

The vapour-liquid fractionation of Cu stable isotopes: a new tool for porphyry research

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Copper is an essential element for green technologies such as long-life Cu batteries, thin films and other highly conductive materials, while porphyry Cu-Mo deposits are a major source of other metals crucial to green industry (Mo and Re). The formation of these deposits typically involves a two-phase magmatic fluid comprised of aqueous vapour and liquid, and significant quantities of Cu may be transported in both of these phases. The stable isotope signature of Cu in each fluid phase could be of use in tracking the evolution of the fluid system, or in identifying zones of a porphyry deposit formed from the vapour- and liquid-dominated fluid regimes. In order to investigate these possibilities, we have conducted an experimental study of the vapour-liquid (V-L) fractionation of Cu and its stable isotopes (⁶⁵Cu/⁶³Cu).

Closed-system V-L fractionation was measured experimentally at P-T conditions applicable to porphyry formation (up to 450°C and 400 bar) by the removal of V and L sample pairs from a batch of bulk fluid contained within an autoclave, with each pair taken at successively lower total pressure. For most sample pairs, the isotopic compositions of the vapour and liquid were equal within uncertainty.

However, from the initial compositions of the bulk start solutions to those of the final, lowest-pressure V and L sample pairs extracted from the autoclave, a shift to heavier values of $\delta^{65}\text{Cu}$ was seen. Specifically, between the starting compositions and those of the lowest-pressure vapour samples, the increases in $\delta^{65}\text{Cu}$ values were 0.16, 0.69 and 0.10‰ (all $\pm 0.07\%$) at 350, 400 and 450°C, respectively. This compositional shift is roughly proportional to the volume of vapour extracted between sample pairs in order to decrease total pressure (6-35% of the total bulk fluid removed as vapour), indicating that ⁶⁵Cu/⁶³Cu fractionation may be described by a Rayleigh distillation process.

These results suggest that in a closed, boiling hydrothermal ore-forming environment, Cu isotopes exhibit conservative fractionation, and coexisting V and L will preserve the isotopic signature of the fluid source. However, in a structurally open system in which periodic vapour removal occurs, the movement of the escaped vapour outward from the magmatic source will result in cooling and condensation of liquid droplets with heavier $\delta^{65}\text{Cu}$ values. This process will give the evolving vapour a progressively lighter $\delta^{65}\text{Cu}$ than the residual fluid near the source, although individual liquid droplets will be only marginally heavier in composition than the vapour from which they condensed. It follows that V and L fluid inclusions trapped at shallower depths (e.g., epithermal vein systems), or primary Cu(I) minerals deposited from those fluids, will have lighter $\delta^{65}\text{Cu}$ values than their deeper magmatic counterparts and the ore fluid source.

Glacial-interglacial simulations of ϵ_{Nd}

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The Atlantic Meridional Overturning Circulation (AMOC) is an important component of the climate system. Reconstructions of past changes in AMOC are possible via records of paleocirculation proxies that reflect the distribution of water masses or the rate of ocean circulation and that can be measured in sediment cores. However, their interpretation is not unequivocal in some cases.

Covariation of Nd isotopic composition (ϵ_{Nd}) with salinity and potential temperature, indicates the potential of ϵ_{Nd} as a complementary water mass tracer [1]. Variations of ϵ_{Nd} can be reconstructed from sediment cores and are interpreted as past water mass changes [2].

Numerical simulations may contribute to the quantitative interpretation of such reconstructions. However, to date only few simulations of past ϵ_{Nd} are available [3]. Systematic studies of its paleoceanographic potential were limited by computational costs. We have included Nd isotopes (¹⁴³Nd and ¹⁴⁴Nd) into a cost-efficient climate model of intermediate complexity [4] with which we run 125,000-year simulations of ϵ_{Nd} .

In this study we present results of the first glacial-interglacial simulations of ϵ_{Nd} . Simulated ϵ_{Nd} is in good qualitative agreement with the few available reconstructions from the Atlantic Ocean. Inferences on changes in the AMOC during the entire last glacial cycle are therefore possible. However, our results indicate that relationships between variations in ϵ_{Nd} and overturning strength in the North Atlantic, or in the deep South Atlantic, are not straightforward during the entire last glacial cycle.

Besides allowing to further constrain changes in pattern and strength of the AMOC during the last glacial cycle, our results therefore provide important new insight into the paleoceanographic potential of ϵ_{Nd} .

[1] Goldstein and Hemming (2003) *Treatise on Geochemistry*, Elsevier, Oxford, 453-489. [2] Piotrowski *et al.* (2008) *Earth and Planetary Science Letters* **272**, 394 – 405. [3] Arsouze *et al.* (2008) *Climate of the Past* **4**, 191-203. [4] Rempfer *et al.* (2011) *Geochimica et Cosmochimica Acta* **75**, 5927-5950.