

# Global Biogeochemical Cycles<sup>®</sup>

# **RESEARCH ARTICLE**

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#### **Key Points:**

- Multiple processes influence the distributions of Cu isotope compositions across the North Atlantic (GEOVIDE cruise, GEOTRACES GA01)
- Nd<sub>xs</sub>-8<sup>65</sup>Cu covariation highlights the importance of lithogenic particle dissolution as a source of light Cu
- Continental margins, under the influence of internal tides, contribute significantly to the missing source of light Cu in the ocean

#### **Supporting Information:**

Supporting Information may be found in the online version of this article.

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# Controls on Dissolved Cu Concentrations and Isotopes in the North Atlantic: The Importance of Continental Margins

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Abstract Copper (Cu) is a marine micronutrient whose distribution and budget remain incompletely understood. Here, we present a section of dissolved Cu isotope compositions ( $\delta^{65}$ Cu) across the North Atlantic (GEOVIDE cruise, GEOTRACES GA01). High  $\delta^{65}$ Cu are observed in surface waters and co-vary with carbon uptake rates, indicating light Cu removal by biological activity or complexation of heavy Cu by organic ligands. Beneath the surface, low  $\delta^{65}$ Cu may be partially caused by remineralization. Below 1,500 m, an increase in  $\delta^{65}$ Cu points to removal by particulate scavenging. At greater depths, reversible scavenging, driven by high vertical particulate exports, could explain the increase in Cu concentrations between the surface and deep ocean, mostly in the eastern part of the transect. Investigation of external sources and sinks reveals that anthropogenic aerosols and benthic processes locally supply isotopically light Cu to the ocean, whilst hydrothermal activity above the Reykjanes ridge does not seem to represent a significant source. A striking feature is the low  $\delta^{65}$ Cu observed between 300 and 1,500 m from the Iberian margin to the Icelandic basin, which coincides with elevated non-conservative dissolved neodymium fractions ( $Nd_{x_s}$ ). This comparison suggests that margin inputs are a source of light Cu to the ocean, and that this Cu can be transported over long distances. The Iberian margin is a hotspot of internal tides and their energy triggers sediment resuspension, leading to particle dissolution and Cu release. These results suggest that continental margins contribute significantly to the missing source of light Cu in the ocean.

**Plain Language Summary** Copper (Cu) is an essential micronutrient for living organisms in the ocean, but its marine cycle is not yet fully understood. Here, we use both concentrations and isotopes to better constrain the processes and sources influencing Cu in the North Atlantic. We find that microorganisms in the surface ocean take up Cu along with carbon, as shown by the variation of Cu isotopes. Other processes at depth, such as particle remineralization and (reversible) scavenging onto particles, can also change Cu distributions. We identified features indicating sources of Cu in the ocean: atmospheric deposition, sediments and continental margins. A key aspect of this study is the use of a neodymium tracer to highlight the Iberian margin as a source of Cu to the ocean. Overall, the margin inputs could contribute significantly to the missing source of Cu in the ocean.

#### 1. Introduction

As a cofactor in a number of enzymes, Cu is an essential micronutrient for marine productivity (Twining & Baines, 2013). It is required in many metabolic processes such as the transport of electrons in photosynthetic and respiratory processes (e.g., Chadd et al., 1996; Peers & Price, 2006), the breakdown of toxic oxygen radical species (e.g., Rae et al., 1999), the regulation of Fe uptake (e.g., Annett et al., 2008; Maldonado et al., 2006), and in the promotion of several denitrification steps (e.g., Casciotti & Ward, 2001; Granger & Ward, 2003; Molfett et al., 2012). Yet, Cu is also harmful to phytoplankton in its free, bioavailable form (Cu<sup>2+</sup>), with toxicity thresholds varying between marine species (e.g., Ridge et al., 2008; Sunda & Lewis, 1978). Cyanobacteria are the most sensitive phytoplankton species to Cu<sup>2+</sup> toxicity, with a reproduction rate that is halved at Cu<sup>2+</sup>concentrations of about  $10^{-12}$  mol/L. In contrast, there is no change for most eukaryotes at  $10^{-11}$  mol/L (Brand et al., 1986). As a protective mechanism, phytoplankton species release strong organic ligands that form complexes with Cu<sup>2+</sup>. In the ocean, >99% of dissolved Cu is organically complexed, thereby maintaining Cu<sup>2+</sup> concentrations at around  $10^{-13}$  mol/L (e.g., Coale & Bruland, 1988; Gerringa et al., 1995). Copper is thus described as a "Goldilocks element," with concentrations that should neither be too low nor too high for phytoplankton requirements (Bruland & Lohan, 2003).

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This biological role influences Cu distributions, with lower concentrations observed in surface waters (Boyle et al., 1977). However, unlike other micronutrients, Cu concentrations increase linearly with depth rather than following a typical nutrient-like distribution. This has been attributed to biological export combined with reversible scavenging and/or bottom sediment inputs (Boyle et al., 1977; Bruland, 1980; Little et al., 2013, 2018; Richon & Tagliabue, 2019; Roshan & Wu, 2015; Takano et al., 2014).

