- 1331 Tipper E., Gaillardet J., Galy A., Louvat P., Bickle M. and Capmas F. (2010) Calcium
1332 isotope ratios in the world’s largest rivers: a constraint on the maximum imbalance of
1333 oceanic calcium fluxes. *Global Biogeochem. Cycles* **24**(3).
- 1334 Tipper E., Galy A., Gaillardet J., Bickle M., Elderfield H. and Carder E. (2006) The
1335 magnesium isotope budget of the modern ocean: constraints from riverine magnesium
1336 isotope ratios. *Earth Planet. Sci. Lett.* **250**(1), 241–253.
- 1337 Tribovillard, N., Hatem, E., Averbuch, O., Barbecot, F., Bout-Roumazelles, V., and
1338 Trentesaux, A. (2015). Iron availability as a dominant control on the primary

- 1339 composition and diagenetic overprint of organic-matter-rich rocks. *Chem. Geol.* **401**,
1340 67–82.
- 1341 Trocine R. P. and Trefry J. H. (1988) Distribution and chemistry of suspended particles
1342 from an active hydrothermal vent site on the Mid-Atlantic Ridge at 26 N. *Earth*
1343 *Planet. Sci. Lett.* **88**(1–2), 1–15.
- 1344 Vance D., Archer C., Bermin J., Perkins J., Statham P. J., Lohan M. C., Ellwood M. J. and
1345 Mills R. A. (2008) The copper isotope geochemistry of rivers and the oceans. *Earth*
1346 *Planet. Sci. Lett.* **274**(1–2), 204–213.
- 1347 Vance, D., Little, S. H., Archer, C., Cameron, V., Andersen, M. B., Rijkenberg, M. J., and
1348 Lyons, T. W. (2016a). The oceanic budgets of nickel and zinc isotopes: the importance
1349 of sulfidic environments as illustrated by the Black Sea. *Phil. Trans. R. Soc. A*,
1350 **374**(2081), 20150294.
- 1351 Vance, D., Matthews, A., Keech, A., Archer, C., Hudson, G., Pett-Ridge, J., and
1352 Chadwick, O. A. (2016b). The behaviour of Cu and Zn isotopes during soil
1353 development: Controls on the dissolved load of rivers. *Chem. Geol.* **445**, 36–53.
- 1354 van Geen, A., Zheng, Y., Bernhard, J. M., Cannariato, K. G., Carriquiry, J., Dean, W. E., ...
1355 and Pike, J. (2003). On the preservation of laminated sediments along the western
1356 margin of North America. *Paleoceanography* **18**(4).
- 1357 Wasylenki, L. E., Weeks, C. L., Bargar, J. R., Spiro, T. G., Hein, J. R., and Anbar, A. D.
1358 (2011). The molecular mechanism of Mo isotope fractionation during adsorption to
1359 birnessite. *Geochim. Cosmochim. Acta* **75**(17), 5019–5031.
- 1360 Welch, S. A., Beard, B. L., Johnson, C. M., and Braterman, P. S. (2003). Kinetic and
1361 equilibrium Fe isotope fractionation between aqueous Fe (II) and Fe (III). *Geochim.*
1362 *Cosmochim. Acta* **67**(22), 4231–4250.
- 1363 Wells, M. L., Kozelka, P. B., and Bruland, K. W. (1998). The complexation of dissolved
1364 Cu, Zn, Cd and Pb by soluble and colloidal organic matter in Narragansett Bay, RI.
1365 *Mar. Chem.* **62**(3), 203–217.
- 1366 Werne, J. P., Lyons, T. W., Hollander, D. J., Formolo, M. J., and Sinninghe Damsté, J. S.
1367 (2003) Reduced sulfur in euxinic sediments of the Cariaco Basin: sulfur isotope
1368 constraints on organic sulfur formation. *Chem. Geol.* **195**(1–4), 159–179.
- 1369 Windom, H., Wallace, G., Smith, R., Dudek, N., Maeda, M., Dulmage, R., and Storti, F.
1370 (1983). Behavior of copper in southeastern United States estuaries. *Mar. Chem.* **12**(2-
1371 3), 183–193.
- 1372 Xue, Z., Rehkämper, M., Horner, T. J., Abouchami, W., Middag, R., van de Flierdt, T., and
1373 de Baar, H. J. (2013). Cadmium isotope variations in the Southern Ocean. *Earth*
1374 *Planet. Sci. Lett.* **382**, 161–172.
- 1375 Yarincik, K. M., Murray, R. W., and Peterson, L. C. (2000). Climatically sensitive eolian
1376 and hemipelagic deposition in the Cariaco Basin, Venezuela, over the past 578,000
1377 years: Results from Al/Ti and K/Al. *Paleoceanography* **15**(2), 210–228.
- 1378 Zheng, Y., Anderson, R. F., van Geen, A., and Kuwabara, J. (2000). Authigenic
1379 molybdenum formation in marine sediments: a link to pore water sulfide in the Santa
1380 Barbara Basin. *Geochim. Cosmochim. Acta* **64**(24), 4165–4178.
- 1381 Zhu, P., and Macdougall, J. D. (1998). Calcium isotopes in the marine environment and the
1382 oceanic calcium cycle. *Geochim. Cosmochim. Acta* **62**(10), 1691–1698.

1383 Zhu, X. K., Guo, Y., Williams, R. J. P., O'nions, R. K., Matthews, A., Belshaw, N. S., ...
1384 and Salvato, B. (2002). Mass fractionation processes of transition metal isotopes.
1385 *Earth Planet. Sci. Lett.* **200**(1), 47–62.