



Copper isotope signatures in modern marine sediments

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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 SRM976). 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.

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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; Bruland and Lohan, 2003; Shank et al., 2004a,b; 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;

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Thompson and Ellwood, 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; Wasylenko 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 modern 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, 1991; Tankéré et al., 2001), and variable Cu enrichments have previously been observed in reducing sediments (e.g., Francois, 1988; Calvert and Pedersen, 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 and Ellwood, 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 Husted, 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).

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