Previous theoretical and experimental studies have shown that Cu isotopes fractionate because of a number of low-temperature processes (changes in redox state, ligand complexation, adsorption onto/desorption from particles, cellular uptake; Moynier et al., 2017). But Cu isotope data are scarce and gaps remain in our knowledge of the Cu cycle, notably including an apparently imbalanced marine isotope budget. The isotope compositions of the deep ocean and all known sources are heavier than the known outputs. Moreover, the calculated input flux is too small to balance the output flux, pointing to a missing light source (Little et al., 2017). Recent studies have proposed that the dissolution of lithogenic materials could solve the mass balance problem by delivering light Cu to the ocean (Liang et al., 2023; Little et al., 2018; Roshan et al., 2020). Supply of this isotopically light Cu seems to occur in coastal regions globally (Takano et al., 2022), suggesting a potential particulate source originating from anthropogenic aerosols (Takano et al., 2020), continental slopes, or large estuaries (Little et al., 2018). Such land-ocean transfer would be consistent with what is observed for other tracers such as neodymium (Nd), with net inputs resulting from particle-dissolved exchange processes, named "Boundary Exchange" (Jeandel et al., 2011; Lacan & Jeandel, 2001; Tachikawa et al., 2003).

The North Atlantic is a relatively small ocean basin and is known to receive large lithogenic inputs advected from continental margins and enhanced by atmospheric deposition (Lagarde et al., 2020; Ohnemus & Lam, 2015). Being located between North America and Europe, the North Atlantic is also expected to be under the influence of anthropogenic inputs. Moreover, the North Atlantic witnesses one of the most productive phytoplankton blooms in the world ocean (Longhurst, 2010). Thus, altogether, this area is of great interest for studying the processes influencing the distributions of Cu and its isotopes. The influence of biological processes and (reversible) scavenging on Cu distributions is discussed here in light of other data from the GEOVIDE cruise. The different sources of Cu along this transect are also investigated. A special emphasis is placed on the importance of continental margins under the forcing of internal tides in supplying both Cu and specifically lithogenic tracers, such as Nd, to the ocean.

#### 2. Methods

#### 2.1. Study Area and Sampling

Samples were collected at 6 stations along the GEOTRACES GA01 section (GEOVIDE cruise in May-June 2014; R/V *Pourquoi Pas?*) for measurement of dissolved Cu concentrations and isotope compositions (expressed as  $\delta^{65}$ Cu). The sampling spanned different biogeochemical regions (Sarthou et al., 2018; Figure 1). In the oligotrophic Iberian basin, station 13 is under the influence of the Iberian margin, which has been described as a significant source of lithogenic material (Gourain et al., 2019; Lagarde et al., 2020). In the west European and Icelandic basins, stations 21, 32 and 38 were sampled during phytoplankton bloom development (Lemaitre, Planchon, et al., 2018). The latter station is also located above the Reykjanes Ridge, where hydrothermal activity may influence trace metal distributions (Gourain et al., 2019; Lemaitre, de Souza, et al., 2020; Le Roy et al., 2018; Tonnard et al., 2020). In the Irminger basin, station 44 was sampled close to the bloom maximum, whereas station 69 in the Labrador basin was sampled at the onset of the bloom (Lemaitre, Planchon, et al., 2018). The Greenland and Newfoundland margins exert no influence on ocean chemistry at these stations (Gourain et al., 2019; Lagarde et al., 2020).

At each station, samples were collected using a clean rosette equipped with cleaned 12L GO-FLO bottles, following the GEOTRACES cookbook (Cutter et al., 2017). The rosette was deployed on a 14 mm Kevlar cable with a dedicated, custom-designed, clean winch. Immediately after recovery, the GO-FLO bottles were individually covered at each end with plastic bags to minimize contamination. Bottles were then transferred into a clean container (class-100) for sampling. Seawater samples were filtered through 0.45  $\mu$ m polyethersulfone filters (Pall, SuporTM) mounted in Swinnex polypropylene filter holders (Millipore). Filtrates of either 1 or 4 L were collected in acid-cleaned polyethylene bottles. More details of the sampling procedures can be found in Gourain et al. (2019).



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Figure 1. Map of the GEOVIDE transect with station locations (large symbols) and corresponding depth profiles of dissolved Cu concentrations and isotope compositions ( $\delta^{65}$ Cu). The shaded gray band shows the average Cu isotope composition in the global deep ocean ( $\delta^{65}$ Cu = 0.66 ± 0.08 %, Moynier et al., 2017).

#### 2.2. Analytical Methodology

The methods used here have been described previously (Little et al., 2018; Sun et al., 2021) and only a brief summary is given here. All work was performed in trace metal clean conditions using clean Savillex PFA labware, ultrapure water ( $\geq 18.2$  M $\Omega$ .cm) and ultrapure or double-distilled acids and reagents. Copper was preconcentrated from up to 2 L of pH 2 acidified seawater with the use of an ethylenediaminetriacetic acid chelating resin, sold commercially as Nobias PA-1 (Hitachi Technologies; Sohrin et al., 2008; Takano et al., 2013) to extract the trace metal load from the seawater matrix (Archer et al., 2020; Lemaitre, de Souza, et al., 2020, 2022; Little et al., 2018; Vance et al., 2016; Wang et al., 2019). Samples were first adjusted to pH  $5.0 \pm 0.3$  using an ammonium acetate buffer. After loading on the columns, matrix cations, principally sodium and magnesium, were eluted with the buffer, followed by the elution of the trace metals using 1 mol/L nitric acid

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 $(HNO_3)$ . To separate individual transition metals from each other, the pre-concentrated samples were passed through an anion-exchange column (Bio-Rad AG MP-1M resin) using procedures described in detail previously (Archer & Vance, 2004; Little et al., 2014). This produces relatively pure Cu fractions, which were further purified by a second pass through this anion column.

