

## Copper isotope fractionation during leach layer development on Cu-sulfide minerals

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Previous studies have shown that upon oxidation and release of Cu from chalcocite (Cu<sub>2</sub>S), covellite (CuS) will form after proceeding through a complex series of intermediate phases. Here we investigate the influence of mineral leach layers on Cu isotope fractionation by combining time-resolved X-ray diffraction, *electron dispersive spectroscopy* (EDS), and isotope analysis.

Flow-through capillary reaction cells were packed with pure, naturally occurring chalcocite powders and exposed to various concentrations of aqueous ferric sulfate for up to 6 hrs. Real-time diffraction data were collected at intervals of 2 min at beam line X7B, National Synchrotron Light Source. The  $\delta^{65}\text{Cu}$  values of the leached Cu as well as the starting and final powders were measured using a Finnigan Neptune multi-collector inductively coupled plasma mass spectrometer. Cross sections of leached powders were analyzed using an Oxford Inca 200 EDS to obtain Cu:S ratios.

Isotope analysis and diffraction data revealed that during the initial stages of the reaction when chalcocite was present the average  $\Delta_{(\text{aq-min})}$  value was  $3.19 \pm 0.14\%$ . At the endpoint of the reaction where only covellite appeared the  $\Delta_{(\text{aq-min})}$  value averaged  $-1.15 \pm 0.14\%$ . These values decreased throughout the reaction as intermediate phases formed and disappeared. Preliminary EDS results confirm that Cu:S ratios decrease from the core to the edge of the mineral grains. This evidence supports diffraction data to suggest that oxidation proceeds stepwise from the exterior to the interior of Cu sulfide grains, generating a sequence of intermediate phases that concentrically rim the grains. The formation of these phases and the concomitant changes in  $\Delta_{(\text{aq-min})}$  values indicate that a combination of redox isotope effects and the growth of mineral leach layers control Cu isotopic fractionation during dissolution.

## A review of the main controls on ore-forming carbonatitic magmas

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About one in twenty of the known carbonatite complexes has a mine. The high probability that any particular carbonatite complex will contain minerals of economic interest is firstly because the carbonatite rock-forming minerals themselves, such as apatite used as a source of P for fertiliser, are frequently the ores. Carbonatites are also characteristically enriched in Nb and REE and host the World's most important sources of these elements. Most carbonatite complexes are associated with alkaline rocks and these also contain important ore deposits, including the World's largest apatite mines in the nepheline syenite at Khibiny, Kola Peninsula, Russia.

### Size and Age

Carbonatites are mantle-derived magmas, typically associated with extensional environments; many occur along the East African Rift Valley, for example. Phosphorous, REE, and Nb are all potential deposits in these carbonatites. Some are mined but most are too small for international mining companies to exploit. Large deposits in large carbonatites are required. The role of mantle anomalies, such as plumes, is one possible factor in forming large intrusions and concentrations of intrusions (e.g. Kola Peninsula). However, another factor that links World-class deposits is age. Bayan Obo, China (REE), Phalaborwa, South Africa (Cu, Fe, P, ZrO<sub>2</sub>, PGE) Mt Weld, Australia (REE) and Mountain Pass, USA (REE) are all Proterozoic. Carbonatites have increased in number over time [1] so this is not a coincidence of numbers and may indicate a real change in mantle environment.

[1] Woolley (1989) In: *Carbonatites: Genesis and Evolution* (Bell, ed.), Unwin Hyman, London, 15-37.