## Copper and zinc isotope composition of China and India dust sources

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Copper (Cu) and zinc (Zn) play key roles in aquatic ecosystems. Zinc is an essential trace element limiting the biological productivity in the open ocean and Cu is potentially toxic to phytoplankton. Work to date suggests that the stable isotope systems of these metals can improve our understanding of their aqueous chemistry and behaviour in the marine environment. Significant spatial variability in isotopic ratios was found between and within ocean basins.

At present, one of the major gaps in knowledge is the characteristics of the isotopic composition of Zn and Cu of terrestrial sources into the marine ecosystem, in particular atmospheric deposition, which is the major source of trace elements to the remote open ocean.

Here we present the first characteristics of the Cu and Zn isotope compositions of the major dust sources in China and India, and discuss the findings with respect to (i) the dominant controls (mineralogy size fractions and Enrichment Factor), and (ii) their implication for the application to marine studies, focussing on the North East Pacific Ocean (NEPO).

a) We observe significant Cu and Zn isotopic variations between bulk samples from Chinese dust, Chinese Loess, and Indian dust (error in 2SD), i.e., Chinese deserts (Taklamakan, Badain Jaran, and Tengger): δ<sup>65</sup>Cu<sub>NIST976</sub>= 0.06±0.11‰  $(n=10), \delta^{66}Zn_{Lyon} = 0.19 \pm 0.19\%$  (n=10); Chinese loess:  $\delta^{65}Cu_{NIST976} = 0.27 \pm 0.19\% \quad (n{=}12), \ \delta^{66}Zn_{Lyon} = 0.41 \pm 0.17\%$ (n=15); Thar Desert (India):  $\delta^{65}Cu_{NIST976} = 0.48 \pm 0.12\%$  (n=4),  $\delta^{66} Zn_{Lvon} = 0.49 \pm 0.22\%$  (n=5). b) Cu isotope values seem to be negatively correlated with the abundance of the clay mineral illite at 95% CI  $R^2 = 0.74$ , (n=10). c) The  $\delta^{65}Cu_{NIST976}$ and  $\delta^{66}$ Zn<sub>Lvon</sub> values differ among the various size fractions of Chinese deserts by up to 0.97 % (Tengger Desert) and 0.35 %(Taklamakan Desert), respectively. This implies that bulk isotopic signatures might be misleading for the characterization of dust. d) Enrichment factors (EF) of the dust range between 0.48 (Thar Desert) and 1.86 (Taklamakan Desert) for Cu and between 0.40 (Chinese loess) and 0.70 (Tengger Desert) for Zn, suggesting that the lower EF values, the heavier the isotope signature of the dust. e) The isotope signature of long range transport Chinese dust (≤5 µm) input to the NEPO area has values of  $\delta^{65}$ Cu<sub>NIST976</sub> = 0.16±0.19‰ and  $\delta^{66}$ Zn<sub>Lyon</sub> = 0.29±0.24‰, which are lower for Cu and similar of Zn relative to the isotope signatures of dust input estimated in pervious studied of NEPO surface waters.

## Multiple magma inputs and sulfur sources in the development of the BIC intrusion, Northern Michigan, Midcontinent Rift system

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The BIC intrusion is located in the Marquette-Baraga dike swarm in the Upper Peninsula of Michigan, and is associated with magmatism related to the development of the ~1.1Ga Midcontinent Rift System. The intrusion is currently being evaluated for the presence of economically viable sulfide-rich Ni- Cu-(PGE) mineralization. Rio Tinto's Eagle deposit is located 43 km to the west within the same dike system; the geometric form of the BIC intrusion, however, is distinctly different from those of the intrusions found in the vicinity of the Eagle deposit. The BIC intrusion is funnel-shaped with basal peridotite overlain by clinopyroxenite and gabbro. Sulfide minerals (pyrrhotite, chalcopyrite, pentlandite) are found in all of the units units but massive sulfide mineralization is restricted to the base of the peridotite unit. Country rocks are composed of siltstones and shales that are sulfide-bearing themselves. A smaller satellite intrusion is referred to as Little BIC, which is composed of peridotites with both massive and semi-massive (net-textured) mineralization.

Sulfide distribution in the BIC intrusion is variable. suggesting that multiple pulses of sulfide-saturated magma were involved in its genesis.  $\delta^{34}$ S values of sulfide minerals throughout the intrusion fall within a narrow range of -2 to +2%.  $\delta^{34}$ S values of the sedimentary country rocks show a much wider range of -6 to +20%. The massive sulphides in Little BIC have the same narrow range of  $\delta^{34}$ S values as in BIC, but semi-massive sulphides are considerably higher (~+6‰) and clearly signify a large component of crustally derived sulfur. The BIC system conforms to a growing body of evidence for the importance of multiple sulfur sources in conduit-related Ni-Cu-(PGE) occurrences. We are currently evaluating the possibility that different processes for the attainment of sulfide saturation (e.g. fractional crystallization versus sulfur assimilation) are responsible for the sharp difference in  $\delta^{34}S$  values between semi-massive sulfides at Little BIC and other sulfide occurrences in the system.

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