Isotope analyses were performed using a Thermo-Scientific NeptunePlus multi-collector inductively coupledplasma mass spectrometer (MC-ICP-MS) at ETH Zurich. Copper solutions were introduced into the mass spectrometer in 0.3 mol/L HNO<sub>3</sub> via a Savillex C-Flow PFA nebulizer (50  $\mu$ L/min) attached to a quartz cyclonic spray chamber. Sodium and magnesium concentrations in the final solutions were measured before the isotope analyses. In all cases, the resultant interferences from argide molecular species involving these elements were negligible.

All isotope compositions are given in standard notation relative to the NIST SRM 976 Cu standard as follows:

$$\delta^{65} \text{Cu} (\%) = \left[ \frac{\left( {}^{65} \text{Cu} / {}^{63} \text{Cu} \right)_{\text{sample}}}{\left( {}^{65} \text{Cu} / {}^{63} \text{Cu} \right)_{\text{NIST SRM 976}}} - 1 \right] \times 1000$$

The long-term reproducibility of isotope analyses was  $\pm 0.06 \%$  for the Cu isotope system. This was assessed over the course of this and parallel studies through repeat measurements of a secondary standard (pure Cu ICP standard solution, supplied by A. Matthews, Hebrew University, Jerusalem), giving  $\delta^{65}$ Cu<sub>NIST SRM976</sub> =  $\pm 0.11 \pm 0.06 \%$ (2SD, n = 174 over 30 months). These values compare well with those published:  $\delta^{65}$ Cu<sub>NIST SRM976</sub> =  $\pm 0.10 \pm 0.06 \%$  (Asael et al., 2007). Full duplicate analyses were carried out for 14 GEOVIDE samples. Results were consistent with long-term standard reproducibility. Differences between these replicates averaged  $0.09 \pm 0.15 \%$  ( $\pm 2SD$ ) for Cu isotopes. Procedural blanks were determined from the same chemical separation protocol as for samples (i.e., acidified to pH ~ 2 and passed through the column chromatographic procedure) using 1L of ultra-pure Milli-Q water (>18.2 M\Omega.cm) as the "sample." These procedural blanks were consistently determined to be <1 ng for Cu (including the inventory of Cu in the Milli-Q water) and are therefore negligible compared to the typical sample size (10–120 ng, average of 40 ng). Concentrations of Cu were measured at the same time as isotopes by comparison of sample signals to those of standards of known concentration. Good agreement has been observed between this method and isotope dilution followed by SF-ICP-MS measurements (Little et al., 2018).

Our samples were not UV irradiated prior to analysis but were stored at low pH for more than 3-4 years, which is as effective as UV irradiation (Posacka et al., 2017). Our GEOVIDE Cu isotope data have been approved by the GEOTRACES Standards and Intercalibration (S&I) Committee and have been released in the GEOTRACES IDP2021 (GEOTRACES Intermediate Data Product Group, 2021). The GEOVIDE copper concentrations were not included due to differences with literature data from samples collected relatively close to ours (Figure S1 in Supporting Information S1). In the Iberian basin, the Cu concentrations at the GEOVIDE station 13 are lower than those at GA03 station 3 (average difference of 0.44 nmol/L). This latter station is influenced by saltier surface waters and a more prominent presence of saltier Mediterranean Outflow Waters around 1,000 m. A discrepancy is also observed in Al data, indicating lithogenic inputs that likely explain the difference in Cu concentrations (Figure S1 in Supporting Information S1). In the Labrador Sea, the GEOVIDE station 69 is characterized by lower concentrations than the GN02 station K1, which was influenced by freshwater inputs (Figure S1 in Supporting Information S1). Baconnais and Holmden (2024) also showed that the K1 station is under the influence of shelf currents from the Fram Strait, Baffin Bay and the Hudson Strait. GEOVIDE station 69, however, is located at the center of the subpolar gyre, away from currents flowing above the surrounding margins. Comparisons to the literature are therefore difficult due to various inputs that locally modify Cu concentrations. In order to validate our analytical procedure, three samples from the UK GEOTRACES GA10 section were fully reprocessed, analyzed and compared to published values in Little et al. (2018). No significant differences in either isotope compositions or concentrations (within analytical uncertainty) were found between the two data sets (Table S1 in Supporting Information S1), highlighting the good reproducibility of Cu analyses between labs and the quality of the GEOVIDE data set.

#### 3. Results and Discussion

The new GEOVIDE Cu concentrations and isotope compositions are displayed as depth profiles in Figure 1 with the corresponding data reported in Table S2 in Supporting Information S1. Dissolved Cu concentrations vary from 0.24 to 2.17 nmol/L with the lowest concentrations in surface waters, likely reflecting biological uptake. Concentrations do not reach a mid-water maximum, as is the case of nutrient-like elements, but gradually increase with depth. Variations in depth profiles can, however, be observed across the North Atlantic basins. In the Iberian and west European basins, Cu concentrations increase by 64% and 71% (+0.90 and 1.30 nmol/L respectively) between the shallowest and deepest samples at stations 13 and 21, respectively. In the Icelandic basin, the increase in Cu concentrations is less pronounced, with a difference of 30% and 20% (or +0.33 and 0.16 nmol/L) between surface and bottom waters at stations 32 and 38, respectively. In the Irminger and Labrador basins, Cu concentrations are relatively homogeneous over the entire depth range of the water column, with a variation of only 18% and 15% (or +0.22 and 0.13 nmol/L) between surface and bottom waters at stations 44 and 69, respectively.

