

Laser ablation inductively coupled plasma mass spectrometry - The role of the ion source for quantitative analysis

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Abstract

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is frequently used for spatially resolved chemical characterization of a wide variety of minerals, soils and many other samples. Despite its successful use, accurate quantification of elemental concentrations can still be problematic, due to effects commonly summarized under the term “elemental fractionation”. This is most pronounced when matrix matched calibration standards are not available, which may result in variations of the relative sensitivities of the elements. This has been mainly attributed to non-representative laser sampling due to variations in the ablation process, causing preferential vaporization of elements. Recent reports, however, indicate that vaporization, ionization of the aerosol inside the ICP as well as the transfer of ions through the vacuum interface of the ICPMS are affecting the relative responses of individual elements significantly [1, 2, 3]. To describe these effects in detail the dependence of relative elemental sensitivities on the operating parameters of the ICPMS was studied for different samples using different laser ablation units (266 nm and 193 nm lasers). It can be shown that the relative sensitivities can vary significantly with the particle size distribution of the laser generated aerosol and the total mass load presented to the ICP. These variations are least pronounced when helium is used as carrier gas with 193 nm laser ablation which produces the aerosol with the lowest fraction of particles > 100 nm. Specific optimization of the ICP operating conditions, on the other hand can reduce the variation in the relative sensitivities and significantly improve the quantification even when the aerosol contains a large fraction of bigger particles and for argon as carrier gas. The change in elemental sensitivity was found to be different for two different ICPMS instruments compared. For one instrument sensitivities varied by not more than a factor of two, while for the other instrument the change was up to a factor of 15, depending on the element.

References

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What comes around goes around: Mantle convection and the meaning of mantle isochrons

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The perceived significance of isotopic data arrays for oceanic basalts has long occupied a middle ground between the endmember interpretations of mixing and age. Brooks *et al.* [1] were the first to attach age significance to the correlations between parent-daughter ratios (e.g. ⁸⁷Rb/⁸⁶Sr) and daughter isotope ratios (e.g. ⁸⁷Sr/⁸⁶Sr) that are a regular feature of the geochemistry of OIB and MORB [e.g. 2,3]. Pseudo-isochrons derived from mixed mantle can still have age significance if the various packets of source material have been physically juxtaposed for long periods of time, yet the current paradigm has generally been to focus on daughter ratios alone, and to interpret their variations in terms of multi-component mixing.

Numerous high-quality geochemical data sets now exist, and continue to be generated, for specific regions of OIB and MORB volcanism. In order to take the next step in a more accurate interpretation of this data, a forward model is needed that delimits the bounds of chemical variability and isotopic correlations expected to arise from the major processes operative during terrestrial mantle convection. In this talk, we will present the results of cylindrical 2D convection models with force-balanced plates [4] and examine specifically the role of subduction and convective mixing of oceanic crust.

In these models, melting occurs at divergent plate boundaries and geochemical evolution is recorded by millions of passive (harzburgite) and active (basalt) tracers that record the times, extents of melting, and extents of degassing at every melting event, allowing the geochemical evolution of any isotope system to be easily calculated (and recalculated) in a post-processing algorithm that operates on the tracer data independently from the dynamic calculations. We will explore the range of isotopic variability in these models as functions of partition coefficients, chemical density of basalt tracers, and convective vigor. In particular, these models reveal relationships between mantle isochron “ages” and true tracer ages that is not obtainable from statistical box-model calculations incorporating idealized mixing scenarios [e.g. 3-5].

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