



# Insight into hydrothermal and subduction processes from copper and nitrogen isotopes in oceanic metagabbros

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## ABSTRACT

The transfer of trace elements from external terrestrial reservoirs (*i.e.* atmosphere, hydrosphere, crust) to the mantle is mainly controlled by their geochemical behaviors during hydrothermal alteration of the oceanic crust and subsequent subduction metamorphism. Deciphering fluid–rock partitioning and element pathways during hydrothermal and subduction metamorphism is complicated due to a variety of pressure–temperature conditions and variable compositions of fluids interacting with the lithosphere. Fluid–rock interactions can, however, be traced by coupling multiple isotopic systems in a single and uniform type of lithology. Here we present Cu and N isotope relationships in Alpine metagabbros, which were hydrothermally-altered on the seafloor and subsequently buried to different depths in a subduction zone. Our sample set covers non-subducted, as well as blueschist- and eclogite-facies low-strain metagabbros, and veins and mylonites equilibrated in eclogite facies conditions. The low-strain metagabbros have Cu contents ranging from 22.5 to 73.2 ppm, and  $\delta^{65}\text{Cu}$  values from  $-1.66$  to  $-0.02\%$ . In contrast, eclogite-facies veins and mylonites have lower Cu contents, below 11.1 ppm (except one sample at 27.7 ppm), but a very large range of  $\delta^{65}\text{Cu}$  values from  $-3.12$  to  $1.76\%$ . Nitrogen contents and  $\delta^{15}\text{N}$  values on the same samples were reported in a previous study and vary between 2.6 and 55 ppm, and from 0.8 to 8.1‰, respectively. In Cu vs  $\delta^{65}\text{Cu}$  and N vs  $\delta^{15}\text{N}$  diagrams, the low-strain metagabbros show clear trends, which are not related to subduction-zone metamorphic conditions, and more likely reflect hydrothermal processes. We propose that N and Cu were released concomitantly from metagabbros to hydrothermal fluids. This produced a decrease of N and Cu concentrations in the residual rocks, together with an increase of  $\delta^{15}\text{N}$  and a decrease of  $\delta^{65}\text{Cu}$ . The Cu isotope data, coupled to mineralogical analyses of the metagabbros by SEM, are compatible with partial dissolution of chalcopyrite under oxidative conditions. Nitrogen is not detected in chalcopyrite or in any major or minor mineral phases, probably reflecting the presence of ammonium ( $\text{NH}_4^+$ ) in trace amounts substituting for  $\text{Na}^+$  and/or  $\text{Ca}^{2+}$  in major phases. The release of Cu and N during hydrothermal alteration is best modeled by Rayleigh distillation in an open system, although a batch equilibrium model cannot be completely discarded. During subduction of the oceanic crust, N was further released to fluids, while Cu was mostly retained in the rocks, a conclusion supported from isotopic and mineralogical analyses. This step resulted in a decrease of N concentration with moderate increase of  $\delta^{15}\text{N}$  ( $<0.5\%$ ), and constant Cu contents and  $\delta^{65}\text{Cu}$  values. Accordingly, Cu isotope variability inherited from hydrothermal alteration was preserved in subducted metagabbros, although 90% of the fluids were lost during eclogitization. The present results imply that Cu depletion associated with light isotope enrichments in metagabbros can record the oxidative nature of hydrothermal alteration on the seafloor and be preserved despite late metamorphic overprint.

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## 1. Introduction

The geochemical evolution of Earth's mantle and external reservoirs are highly dependent on the fluxes of material that are

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output from mid-ocean ridges, volcanic arcs and hot spots, and input by lithospheric plates consumed in subduction zones. Chemical exchanges are mediated by magma degassing for volatile species (CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, rare gases, and N<sub>2</sub>; e.g. Marty, 1995; Cartigny et al., 2008), or fluid–rock interaction during hydrothermal alteration on the seafloor and/or metamorphism in subduction zones (e.g. for elements such as Sr, K, Na, Fe, Mn, Cu, Zn, as well as volatile species; e.g. Staudigel, 2003; Bebout, 2013). The behavior and fluxes of elements transferred to the mantle can be explored by studying metamorphic rocks buried in paleo-subduction zones, and exhumed back to the surface by tectonic processes (Bebout and Fogel, 1992; Spandler et al., 2004; Halama et al., 2010). These rocks include various lithologies, which can be grouped as metasediments, metabasalts, metagabbros and meta-peridotites. For a single lithology, the fate of volatiles in subduction zones is mainly controlled by the stability of the main water-bearing phases, which are strongly dependent on the geothermal gradient within the subduction zone (Bebout et al., 1999; Kerrick and Connolly, 2001). For instance, in subducted metagabbros, the dominant water-bearing phase is amphibole and rock dehydration corresponds to eclogitization (e.g. Nadeau et al., 1993). Although the behavior of any element in metagabbros could in theory be simply derived by comparing several samples subducted to different depths, a complication arises from the fact that fluid–rock interactions often occur during both hydrothermal alteration and subduction processes. This potential limit can be overcome by coupling multiple isotope tracers, with variable geochemical behaviors during hydrothermal alteration and subduction. In the present contribution, we illustrate that Cu and N isotopes can be used together as a powerful tracer for distinguishing subduction zone metamorphic effects from hydrothermal chemical modifications, and for understanding the fate of Cu and N in the subducting oceanic crust.