The  $\delta^{65}$ Cu depth profiles are relatively noisy, with values ranging between 0.34 and 0.85% (n = 94). Such variability is also observed in other oceanic regions (0.21–0.99%, n = 350). Indeed, the ranges of the GEOVIDE  $\delta^{65}$ Cu values at depths <1,000 m (0.34–0.82%) and >1,000 m (0.41–0.85%) are consistent with those observed elsewhere (0.4–0.8 % and 0.6–0.9 % respectively; Baconnais et al., 2019; Little et al., 2018; Takano et al., 2014, 2017, 2022; Thompson & Ellwood, 2014; Yang et al., 2020). The deep ocean  $\delta^{65}$ Cu (>1,000 m) across the GEOVIDE section averages 0.64 ± 0.10%, which is indistinguishable from the world ocean average of 0.66 ± 0.14% (shaded band in Figure 1; Baconnais et al., 2019; Little et al., 2018; Takano et al., 2014, 2017, 2022; Thompson & Ellwood, 2014; Yang et al., 2020) and the reference value defined by Moynier et al. (2017;  $\delta^{65}$ Cu = 0.66 ± 0.08%).

The scatter observed for the GEOVIDE and literature data can be attributed to the complex mixtures of processes affecting Cu distributions in the ocean. Below, we attempt to disentangle the different processes controlling Cu concentration and isotope distribution along the GEOVIDE section. First, the internal cycle of Cu is discussed by examining the influence of biological processes and adsorption/desorption processes. Then, the various sources of Cu along the GEOVIDE section are investigated at the different ocean interfaces (atmosphere, ridge, bottom sediments and Iberian margin).

#### 3.1. Internal Cycle

#### 3.1.1. Biological Processes

At shallow depths (between 15 and 30 m depending on the station, Figure 1), the Cu isotope composition averages  $0.63 \pm 0.06\%_0$ , which is generally heavier than the samples beneath. The exception is station 38, where  $\delta^{65}$ Cu is as low as  $0.43\%_0$  at the surface (discussed in Section 3.2.1). Although there is no clear isotope fractionation in the surface at the scale of the global ocean, other studies have also observed heavy dissolved Cu isotope composition at shallow depths, possibly resulting from biological uptake of the light isotope (Baconnais et al., 2019; Little et al., 2018; Maharaj et al., 2025; Takano et al., 2017; Thompson & Ellwood, 2014). The GEOVIDE sampling covered several phases of the phytoplankton bloom, which makes this section of great interest for the study of Cu fractionation during biological uptake. At the time of sampling, the bloom was declining in the Iberian and Labrador basins (stations 13 and 69), was developing in Icelandic basins (stations 32 and 38), and was close to its maximum in the west European and Irminger basins (stations 21 and 44; Lemaitre, Planchon, et al., 2018). Interestingly,  $\delta^{65}$ Cu values within the primary production zone (corresponding to the zone over which in situ fluorescence is elevated; Lemaitre, Planchon, et al., 2018; Owens et al., 2015) co-vary with carbon uptake rates measured at similar depths ( $\pm 10$  m; Fonseca-Batista, 2017, 2019; Figure 2; Table S3 in Supporting Information S1). Stations with higher carbon uptake rates (21, 44) are characterized by the heaviest Cu isotope composition south the primary production zone.

Two specific kinds of biologically related processes could contribute to this heavy surface signature. On the one hand, culturing studies have demonstrated removal of isotopically light Cu from the dissolved phase either due to sorption or cellular uptake (Cadiou et al., 2017; Coutaud et al., 2018; Navarrete et al., 2011; Pokrovsky et al., 2008). On the other hand, Cu complexation by organic ligands is another possibility for biologically related Cu isotope fractionation. Indeed, some phytoplankton species have the ability to release organic ligands to reduce the concentration of toxic free Cu<sup>2+</sup> (Brand et al., 1986; Moffett et al., 1990; Moriyasu & Moffett, 2022). The





Figure 2. Comparison of  $\delta^{65}$ Cu and carbon (C) uptake rates (data from Fonseca-Batista, 2017; Fonseca-Batista et al., 2019) within the primary production zone, that is, the zone over which fluorescence is elevated (Lemaitre, Planchon, et al., 2018; Owens et al., 2015). Station 38 is not shown because its surface waters are influenced by other processes (see Section 3.2.1). The regression (solid blue line) is defined as  $y = (4.219 \times 10^{-5} \pm 9.918 \times 10^{-6}) * x + (0.506 \pm 0.020)$ , with  $R^2 = 0.81$  and p-value = 0.016. The dashed blue lines correspond to the 95% confidence intervals on the regression.

complexation of Cu by these strong organic ligands, forming kinetically non-labile compounds (i.e., compounds that are not exchangeable between pools), stabilizes the heavy isotopes in the dissolved phase (Fujii et al., 2013; Ryan et al., 2014; Sherman, 2013; Vance et al., 2008).

In the mesopelagic layer, deviations toward lighter Cu isotope compositions (minimum  $\delta^{65}$ Cu as low as 0.34–0.58 ‰ along the transect) often mirror high apparent oxygen utilization (AOU; Figure S2 in Supporting Information S1), linking this isotope minimum to the remineralization of sinking particles. This is especially clear between 600 and 1,200 m at stations 13 and 21, and between 300 and 800 m at station 32. Remineralization, however, has been reported to be highest in the western subpolar part of the transect (stations 44 and 69; Lemaitre, Planquette, et al., 2018) where this mirror effect is not seen. This suggests that additional processes may control the observed light Cu isotope compositions in the Eastern Atlantic Ocean (e.g., light Cu input, see Section 3.2.4).

