

# The oceanic mass balance of copper and zinc isotopes, investigated by analysis of their inputs, and outputs to ferromanganese oxide sediments <sup>☆</sup>

S.H. Little <sup>a,b,\*</sup>, D. Vance <sup>a,b</sup>, C. Walker-Brown <sup>c</sup>, W.M. Landing <sup>d</sup>

<sup>a</sup> Bristol Isotope Group, School of Earth Sciences, University of Bristol, Wills Memorial Building, Queen's Rd, Bristol BS8 1RJ, UK

<sup>b</sup> Institute of Geochemistry and Petrology, Department of Earth Sciences, NW D81.4, Clausiusstrasse 25, 8092 Zürich, Switzerland

<sup>c</sup> School of Environmental Sciences, University of East Anglia, Norwich Research Park, Norwich NR4 7TJ, UK

<sup>d</sup> Department of Earth, Ocean, and Atmospheric Science, Florida State University, 117N. Woodward Ave., Tallahassee, FL, USA

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## Abstract

The oceanic biogeochemical cycles of the transition metals have been eliciting considerable attention for some time. Many of them have isotope systems that are fractionated by key biological and chemical processes so that significant information about such processes may be gleaned from them. However, for many of these nascent isotopic systems we currently know too little of their modern oceanic mass balance, making the application of such systems to the past speculative, at best. Here we investigate the biogeochemical cycling of copper (Cu) and zinc (Zn) isotopes in the ocean. We present estimates for the isotopic composition of Cu and Zn inputs to the oceans based on new data presented here and published data. The bulk isotopic composition of dissolved Cu and Zn in the oceans ( $\delta^{65}\text{Cu} \sim +0.9\text{‰}$ ,  $\delta^{66}\text{Zn} \sim +0.5\text{‰}$ ) is in both cases heavier than their respective inputs (at around  $\delta^{65}\text{Cu} = +0.6\text{‰}$  and  $\delta^{66}\text{Zn} = +0.3\text{‰}$ , respectively), implying a marine process that fractionates them and a resulting isotopically light sedimentary output. For the better-known molybdenum isotope system this is achieved by sorption to Fe–Mn oxides, and this light isotopic composition is recorded in Fe–Mn crusts. Hence, we present isotopic data for Cu and Zn in three Fe–Mn crusts from the major ocean basins, which yield  $\delta^{65}\text{Cu} = 0.44 \pm 0.23\text{‰}$  (mean and 2SD) and  $\delta^{66}\text{Zn} = 1.04 \pm 0.21\text{‰}$ . Thus for Cu isotopes output to particulate Fe–Mn oxides can explain the heavy isotopic composition of the oceans, while for Zn it cannot. The heavy Zn in Fe–Mn crusts (and in all other authigenic marine sediments measured so far) implies that a missing light sink is still to be located. These observations are some of the first to place constraints on the modern oceanic mass balance of Cu and Zn isotopes.

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## 1. INTRODUCTION

The isotope systems of the transition metals are increasingly being developed in the Earth Sciences (e.g. Albarède, 2004; Anbar and Rouxel, 2007). The biogeochemistry of these elements suggests two obvious potential applications of their isotope systems in the marine realm. Firstly, many trace metals are well-known to be biologically-active (Bruland and Lohan, 2003; Morel and Price, 2003) so that the attendant isotopic fractionations (e.g. Beard et al., 1999; John et al., 2007a; Navarrete et al., 2011) may have some utility in understanding the detailed processes controlling

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\* Corresponding author at: Institute of Geochemistry and Petrology, Department of Earth Sciences, NW D81.4, Clausiusstrasse 25, 8092 Zürich, Switzerland. Tel.: +41 44 632 6455.

E-mail address: [susan.little@erdw.ethz.ch](mailto:susan.little@erdw.ethz.ch) (S.H. Little).

their biological cycling on the modern and ancient Earth. Secondly, the speciation and oxidation state of the transition metals in the oceans is redox-sensitive, and this is important to their biogeochemical cycling because of the control on the reactivity of the metals concerned, such as their solubility or their susceptibility to scavenging (e.g. [Algeo and Maynard, 2008](#); [Helz et al., 2011](#)). Given that speciation and oxidation state changes also induce isotopic fractionations, a second potential application of the new isotope systems is in tracking past ocean redox state. With regard to the latter potential application, most progress has been made with molybdenum isotopes, where the speciation in oxic versus euxinic (free H<sub>2</sub>S-bearing) aqueous solutions is fundamentally different, where the rate of output is controlled by this speciation, and where speciation-related isotopic fractionations are imprinted on sediments, both ancient and modern (reviews in: [Anbar and Rouxel, 2007](#); [Scott and Lyons, 2012](#)).