Nitrogen geochemical data on mafic and ultramafic rocks buried in subduction zones are scarce. Nitrogen concentrations and  $\delta^{15}\text{N}$  values ( $\delta^{15}\text{N} = [(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{standard}} - 1] \times 1000$ , where the standard is atmospheric N<sub>2</sub>) of serpentinitized meta-peridotite analyzed to date range from 1.4 to 15 ppm, and 4 to 15‰, respectively (Halama et al., 2014; Philippot et al., 2007). In contrast, the N concentration in unaltered lithospheric peridotites is always lower than 1 ppm (Yokochi et al., 2009), supporting N enrichment during interaction with hydrothermal fluids on the seafloor. Although serpentinitized metaperidotites may transfer a significant amount of N to the deep mantle, this N flux has never been assessed because of the poorly constrained mass flux of total subducting serpentinites. Interaction of seawater with the basaltic part of the oceanic crust produces secondary mineral phases that are able to store N. The concentrations of N in altered oceanic basalts vary from ~1.3 to 18.2 ppm, with  $\delta^{15}\text{N}$  values from –11.6 to 8.3‰ (Busigny et al., 2005a; Li et al., 2007). Nitrogen concentrations and  $\delta^{15}\text{N}$  values of eclogitic metabasalts (2–20 ppm and –1 to 8‰, respectively) have similar ranges as altered oceanic basalts, suggesting that N that is added during hydrothermal processes on the seafloor is largely preserved during metamorphism in subduction zones (Halama et al., 2010). To our knowledge, N concentrations and isotope compositions of fresh/unaltered gabbros have never been measured. In a companion study, we analyzed ophiolitic metagabbros that were subducted to different depths in the Alps and found N contents and  $\delta^{15}\text{N}$  values of 2.6 to 55 ppm and 0.8 to 8.1‰, respectively (Busigny et al., 2011).  $\delta^{15}\text{N}$  values of low-strain metagabbros showed a negative correlation with Cu concentrations, interpreted as resulting from a release of a Cu–N chemical compound during hydrothermal alteration on the seafloor. No specific relation with metamorphic grade in subduction was observed, suggesting that minor modification affected Cu and N during burial metamorphism.

In order to further understand the origin of the relations between N and Cu, and to determine their fate during hydrothermal alteration and subduction, we measured Cu isotope compositions in the same sample set as reported in Busigny et al. (2011). We also conducted petrological analyses by optical and scanning electron microscopy (SEM) to determine the Cu-hosting minerals in Alpine metagabbros, which is crucial for interpreting the isotopic data. Primary igneous rocks generally display a restricted range of Cu isotope composition, with  $\delta^{65}\text{Cu}$  values averaging  $\sim 0.07 \pm 0.10\text{‰}$  (Larson et al., 2003; Dekov et al., 2013; Liu et al., 2015; Savage et al., 2015; see compilation in Moynier et al., 2017). In contrast, significant Cu isotope variability is inherited from redox reactions during low-temperature supergene and hydrothermal alteration of primary Cu minerals (Larson et al., 2003; Rouxel et al., 2004; Mathur et al., 2005; Markl et al., 2006; Mathur and Fantle, 2015), with a total range of  $\delta^{65}\text{Cu}$  values from –16.5 to 10‰ (Moynier et al., 2017). Experimental determination of Cu(II)<sub>aq</sub>–Cu(I)<sub>sulfide</sub> isotope fractionation shows enrichment of aqueous Cu(II) in the heavy isotope by ~2.5 to 3.5‰ for the temperature range between 0 and 100 °C (Ehrlich et al., 2004; Mathur et al., 2005; Asael et al., 2007). Slightly lower Cu isotope fractionation of ~1.4‰ was obtained for chalcopyrite leaching under abiotic oxidative conditions at low pH (~2) and a temperature of 25 °C, which possibly resulted from a kinetic isotope effect (Mathur et al., 2005; Kimball et al., 2009). Laboratory experiments of Cu partitioning between chalcopyrite and fluid at high temperature (250 and 300 °C) showed that the Cu isotope fractionation is controlled by several parameters such as pH, salinity, and partitioning between liquid and vapor phases (Maher et al., 2011). Additionally, Cu isotope fractionation between minerals and fluids depends heavily on the Cu speciation in the fluid, and therefore on the fluid composition. This is also illustrated by thermodynamic calculations of the equilibrium isotope fractionation for Cu complexes relevant to hydrothermal ore-forming fluids (Seo et al., 2007), Cu-bearing minerals and various aqueous Cu complexes and organic compounds (Sherman, 2013; Fujii et al., 2014). Overall, the mobility of Cu during fluid–rock interactions and associated isotope fractionation provide a strong potential for tracing hydrothermal alteration of the oceanic crust and subduction processes.

## 2. Sample description

The samples have been described in detail previously (Busigny et al., 2011) and are only briefly presented here. They correspond to ophiolitic metagabbros embedded in pelagic metasediments from the Schistes Lustrés nappe of the Piemonte-Ligurian domain, western Alps. The metagabbros experienced hydrothermal alteration on the seafloor and some of them were subsequently subducted in a cold slab environment (~8 °C/km; Le Pichon et al., 1988). Samples have been collected in three different zones: the Chenaillet Massif, the Queyras Valley, and the Monviso Massif. Two samples from the Chenaillet Massif are undeformed metagabbros that escaped subduction zone metamorphism (Mével et al., 1978; Manatschal et al., 2011). These rocks have experienced oceanic hydrothermal alteration under greenschist- to amphibolite-facies conditions. Four samples from the Queyras Valley are low-strain glaucophane-bearing metagabbros, which have been subducted down to blueschist facies conditions. Seven omphacite- and garnet-bearing samples from the Monviso Massif have been subducted down to eclogite facies conditions (Messiga et al., 1999). These samples include two low-strain metagabbros, with one being undifferentiated (as indicated by its particularly high Mg–Cr content), as well as three mylonites and four veins collected in highly strained domains (Nadeau et al., 1993). The comparison between low-strain rocks, which experienced quasi-static metamorphism,

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