#### **3.1.2.** Adsorption/Desorption Processes

An increase in  $\delta^{65}$ Cu can be observed below 1,200–1,500 m, with the heaviest isotope composition reaching between 0.77 and 0.85% along the transect (Figure 1). These high  $\delta^{65}$ Cu values are co-located with net neodymium (Nd) removal by scavenging reported by Lagarde et al. (2024; Figure 3). Similarly, the heavy Cu signals could be associated with scavenging, consistent with the removal of light Cu onto particles (Takano et al., 2017; Vance et al., 2008). As mentioned by Little et al. (2018), however, the precise mechanism involved is not yet clear. It could be either a fractionation of Cu isotopes between the particle surface and the dissolved pool or a fractionation in the dissolved phase between the pool of labile isotopically light Cu and that of non-labile isotopically heavy Cu, with only the former being scavenged (Liang et al., 2023). Scavenging occurs everywhere, but more effective removal is expected in regions of high particle flux. During GEOVIDE, the highest particulate Cu export flux was determined at station 21 (Lemaitre, Planquette, et al., 2020) where the average  $\delta^{65}$ Cu is higher than elsewhere on the transect, suggesting that Cu scavenging may be more pronounced at this station. Such vertical transport through sinking particles can lead to reversible scavenging at particle-poor depths (Lanning et al., 2023; Olivelli et al., 2024). Reversible scavenging has been suggested as an important process controlling oceanic Cu distributions (Cui & Gnanadesikan, 2022; Liang et al., 2023; Little et al., 2013; Richon & Tagliabue, 2019) and is likely to be intense in particle-rich regions, such as the North Atlantic. The variability in Cu concentration depth profiles may indicate that the balance of these continuous dissolved-particulate exchanges varies with depth. This is more pronounced at stations 13 and 21. Moreover, the overall increase in Cu



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**Figure 3.** Cu isotope compositions ( $\delta^{65}$ Cu) versus dissolved non-conservative Nd concentrations (Nd<sub>xs</sub>) for the GEOVIDE stations. Concentrations of Nd<sub>xs</sub> were obtained by subtracting the preformed Nd (calculated using an extended Optimum Multiparameter Analysis, García-Ibáñez et al., 2018) from the measured concentrations. The smaller, paler symbols show samples for which Nd<sub>xs</sub> concentrations are not significantly different from 0 (Lagarde et al., 2024, their Figure S10). The influence of the Iberian margin is shown by the brown oval (Nd<sub>xs</sub> > 0 and  $\delta^{65}$ Cu < 0.58‰) while the influence of benthic processes (Nd<sub>xs</sub> < 0 and  $\delta^{65}$ Cu < 0.58‰) and scavenging (Nd<sub>xs</sub> < 0 and  $\delta^{65}$ Cu ≥ 0.6‰) are shown by the black oval and black dotted rectangle, respectively. The average  $\delta^{65}$ Cu of the deep ocean is shown by the shaded gray band.

concentrations between surface and bottom waters, especially at these two easternmost stations, may indicate deep desorption of Cu from sinking particles. However, at present there is no clear understanding of how reversible scavenging affects Cu isotopes either along the GEOVIDE transect or in other studied locations.

#### 3.2. Processes at Ocean Interfaces

#### 3.2.1. Atmospheric Deposition

Along the GEOVIDE transect, the highest percentage of soluble aerosol Cu was observed near station 38 (Shelley et al., 2018; Zhang et al., 2024), indicating an influence of aerosols of anthropogenic origin, given the latter's higher solubility (Mahowald et al., 2018). This most anthropogenically influenced aerosol fraction coincides with the lowest  $\delta^{65}$ Cu value determined at the surface of station 38 (0.43 ± 0.03‰; Figure 4). In the North Atlantic, the few available measurements of  $\delta^{65}$ Cu for aerosol leachates vary between -0.03 and +0.27% (Little et al., 2014; Packman et al., 2022), a range that is lighter than the global deep ocean ( $\delta^{65}$ Cu =  $0.66 \pm 0.08\%$ ), and also lighter than the average surface ocean along the GEOVIDE transect ( $\delta^{65}$ Cu =  $0.63 \pm 0.06\%$ ). Elsewhere, light Cu has been shown to be added to the surface ocean by anthropogenic inputs through aerosols ( $\delta^{65}$ Cu as low as -0.23%; Takano et al., 2021). Variable Cu isotope compositions have been determined among anthropogenic sources, with  $\delta^{65}$ Cu ranging between 0.3 and 0.7% in brake pads, -1.35 and -0.35% in coal, or -0.5% in smelting wastes (Packman et al., 2022). All these anthropogenic materials could partially explain the locally low  $\delta^{65}$ Cu value in surface of the station 38.

#### 3.2.2. Hydrothermal Activity

The Cu distribution at the bottom of station 38 deviates from the water column above, with a decrease in concentration mirroring an increase in  $\delta^{65}$ Cu values (Figure 1). The deepest sample at this station is slightly heavier than the average GEOVIDE deep ocean (0.77 ± 0.07% compared to 0.64 ± 0.10%). At this station, a significant maximum in Zn, transported over 1,000 km eastward off the Reykjanes ridge, was attributed to hydrothermal venting (Lemaitre, de Souza, et al., 2020). Enrichment in particulate and dissolved iron as well as high dissolved radium-226 activities were also detected above the ridge at station 38 (Gourain et al., 2019; Le Roy et al., 2018;



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**Figure 4.** Variability of surface  $\delta^{65}$ Cu (yellow diamonds) and Cu solubility in aerosols (black crosses; data from Shelley et al. (2018) and Zhang et al. (2024)) along the GEOVIDE transect. The soluble Cu fraction is the ratio of the Cu concentration from an ultra-high-purity water (18.2 M $\Omega$ /cm) leachate to the total Cu concentration (Shelley et al., 2018). The longitude of station 38 (-31.3°E) is indicated by the black arrow.

