

The accuracy and precision of *in situ* Re-Os isotopic measurements by laser ablation MC-ICPMS

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The development of *in situ* techniques for the measurement of Re-Os isotopes using laser ablation multi-collector ICP-MS has provided a stimulus to mantle geochronology by analysis of sulfides in mantle-derived peridotites (e.g. [1-3]) and platinum group alloy grains (e.g. [4-7]). The principal contribution to method development for laser ablation analysis of mantle sulfides is Pearson *et al.* [1] but the recent contribution of Nowell *et al.* [7] has identified issues that warrant a review of the original method. Accuracy and precision of the measurements depend on corrections for instrumental mass fractionation and isobaric overlap of ¹⁸⁷Re on ¹⁸⁷Os, as well as signal intensity, analysis time and laser-induced inter-element fractionation. Pearson *et al.* [1] and Nowell *et al.* [7] relied on solution experiments to establish reliability of Re corrections, and improvement of the *in situ* method continues to be hampered by lack of suitable elemental and isotopic reference materials. This problem is now addressed by the synthesis of a suite of NiS beads doped with different Re/Os ratios. Results from these beads demonstrate the validity of the Re correction methods, independently showing how accuracy and precision are affected by the total beam intensities of Re and Os, the Re/Os ratio, detector calibration and linearity, and the degree of Re/Os fractionation during ablation.

[1] Pearson, N.J. *et al.* (2002). *Geochim. Cosmochim. Acta* **66**, 1037-1050. [2] Alard, O. *et al.* (2005). *Nature* **436**, 1005-1008. [3] Griffin, W.L. *et al.* (2002). *G3*, 2002-11-21. [4] Hirata, T. *et al.*, (1998). *Chem. Geol.*, **144**, 269-280. [5] Shi, R. *et al.* (2007) *Earth Planet. Sci. Lett.* **261**, 33-48. [6] Walker, R.J. *et al.* (2005). *Earth Planet. Sci. Lett.* **230**, 211-226. [7] Nowell, G. *et al.* (2008). *Chem. Geol.*, **248**, 394-426. [8] Griffin, W.L. *et al.* (2004). *Chem. Geol.*, **208**, 89-118.

Exploring the world of high repetition rate femtosecond laser ablation coupled to ICPMS for trace element analysis in solids

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The increasing need to characterize complex solid specimens, including environmental samples, geochemical materials, archaeological objects, gemstones, is forcing the development of laser ablation sampling for chemical analysis as this technique allows the characterization of solid materials both in bulk and in spatially resolved analysis.

The arising of new compact femtosecond laser sources represents new advances in LA-ICP-MS. Such sources can deliver pulses at very high repetition rate (typically <10 kHz) though with a limited energy (<100µJ per pulse at 10 kHz). This contrasts with more conventional laser ablation systems operating at low repetition rates (few Hz) and high energy (few mJ per pulse). High repetition rate can be fully exploited for LA-ICP-MS analysis by using a fast scanning beam system (up to 300 mm s⁻¹) allowing sample ablation according to 2-dimensions trajectories. This opens a wide field of investigation in sampling strategies both in microscale and macroscale. Large volume of sample can be ablated in few seconds only providing the introduction of large amount of material into ICPMS enhancing the signal to noise ratio of the coupling. An original approach of in-cell isotope dilution has been developed : here, the quasi-simultaneous ablation of an isotopically-enriched solid spike and the sample to be analyzed placed together into the ablation cell allows the on-line isotope dilution process to occur very rapidly. This concept was successfully applied to soils analysis and will be presented.

As an illustration of these ablation approaches, the determination of trace element and isotope distribution in crude oils, fish otoliths, or uranium containing-micrometric particles will be presented. In addition, elemental and isotope fractionation phenomena have also been studied in these sampling conditions and will be presented.