Cu isotopic anomalies around porphyry Cu deposits

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Significant isotopic fractionation of Cu is generally considered to be associated mainly with supergene redox processes rather than hypogene processes. Here we report large, systematic Cu isotopic variations in the Northparkes Cu-Au deposit, NSW, Australia, which is a typical orthomagmatic porphyry Cu deposit.

Copper isotopes have been measured in sulfide minerals by solution MC-ICP-MS and laser ablation MC-ICP-MS. The results from both methods show a variation in δ^{65}Cu of hypogene sulfide minerals (chalcopyrite and bornite) greater than 1.2‰ (relative to NIST976). Significantly, the results from four drill holes through two separate ore bodies show strikingly similar patterns of Cu isotope variation with depth (Fig. 1). The patterns are characterized by a sharp down-hole decrease from ~ 0.8‰ to ~ -0.3‰ at the margins of the most mineralized zones (Cu grade > 1wt.%). Below the margin, the compositions are more consistent (around 0.2‰). Sulphur isotopes show no such concomitant variation and the mechanism(s) responsible for the Cu isotopic distribution is not yet clear. Nevertheless, this work demonstrates that Cu isotopes show a large response to high-temperature porphyry mineralizing processes, and that they may act as a vector to buried mineralization.

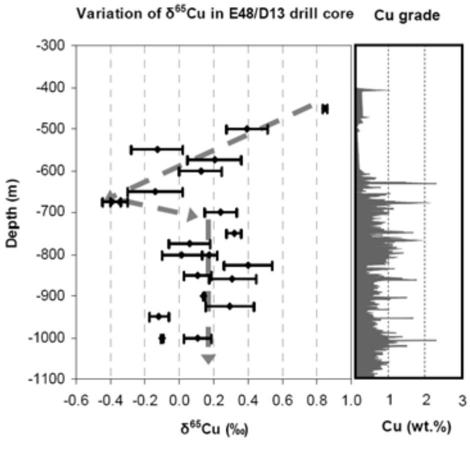

Figure 1: Variation of Cu isotope ratio and Cu grade with depth in drill hole E48/D13 from Northparkes Cu-Au porphyry deposit, NSW, Australia.

Interactions of Nitrate, Iron, Uranium and Technetium during bioremediation

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Immobilization of radionuclides including uranium and technetium in subsurface aquifers can be achieved through microbial reductive processes. Reduction of U(VI) to U(IV) and Tc(VII) to Tc(IV) are known to be carried out by anaerobic bacteria and the processes can be stimulated in aquifers by addition of soluble electron donors such as ethanol or acetate.

Sediments contaminated with radionuclides are often co-contaminated with nitrate. Our results show that during ethanol biostimulation of sediments, reduction of nitrate must occur prior to the reduction of Tc(VI) and U(VI). We have investigated the microbial community during ethanol biostimulation at a US Dept of Energy site contaminated with >130 mM nitrate along with radionuclides in Oak Ridge, TN. A *Castellaniella* species, a β-proteobacterium dominanted in biostimulated 16S rRNA and *nir*K clone libraries and was the most abundant cultivatable species capable of denitrification. Physiological tests along with the above results suggest that this species is important for *in situ* nitrate removal at this site.

We have also investigated factors influencing microbial reduction of Tc(VII) in nitrate contaminated aquifer sediments. To investigate the mechanisms of Tc(VII) reduction under these conditions, several strains were isolated from sediment microcosms undergoing Tc(VII) reduction. Nitrate reducing bacteria reduced Tc(VII) effectively only in the presence of Fe(III) and after nitrate was reduced , implying a major role for Fe(II) as an electron shuttle in Tc(VII) reduction. It is likely that accumulation of NO_2^- blocks Fe(II) production and hence Tc(VII) reduction during the active nitrate reduction phase. The pure culture of *Clostridium* FRC-C11 is able to reduce Tc(VII) enzymatically with H_2 or glucose as electron donor and deposits insoluble Tc compounds within the cells in a manner that is not significantly influenced by the presence of NO_3^-. These results provided another possible mechanism for Tc(VII) reduction that is independent of Fe(III) and not influenced by nitrate.