Tonnard et al., 2020). The heavier Cu isotope composition above the Reykjanes ridge could therefore be related to hydrothermal vents. Little et al. (2018) also observed a slight increase of  $\delta^{65}$ Cu above the mid-Atlantic ridge in the South Atlantic but without variation in Cu concentrations. Other studies have suggested that hydrothermal activity could be a weak source of Cu (over the Southeast Pacific Rise; Roshan & Wu, 2018) or might even represent a sink because of the Cu scavenging or coprecipitation with Fe-oxyhydroxides (over the mid-Atlantic Ridge; Jacquot & Moffett, 2015; Roshan & Wu, 2015). Recently, Wang et al. (2024) observed heavier isotope signatures in plume samples relative to hydrothermal fluids, confirming Cu adsorption onto particles when fluids mix with seawater. Similarly, Cu over the Reykjanes ridge might be trapped within the hydrothermal system because of its scavenging onto particles, thereby supporting the limited role of hydrothermal activity in Cu cycling.

#### 3.2.3. Benthic Processes

While Cu concentrations do not show anomalous behavior near the sediment-water interface, lower  $\delta^{65}$ Cu are observed in bottom water for all GEOVIDE stations (except at station 38, see Section 3.2.2). Isotope compositions are below the average deep ocean in the bottom waters of the Icelandic, Irminger and Labrador basins (between 0.42 and 0.52 %), but are not significantly different in the Iberian and west European basins (Figures 1 and 3). Deviations toward light Cu isotope compositions have been observed near the sediment-water interface in the South Atlantic and are also not accompanied by anomalous Cu concentrations (Little et al., 2018). The hypothesis of a benthic source of Cu is long-standing, in particular to explain the linear increase of Cu concentrations with depth, suggesting a "bottom-up" control on Cu distributions (e.g., Boyle et al., 1977; Heller & Croot, 2014; Roshan & Wu, 2015). Release of Cu from bottom nepheloid layers (Gerringa et al., 2020) and pore waters (Skrabal et al., 2000) has been demonstrated and this benthic source has been proposed to close the marine Cu mass balance (Liang et al., 2023; Roshan et al., 2020). However, the sedimentary source of such a benthic flux is not yet constrained and could either correspond to organic matter remineralization (i.e., a recycled source; Sawlan & Murray, 1983; Shaw et al., 1990) or lithogenic particulate dissolution (i.e., a new source to the oceanic dissolved pool; Little et al., 2018, 2024). It may also be a mix of processes as suggested by the longitudinal variability of the GEOVIDE bottom  $\delta^{65}$ Cu values. Relatively higher  $\delta^{65}$ Cu values are observed close to the seafloor in the Iberian and west European basins where Ra enrichments were also found, suggesting upward diffusion from pore waters (Le Roy et al., 2018). In the western basins, sediment resuspension and dissolution may explain the lower  $\delta^{65}$ Cu observed near the sediments, in agreement with the high concentrations of particulate iron and manganese determined at the same stations (Gourain et al., 2019).

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#### 3.2.4. Inputs From Continental Margin

A striking feature of the GEOVIDE  $\delta^{65}$ Cu section is the light isotope composition between 300 and 1,500 m from the Iberian margin to station 32. Although this light Cu may be due to remineralization of biological particulates from the surface ocean, there is another process that has been identified for other tracers that may play a more significant role. In this respect, other tracer data (iron, manganese, rare earth elements) have revealed the occurrence of intermediate nepheloid layers, hosting up to 100% of particulate rare earth elements and iron of lithogenic origin (Gourain et al., 2019; Lagarde et al., 2020). Using an Optimum Multi Parameter Analysis, Lagarde et al. (2024) estimated the non-conservative dissolved neodymium fractions ( $Nd_{xs}$ ), calculated as the difference between theoretical concentrations resulting from water masses mixing only (García-Ibáñez et al., 2018) and measured concentrations. These revealed significant Nd enrichment (Nd<sub>xs</sub> > 0) propagating from the Iberian margin to the middle of the west European basin. Neodymium being a lithogenic tracer, these inputs were interpreted as due to the dissolution of resuspended particles transported into intermediate nepheloid layers (Lagarde et al., 2024). These nepheloid layers, comprising sediments remobilized from the continental slope by the energy dissipation of internal waves, are then transported by the circulation toward the open ocean (Barbot et al., 2022). Interestingly, high Nd<sub>xx</sub> concentrations coincide with low  $\delta^{65}$ Cu values (Figure 3). Given the average lithogenic Cu isotope composition of  $0.08 \pm 0.17$  % (Moynier et al., 2017), the observed low  $\delta^{65}$ Cu in GEOVIDE samples could be associated with lithogenic inputs. At station 13, the transported particles are of lithogenic origin at shallow depths (200 m), and of mixed origin (biogenic + lithogenic) at 500 and 800 m. Station 21 is, however, not connected to the Iberian margin, as evidenced by streamlines from velocity fields at different isopycnals, suggesting that the lithogenic inputs observed at this station could originate from the North American margins rather than from the Iberian margin (Barbot et al., 2022). This long-distance transport of lithogenic material due to internal tides has also been proposed to represent a source of iron at the Peruvian margin (Lam et al., 2020).

Consistent with our observations, Little et al. (2018) observed isotopically light dissolved Cu isotope compositions associated with local enrichment in particulate Cu concentrations in both surface and deep waters close to the continental margin of the western Argentine slope. This signal was attributed either to a source in porewater or to partial dissolution of particulate material upon its suspension and interaction with seawater. Similarly, in the surface and subsurface of the GA03 transect, Roshan and Wu (2015) suggest strong shelf inputs from the North American and European continents. Here, the consistency between high Nd<sub>xs</sub> concentrations and low  $\delta^{65}$ Cu demonstrates a particle-associated input of isotopically light dissolved Cu from the continental margin, and highlights the important role of lithogenic inputs in the Cu cycle.

