

Microanalysis of oxygen isotopes

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The preferred techniques for microanalysis of oxygen isotope ratios are laser fluorination/gas-source mass-spectrometry and ion microprobe/SIMS. These techniques are complementary.

IR-laser fluorination of mg-size chips or powder provide the most accurate and precise analyses ($\sim\pm 0.05\%$, 1SD). From 2 to 5 analyses/hour are routine and, unlike with Ni-reaction vessels, all components of the reaction line are evaluated by analysis of standards. Analysis at 50 μg scale requires transfer of O_2 to avoid fractionation during conversion to CO_2 and has less precision. In situ analysis by UV-laser carries the same trade-off of precision to sample size. Spatial resolution of 300 μm ($\sim 50 \mu\text{g}$) is possible at 0.1-0.2%. However, in situ analysis requires that the entire sample is exposed to reagent, and room temperature fluorination of grain boundary alteration and other reactive phases that are not in the laser spot can be a problem.

Stable isotope analysis by ion microprobe attains the smallest sample size and best spatial resolution. Instrumental mass-fractionation varies with instrument and mineral. Careful use of appropriate standards, bracketing unknown analyses, allows accuracy to approach precision. Analytical precision is greatly improved by use of multiple Faraday cup or electron multiplier detectors. Under favorable conditions, reproducible precision of 0.1-0.2% (1SD, $\delta^{18}\text{O}$, spot to spot) has been attained for 10-20 μm spots ($\sim 1 \text{ ng}$) in many silicate minerals (5-20 min./analysis) in at least four labs by Cameca ims-1270 with dual Faradays. Linear spatial resolution can be better than 1 μm in depth profile mode. Spot size of 0.3 μm is possible and, even at poorer precision, is useful for isotopically labelled experiments. Design improvements to the Wisconsin Cameca ims-1280 are intended to enhance reliability and precision of analysis, including: digital electronics; PC control; continuous monitoring of primary beam intensity; automatic focusing of the secondary beam in the field aperture and entrance slit, and of the objective lens; and better control of stray magnetic fields in the sample chamber and secondary column.

Ion microprobe analysis is required for samples that are zoned, precious, or rare. Published studies include coesite inclusions in diamond, zoned zircons, meteorites, quartz overgrowths, and speleothems. Future studies will explore new applications including biological targets. Most traditional and non-traditional stable isotope systems will enjoy the same advantages of small spot size and enhanced accuracy by multiple collector ion microprobe.

In situ-Fe isotope determination using femtosecond LA-MC-ICP-MS

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The *in situ* determination of stable iron isotopes by laser ablation coupled to multiple collector ICP-MS requires a precision of better than 100 ppm if the small variations expected in minerals shall be resolved. However, nanosecond laser systems that are common in geochemical laboratories are likely to produce an instrumental mass bias that is notoriously difficult to control and correct for. We expect that femtosecond lasers operated in the UV range produce ablation conditions that are by far superior in terms of aerosol size, stability, and ionisation efficiency.

Stable Fe isotope data of a variety of different matrices measured with our in-house build femtosecond laser ablation system are compared to standard solution ICP-MS measurements after chemical purification (Schoenberg & von Blanckenburg 2005) in order to evaluate the potential and advantages over traditionally employed nanosecond laser ablation. A pure Fe-metal standard (Puratronic) has been calibrated versus IRMM-14 yielding a $\delta^{56}\text{Fe}$ of $+0.085 \pm 0.03\%$ in solution. Using laser ablation we obtained a $\delta^{56}\text{Fe}$ of $-0.06 \pm 0.04\%$ (2σ) for this pair. We used this metal as a bracketing laser standard for all types of matrices including the iron meteorite phases taenite and kamacite, and the mineral phases hematite, siderite, goethite and biotite. A short term precision of 0.057% has been achieved on iron meteorites when bracketed against this metal.

Without a matrix match (e.g. bracketing an oxide, carbonate, or silicate against a metal) no significant degradation of either precision nor accuracy could be observed. Goethite yields an average $\delta^{56}\text{Fe}$ of -0.515% (LA) which compares well to the average value of -0.510% determined conventionally from solution. Siderite shows a $\delta^{56}\text{Fe}$ of -0.838% (LA) which again compares well to the $\delta^{56}\text{Fe}$ value of -0.854% determined conventionally.

However many of the low-temperature minerals analysed so far show significant zonations or large-scale inhomogeneities which can now be resolved by using femtosecond laser ablation. This provides us with a spatial resolution that adds a further dimension to our interpretation of stable metal isotope fractionation.

Reference

Schoenberg, R. and von Blanckenburg, F. (2005) *Int. J. Mass Spec.* in press.