Double spiking and the analysis of non-traditional stable isotopes by MC-ICPMS: An update

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In recent years, the use of a double spike for the correction of analytical mass bias in stable isotope ratio measurements by MC-ICPMS has become increasingly popular. This mass bias is usually an order of magnitude higher than natural isotope fractionation and therefore has to be corrected rigorously. After initial usage for the analysis of Mo isotopes, double spikes have recently been used for the analysis of Cr, Zn, Ca and Fe isotopes. The technique offers a number of significant advantages if compared to bracketing standards and “element doping” techniques. 1) unsystematic variations of the analytical mass bias with time are accounted for within analyses, as well as differences in matrix between standard and sample. 2) The mass range is restricted to the isotopes of the target element which is favorable for static measurements. 3) Problems effecting the isotope ratio of a doping element relative to the element to be analysed are avoided. However, with the introduction of second or third generation MC-ICPMS instruments and refined chemical and analytical techniques, all three techniques for mass bias correction or combinations thereof can produce similar instrumental precision. A drawback of double spiking is that extra care has to be taken to avoid memory effects particularly in sample introduction systems (e.g. DSN). These effects can considerably influence the precision of isotope ratio measurements. Rinsing protocols using different types of solutions as well as “pre-contamination” (i.e. rinsing with a sample aliquot before starting data aquisition) of the membrane have been proven useful to avoid memory.

The biggest advantage of the double spike technique today is therefore its capability to account for any isotope fractionation during chemical treatment of a wide variety of samples before analysis in a mass spectrometer. This allows for example the optimisation of ion chromatographic separations or non-quantitative recovery of the element in question from natural solutions after spike sample homogenisation. Use of a double spike can also significantly improve the accuracy, precision and flexibility of less common sample introduction techniques such as hydride generation and HPLC.

Regulation of Arsenic mobility on basaltic glass surfaces by speciation and pH

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The importance of geothermal energy as a source for electricity generation and district heating has increased over the last decades as demand for non fossil fuel energy sources has expanded. Arsenic can be a significant constituent of the geothermal fluids pumped to the surface during power generation. The aim of this project is to study the interaction of arsenic and basaltic glass surface, to allow prediction of arsenic mobility in volcanic aquifers.

Dissolved As exists in different oxidation states, mainly as the oxyanions arsenite (As(III)) which is more toxic than the oxidised from, arsenate (As(V)), with the charge of individual species varying with pH. Geothermal waters are frequently sulphidic and therefore the primary form of arsenic are thioarsenic species where oxygen surrounding a central arsenic atom is replaced by sulphur.

Basaltic glass is one of the most important rock types in many high temperature geothermal fields. The basaltic glass surface may be considered to by primarely composed of silanol and aluminol surfaces and to lesser but variable extent ironhydoxide surfaces.

Arsenic can form i) surface precipitates, ii) strong inner sphere complexes or iii) weaker outer sphere complexes on surfaces and the extent and type of sorption depends on surface type, pH (protonation of surface) and surface charge. Arsenic has the highest affinity for Fe(III) surfaces, followed by aluminol and finally silanol surfaces.

Static batch and dynamic column experiments were combined to generate and validate sorption coefficients for the As(III) and As(V) oxyanions in contact with basaltic glass at pH 3 to 10. Mobility of As(III) decreased as pH was shifted from pH 3 to pH 10. The opposite was true for As(V) being nearly immobile at pH 3 to having very limited interaction with the basaltic glass at pH 10. Incorporation of sorption coefficients, based on measured pH and Eh of geothermal fluids, into a regional groundwater-flow model was carried out and the modeled data will be validated with field measurements.