#### 3.3. Importance of the Margin Source on the Cu Budget

In common with other trace elements, the oceanic Cu isotope mass balance, as currently understood, is missing a budget term (Jeandel & Vance, 2018). The known sources of Cu to the ocean are rivers and atmospheric deposition, the latter being a minor input (Little et al., 2014). The calculated isotope composition of the combined riverine and atmospheric sources (0.63%; Little et al., 2014) is similar to that of the ocean (+0.66%; Moynier et al., 2017). All are heavier than the known outputs at +0.3%, which are represented by ferromanganese sediments in oxic environments, organic-rich sediments in reducing environments and sulfidic sediments in euxinic environments (Little et al., 2017, 2024). Together, these sinks represent an output flux that is at least a factor of two larger than the input flux. Therefore, assuming that the dissolved Cu pool is in a steady state with regard to inputs and outputs, a major isotopically light Cu source is missing.

This missing source has been attributed to a larger aerosol deposition flux (Takano et al., 2014), hydrothermal vents (Little et al., 2017; Wang et al., 2024) or the dissolution of particles originating from rivers, continental margins or benthic nepheloid layers (Liang et al., 2023; Little et al., 2017; Roshan et al., 2020). Lithogenic particulate dissolution has long been put forward as a source of Cu over shelves, based on Cu concentrations in both seawater and pore waters (Heggie et al., 1987; Skrabal et al., 2000), and is supported by recent isotope studies suggesting a source of light Cu in coastal regions (Little et al., 2018; Takano et al., 2022). Thanks to the GEOVIDE data, the net flux from the margins (taking into account the margin input and the scavenging output of Cu) can be quantified both in concentration and isotope composition using Equations 1 and 2. The data required for this calculation are available at station 13 at 200 m, where lithogenic particles originate from the sediment resuspension site of La Coruña in the north of the Iberian margin (Barbot et al., 2022).

Table 1

Parameters Used to Calculate Cu Fluxes ( $F_{margin}$  and  $F_{scavenging}$ ) at 200 m at Station 13

		$W = 200 \text{ m}^3/\text{s}$	$W = 500 \text{ m}^3/\text{s}$
[Cu] <sub>ENACW</sub>	(nmol/L)	0.59	0.59
[Cu] <sub>ENACW</sub>	(nmol/m <sup>3</sup> )	590	590
[Cu] <sub>13</sub>	(nmol/L)	0.47	0.47
[Cu] <sub>13</sub>	(nmol/m <sup>3</sup> )	470	470
$\delta^{65}Cu_{\rm ENACW}$	(%0)	0.65	0.65
$\delta^{65}Cu_{13}$	(%0)	0.44	0.44
$\delta^{65}Cu_{margin}$	(%0)	0.10	0.10
$\delta^{65}Cu_{scavenging}$	(%0)	0.30	0.30
F(Cu) <sub>scavenging</sub>	(nmol/sec)	1.6 E + 05	4.1  E + 05
F(Cu) <sub>margin</sub>	(nmol/sec)	1.4 E + 05	3.5 E + 05
F(Cu) <sub>scavenging</sub>	(mol/year)	5.2 E + 03	1.3 E + 04
F(Cu) <sub>margin</sub>	(mol/year)	4.4 E + 03	1.1 E + 04

$$W \times [Cu]_{ENACW} + F_{margin} - F_{scavenging} = W \times [Cu]_{13}$$
(1)

$$\times \delta^{65} Cu_{scavenging} \times \delta^{65} Cu_{scavenging}$$

$$= W \times [\mathrm{Cu}]_{13} \times \delta^{65} \mathrm{Cu}_{13} \tag{2}$$

where: W represents the water mass flow rate from the resuspension site to station 13-200 m and ranges from 200 to 500 m<sup>3</sup>/s (corresponding to current speeds of 2 and 5 cm/s; Zunino et al., 2017; Barbot et al., 2022, for a section of 100 m by 100 m centered on the depth of interest).

 $[Cu]_{13}$  and  $\delta^{65}Cu_{13}$  respectively represent the Cu concentration and the isotope composition measured at 200 m at station 13 (see Table S2 in Supporting Information S1).

 $[Cu]_{ENACW}$  and  $\delta^{65}Cu_{ENACW}$  represent the same parameters prior to margin inputs in the dominant water mass, the East North Atlantic Central water (ENACW), which is the only water mass identified at 200 m at station 13 by García-Ibáñez et al. (2018). The ENACW parameters are estimated by

averaging the concentrations and isotope compositions at station 13–300 m, station 21–100 m and station 21–200 m where the ENACW contribution is  $\geq$ 94% (Garcia-Ibanez et al., 2018), and where  $\delta^{65}$ Cu and Nd<sub>xs</sub> do not point to lithogenic inputs

 $F_{\text{margin}}$  represents the flux supplying Cu from the margin and  $\delta^{65}$ Cu<sub>margin</sub> its isotope composition, set at 0.1% (Moynier et al., 2017).

 $F_{\text{scavenging}}$  is the scavenging removal flux and  $\delta^{65}$ Cu<sub>scavenging</sub> its isotope composition, set at 0.3% (Moynier et al., 2017).

