Stable isotope tracing of the natural and anthropogenic sources of Zn and Cu to Atlantic aerosols

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Aerosols supply Zn and Cu to the surface ocean[1]. In this study, we test the hypothesis that the stable isotope signatures of Zn and Cu can be used to trace the external sources that contribute to this atmospheric supply route. External sources include natural mineral dust and anthropogenic activities such as factory and traffic emissions. High temperature processes, for example those in Pb-Zn smelting, fractionate metal isotopes [2] and may therefore influence the isotope compositions of aerosols.

This study presents Zn and Cu isotope data for aerosols collected during the GEOTRACES GA06 cruise in the eastern tropical Atlantic Ocean. The aerosol $\delta^{66}Zn_{JMC\text{-}Lyon}$ values fall in the range -0.05 to +0.63‰, with the majority of the samples yielding an isotope composition lighter than the measured North African mineral dust value of about +0.3‰. These comparatively light values, together with the large enrichment factors determined for Zn, suggest a significant anthropogenic contribution.

The aerosol $\delta^{65}Cu_{NIST\ SRM\ 976}$ isotope values range from -0.34 to +0.27‰ and hence do not differ significantly from the isotope composition of lithogenic Cu isotope values (+0.08 ± 0.20‰)[3]. Copper is less volatile than Zn and thus does not fractionate to the same extent during high temperature processes. The combination of a remote sampling location and the high boiling point results in the sources of aerosol-borne Cu being more ambiguous.

The atmospheric data of this study highlights the potential for perturbation of the natural cycles of trace elements in the ocean by anthropogenic emissions. The isotopic evidence of this perturbation will vary between elements depending on their chemical properties.

[1] Duce R A *et al*. (1991) *Global Biogeochem. Cy*. **5 (3)**, 193-259. [2] Mattielli N *et al*. (2009) *Atmos. Environ*. **43**, 1265-1272. [3] Moynier F, Vance D, Fujii T, Savage P (2017) *Rev. Mineral. Geochemistry* **82 (1)**, 543-600.