A novel ion exchange separation for Cu prior to stable isotope analysis by MC-ICPMS

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The acquisition of stable isotope data with a precision of better than ±0.10‰ using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) requires that target elements are separated from the sample matrix to enhance sensitivity, avoid spectral interferences and minimize matrix effects.

At present, the isolation of Cu is generally performed using anion exchange chromatography, with Cu in the +2 oxidation state. These methods suffer from the incomplete separation of Cu from matrix elements and multiple stages of column chemistry are therefore often required to produce a sufficiently purified Cu sample for isotopic analysis. Such problems appear to be particularly prominent for biological materials because (i) of the major interference of $^{40}Ar^{23}Na^+$ on $^{63}Cu^+$ and (ii) samples with high organic content appear to increase the overlap between the elution of Cu^{2+} and the bulk sample matrix.

To avoid these problems, we have developed a novel procedure that makes use of the different distribution coefficients of Cu (I) and Cu (II) to anion exchange resin, to significantly improve the separation of Cu from biological materials. The method was found to yield sufficiently pure Cu fractions for isotopic analyses after a single pass through the anion exchange columns and it routinely achieves recoveries of 100% ± 2%. Subsequent isotopic analyses of the Cu by MC-ICPMS, using admixed Ni for mass bias correction, yielded accurate Cu isotope data with a reproducibility of about ±0.05‰ (2s) for pure standard solutions and ±0.10‰ (2s) for samples.

Schwertmannite and Fe oxides formed by biological low-pH Fe(II) oxidation versus abiotic neutralization

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We studied the mineralogy of three low-pH coal mine drainage (CMD) sites in central Pennsylvania. Water from one site was used in discontinuous titration/ neutralization experiments to produce Fe (III) minerals by abiotic precipitation for comparison with the field precipitates that were produced by biological low-pH Fe (II) oxidation. Sediments were characterized using X-ray diffraction, Fe K-edge extended X-ray absorption fine structure spectroscopy, and scanning electron microscopy with energy dispersive spectroscopy. Even though the hydrology and concentration of dissolved metals of the CMD varied considerably between the three field sites, the sediment mineralogy of the three iron terraces was found to be very similar. Schwertmannite was the predominant mineral phase precipitated at low-pH (2.5–4.0) along with lesser amounts of goethite. Schwertmannite particles occurred as micron sized spheroids with characteristic 'hedgehog' morphology at all sites. No trace metal incorporation was detected in sediments from the field sites, and no metals (other than Fe) were removed from the CMD at any of the field sites. Minerals formed by abiotic neutralization/precipitation (pH 4.4 – 8.4) were found to contain (in order of predominance) ferri-hydrite, schwertmannite and goethite. In contrast to low-pH precipitation, substantial trace metal removal occurred in the neutralized CMD. Biological low-pH Fe (II) oxidation can improve CMD treatment by reducing armouring and clogging of downstream limestone beds. A further benefit is that solids formed under these conditions may be of industrial value because they do not contain trace metals.