Note that the constraints on the parameters describing ENACW parameters are associated with large uncertainties because of the low data resolution and the numerous processes affecting and modifying Cu concentrations and isotope compositions. Though the results of these calculations have to be used with caution, the estimated input Cu flux from the La Coruña resuspension site ( $F_{margin}$ ) ranges from 4.4 to  $11 \times 10^3$  mol/year and a scavenging flux ( $F_{scavenging}$ ) between 5.2 and  $13 \times 10^3$  mol/year, depending on the water mass transport rate (200 and 500 m<sup>3</sup>/ s respectively; Table 1). The ranges obtained for the margin and scavenging fluxes are quite similar, and it seems that Cu supplied by the dissolution of lithogenic particles originating from the margin sediments is then removed by scavenging. These exchanges at the margin may not significantly change the in situ concentrations but would influence the dissolved isotope composition (as observed at station 13 at 200 m). This description of the process is, of course, the definition of boundary exchange. As part of the various processes encompassed in this term (Jeandel, 2016), the combination of lithogenic input with dissolution and removal reveals unaccounted Cu sources and sinks, as observed for Nd (Du et al., 2022; Jeandel, 2016; Lacan & Jeandel, 2001; Tachikawa et al., 2003) and as may be the case for other trace elements.

The margin flux calculated here accounts for 0.0003%-0.0008% of the global flux needed for balancing the oceanic Cu mass balance ( $14 \times 10^8$  mol/year; Little et al., 2024). Our calculation nevertheless takes into account only one resuspension site on the Iberian margin and only one depth. Along the Iberian margin, Barbot et al. (2022) identified 19 resuspension sites between 50 and 500 m depth, with sediments having a lithogenic or a mixed (biogenic and lithogenic) origin. Based on the tentative assumption that the Cu flux is similar from one site to another, the input flux from the Iberian margin would be  $8.4-21 \times 10^4$  mol/year of Cu. This source would then account for 0.006%-0.015% of the missing Cu flux. Compared to the fact that the Iberian margin approximately covers 0.005% of the total length of the combined world's ocean continental slopes, this flux does not appear negligible, and emphasizes previous conclusions that this margin is an active source of trace elements (Gourain et al., 2019; Lagarde et al., 2020, 2024). Overall, in order to better constrain the global input of Cu to the ocean, a focus should be placed on continental margins, with particular attention on those playing an important role in dissipating internal tide energy.

#### 4. Conclusions

This study reports dissolved Cu concentrations and isotope compositions ( $\delta^{65}$ Cu) along the GEOVIDE transect (GEOTRACES GA01 section) in the North Atlantic. Different data sets concerning physical circulation, biological productivity and various trace element cycling have already been published in the framework of this cruise, allowing us to better interpret the Cu distributions.

Heavy isotope compositions in the upper ocean (within the primary production zone) co-vary with carbon uptake rates, and are suggested to arise through the removal of light Cu during biological uptake. Complexation to organic ligands, produced by microorganisms, could also favor the stabilization of the heavy Cu isotopes in the dissolved phase. Below the surface, deviations toward light Cu isotope compositions may partially be explained by the remineralization of sinking biological particles. Scavenging onto and reversible scavenging from particles are known to play an important role in shaping Cu depth profiles. Here, we observe an increase of  $\delta^{65}$ Cu, pointing to Cu net removal by scavenging. Reversible scavenging, driven by high vertical particulate exports, could explain the greater increase of Cu concentrations between the surface and deep ocean in the eastern part of the transect.

External sources also influence the Cu distributions. At the atmosphere interface, we suggest that the local low  $\delta^{65}$ Cu determined at station 38 could be due to anthropogenic aerosol deposition. At the Reykjanes ridge, a decrease in Cu concentration mirrors an increase in isotope compositions that we interpret as the removal of Cu by scavenging in the hydrothermal plume. At the sediment-water interface, lower  $\delta^{65}$ Cu are observed compared to the overlying samples. This deviation toward light Cu near the seafloor is more pronounced in the western part of the transect where particulate resuspension and dissolution occurs. This input of Cu to seawater could represent either a recycled source through the dissolution of authigenic and biogenic material at the seabed or a new source via the dissolution of crustal particles. Interestingly, elevated Nd<sub>xx</sub> fractions, evidencing lithogenic Nd supply, are observed alongside with low  $\delta^{65}$ Cu between 300 and 1,500 m from the Iberian margin to the Icelandic basin. At station 13, in the Iberian basin, the lithogenic input originates from the Iberian margin, where particles have been resuspended due to internal tide energy dissipation and advected offshore via the circulation. Station 21, in the west European basin, also undergoes lithogenic inputs but is not connected to any resuspension sites from the Iberian margin, suggesting that lithogenic inputs can be transported over longdistances. The  $Nd_{xs}\delta^{65}Cu$  covariation highlights the importance of lithogenic particle dissolution in representing a source of light Cu, confirming hypotheses from the literature. Continental margins, under the influence of internal tides, are important contributors of lateral lithogenic inputs and should therefore be considered in the Cu cycle. A quantification of this input flux is attempted for one sediment resuspension site influencing the upper water column of station 13. More Cu data from continental margins are needed for estimating a global flux.

#### **Data Availability Statement**

The new GEOVIDE dissolved Cu isotope compositions ( $\delta^{65}$ Cu) and concentrations together with macronutrient concentrations and CTD data are available in Table S2 in Supporting Information S1 and also publicly available through the GEOTRACES intermediate data product 2021 at BODC (https://www.bodc.ac.uk/geotraces/data/idp2021/). Non-conservative dissolved neodymium fractions (Nd<sub>xs</sub>) are available in Lagarde et al. (2024). Carbon uptake rates can be found in Table S3 in Supporting Information S1 and in Fonseca-Batista (2017) and Fonseca-Batista et al. (2019).

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