Pb purification by HBr-HCl and HBr-HNO_3 chemistry – A comparison

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Precise and accurate isotope ratio analysis by MC-ICP-MS requires effective matrix removal to minimize unwanted fractionation effects, particularly when using a desolvating nebulizer. We present a comparison of two anion-exchange resin based techniques for Pb purification. The first is the conventional approach employing HBr and strong HCl, the second was proposed for low blank separation of Pb from achondites, eluting Pb with weak HNO_3.

Identically sized columns were made from pre-cleaned commerical pipette tips into which a bed of ca. 10 mm resin (AGX-1*8, 200-400 mesh) is loaded. Columns were charged with a solution corresponding to 100 mg dissolved rock (AGV-2, BIR-1 & BCR-2). Elution acids were collected in 0.1mL steps and analyzed by quadruople ICP-MS.

For the HBr-HCl method, these analyses showed that all major elements were eluted effectively in the first 2 mL of weak HBr, and that less than 0.1% of major elements were collected with the Pb fraction. By contrast, the HBr-HNO_3 method was not as effective at removing the matrix elements Na, Mg and Al. Their retention behavior differs from one rock type to another. A careful single pass purification on HBr-HCl columns is sufficient for removal of >99.9% matrix.

We also compared yields. These were 71 % for the HBr-HCl method and 82 % for the HBr-HNO_3 method. The missing 20-30% of Pb is left behind in the undissolved residue that remains after centrifugation. Yields could be improved by a sequential extraction into more dilute HBr.

Column blanks were only marginally lower (8±3 pg) for the HNO_3 based method compared to the HBr-HCl method (12±3 pg). For the latter, we eluted Pb with 0.4 mL of 13.2 M triple sub-boiling distilled low-blank HCl, which is the key to minimizing blank of the HBr-HCl method.

For routine analyses, our digested samples are taken up in 10 mL of 20% HNO_3, from which a small aliquot is further diluted for full trace element analysis by quadrupole ICPMS. This yields the following long-term reproducibilities (1 sigma): Th/U (0.6%), U/Pb (1.2%) and Th/U (1.1%) for USGS standard BCR-2 and bviates the need for isotope dilution analysis and spiking. The remaining solution is then dried down and Pb purified. The eluted Pb is taken up in 2% HNO_3 for isotope ratio analysis. The knowledge of column yield and Pb concentration in the rock allows us to accurately predict the Pb concentration for optimal Tl spiking and optimal ion signal.

Defining biomineralization from the bacterial cell wall to the bulk solution

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The fate of metals in natural systems results from the complex interplay between processes mediated by bacteria and abiotic reactions in the bulk extracellular solution. It can be challenging to distinguish biotic from abiotic factors, making it difficult to articulate the pathways and identify the extent to which microorganisms control subsurface geochemistry. We have investigated the dissimilatory reduction of Fe, Mn, V and U by *S. putrefaciens* using microspectroscopy and electron microscopy techniques. Scanning transmission X-ray microscopy in particular has allowed us to decipher the path of metal ions from mobilization to bioreduction and precipitation as new mineral phases by providing critical information on metal distribution and speciation. The reaction of metals and minerals at the cell wall is of particular interest, and we have observed that the reaction of the metal with the cell wall – in terms of sorption, uptake or expulsion – cannot be explained solely by electrostatic or size factors. In addition, exposure of the bacteria to solid rather than soluble metals as the electron acceptor as well as the presence of competing ions strongly impacts the partitioning of metals between the bacteria, the bacteria-mineral interface, and the bulk solution. Nanometre-scale imaging and spectroscopy techniques are essential for understanding the suite of mineralization processes that take place consequent to bacterial metal reduction. This knowledge is vital to identifying sinks for trace metals in natural environments and estimating the potential for their long term immobilization.