However, the Mo isotope system also highlights complexities in using isotope systematics to probe past redox conditions, for example with regard to the intermediate isotopic fractionations observed in both anoxic but non-euxinic ([McManus et al., 2006](#); [Poulson et al., 2006](#); [Siebert et al., 2006](#); [Poulson-Brucker et al., 2009](#); [Scott and Lyons, 2012](#)) and mildly euxinic ([Nägler et al., 2011](#)) settings. There is a clear need, therefore, to harness the potentially complementary information that may be held in less-developed transition metal isotopic systems. Moreover, though Mo is certainly a biologically-active transition metal, its direct involvement in biology is not quantitatively important to its oceanic biogeochemical cycling ([Nakagawa et al., 2012](#)). In contrast it is well-known that biological uptake and regeneration determines Zn depth profiles in the modern ocean ([Bruland and Lohan, 2003](#)), and early isotopic data ([Bermin et al., 2006](#); [John et al., 2007a](#); [Peel et al., 2009](#); [Zhao et al., in press](#)) hints that this may also be the case for the Zn isotopic system. Copper distributions in the modern ocean are thought to be strongly influenced by both biological recycling and scavenging processes ([Bruland and Lohan, 2003](#)), and the first data for Cu isotopes in rivers and oceans has suggested that organic complexes with biologically-produced ligands are an important control on dissolved oceanic isotopic compositions ([Vance et al., 2008](#)). It seems likely, therefore, that the isotopic systems of Cu and Zn could be useful in understanding the biogeochemical cycling of these metals in the modern ocean (e.g. [Albarède, 2004](#)), with applications to the quantification of key processes in the past ocean through their analysis in sedimentary outputs.

The development of Cu and Zn isotopes as sources of biogeochemical information, however, requires a much better understanding of the modern oceanic isotopic mass balance of these two metals than we currently have. This paper adopts a two-pronged approach to bridging this gap. We present new isotopic data for riverine Zn isotopes, and for both Cu and Zn isotopes in Atlantic marine aerosol, allowing us to summarise the current state of knowledge with respect to the inputs of Cu and Zn to the modern ocean. The main outcome of this, as has already been suggested for Cu isotopes ([Vance et al., 2008](#)), is that there

must be isotopic fractionation during marine cycling, such that the isotopic composition of Cu and Zn in the dissolved oceanic pool are driven away from the input composition by one or more of the sedimentary outputs. Similar patterns of marine source-sink isotopic fractionation have previously been observed for other metal isotope systems, including Mg and Ca ([Tipper et al., 2006, 2010](#)), and the better established transition metal isotope system of Mo, with the isotopic mass balance in this case closed by fractionation during sorption to Fe–Mn oxides ([Siebert et al., 2003](#)). In pursuit of an understanding of this issue, then, the second part of this study begins to address the nature of the outputs. Cu and Zn isotopic analyses are reported from the sedimentary record of one of the main sinks, the Fe–Mn crust record of sorption to particulate Fe–Mn oxides. Finally, we assess the implications of the new data for the oceanic mass balance of Cu and Zn and their isotopes.

## 2. BACKGROUND: THE MARINE BIOGEOCHEMISTRY OF CU AND ZN

The interpretation of much of the isotopic data presented later in this paper will be grounded in what we know of the marine chemistry of Cu and Zn, so before proceeding to those data we first present a short review of the most important aspects of that marine chemistry, which will serve as a template for the interpretation of the isotopic data.

Copper and Zn are both strongly cycled between the surface ocean and the deep (e.g. [Boyle et al., 1977b](#); [Bruland, 1980](#)). Zn concentrations in the deep Atlantic and Pacific are around 2 and 10 nM respectively (e.g. [Bruland, 1980](#); [Bruland and Franks, 1983](#); [Bruland et al., 1994](#); [Boyle et al., 2012](#)), but are often <0.1 nM in the photic zone (e.g. [Bruland, 1980](#); [Lohan et al., 2002](#)). The strong depletion of Zn in the surface ocean has been attributed to biological uptake (e.g. [Morel and Price, 2003](#)), with regeneration in the deep ocean driving up concentrations. Zn concentration profiles, however, exhibit deeper regeneration maxima than the major labile nutrients and closely resemble those of dissolved silica (e.g. [Bruland, 1980](#)). Copper concentration profiles also show surface depletion and deep enrichment but, whereas the deep/surface concentration ratio can be several hundred for Zn, it is never more than about 5–10 for Cu. In addition, depth profiles for Cu are also much more linear than those of both Zn and the major nutrients (e.g. [Boyle et al., 1977b](#); [Bruland, 1980](#); [Martin et al., 1993](#)). [Bruland and Lohan \(2003\)](#) attribute this to the particle reactivity of Cu, and the importance of scavenging (in addition to biological recycling) in controlling dissolved Cu distributions.

A key aspect of the dissolved chemistry of both Cu and Zn is organic complexation. Copper is well-known to be strongly complexed to organic ligands (e.g. [Coale and Bruland, 1988](#); [Moffett and Dupont, 2007](#)) such that <0.1% of the total dissolved fraction (operationally-defined as passing through a 0.2 or 0.4 μm filter) is free Cu<sup>2+</sup>. Culture experiments have shown that the ligands that bind Cu are produced by a range of phytoplankton groups, including cyanobacteria ([Moffett and Brand, 1996](#); [Croot et al.,](#)

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