

Characterization of laser-induced aerosol for quantitative analysis of solids using LA-ICP-MS

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Over the last 20 years of existence of LA-ICP-MS a lot of fundamental insights into the ablation process, aerosol transport and the atomization, vaporization and ionization within the ICP have been gained. However, the source of elemental fractionation as the most significant limitation of this technique and their influence on the quantification and isotope ratio measurements is still in controversial discussion.

Different methods to measure the particle size distribution were applied to characterize the structure of aerosols produced from various silicate matrices. Results show that the nano-particles generated within the ablation cell already agglomerate to nano-particles clusters up to a size of 1 micron before leaving the ablation cell (193 nm) whereas the aerosols generated at 266 nm contain agglomerates and a significant portion of single particles in the order of 1 micron. Furthermore, the total composition of the aerosol entering the ICP was collected and analysed using solution nebulization-ICP-MS. The collected aerosol generated at 266 nm and 193 nm in helium and argon represents the stoichiometric composition of the original sample (except Be, Fe and Cd). However, the size dependent composition of the aerosol (generated using 266 nm) entering the ICP-MS shows significant enrichment of volatile elements within the particle fraction below 340 nm and 125 nm, which indicates that the ion formation within a broader particle size distribution with highly variable composition can lead to matrix effects, especially when the absorptivity between the external calibration standard and the sample of interest differs.

To validate that 193 nm generated aerosols are less influenced by these matrix effects liquid calibration standards were applied to quantify solids. It will be shown that 193 nm laser aerosols and desolvated liquids behave similar within the ICP and can therefore be used for quantification.

Laser ablation MC-ICP-MS: Shedding new light on *in-situ* isotope ratio measurement

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The development of the multi-collector ICP-MS has greatly enhanced the capability for *in-situ* high precision isotope ratio analysis. Although we can build on experience from laser ablation trace element analysis on single-collector ICPMS, there are additional and complex issues to be considered in LAM-MC-ICPMS. Some are common to solution analysis (eg mass bias) but others are a consequence of the complex matrix of natural samples.

Accurate analysis requires rigorous correction procedures for mass bias and isobaric interferences. Instrument sensitivity, elemental concentration and grain size are the main controls in determining laser conditions and ablation times, and thus analytical precision. Signals produced by laser ablation are transient, but operating conditions for the laser can be chosen to achieve near steady-state signals. Frequency, laser fluence and spot size settings all contribute to signal stability and intensity.

In the analysis of major elements in common rock-forming minerals (eg Mg in olivine; Fe in pyrite) sensitivity is not a problem and isobaric interferences are negligible. In analyses of the Hf isotopic composition of zircon, corrections for REE interferences are critical. The measurement of isotopic ratios of trace elements presents greater problems; successful applications include Os in mantle sulfide; Sr in cpx, plagioclase and carbonate; Pb in feldspar. In some cases the best precision has been obtained at the expense of spatial resolution or in minerals with very low parent/daughter ratios. Further improvements will come with wider use of multi-ion counting systems; this will require the development of more stable detectors and more complex calibration routines. Laser-induced isotopic fractionation remains poorly documented and understood. It is unclear if fractionation occurs during ablation, during transport or within the plasma due to particle size distribution and/or matrix effects.

Compared with SIMS, a much wider range of isotopic systems has been developed on the LA-MC-ICPMS. There is a critical need for isotopically homogeneous reference materials that can be used to verify accuracy and for standard-sample bracketing in the measurement of mass-dependent isotopic fractionation.