Femtosecond laser ablation ICP-MS analysis of trace elements in solids

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The shorter duration of femtosecond laser pulses relative to the timescales for (1) heat transfer in ablated solids and (2) the time required for formation of a laser-induced plasma should lead to theoretically simpler laser-matter interaction processes compared to the commonly-used nanosecond laser ablation. Femtosecond laser ablation craters show much more limited thermal effects, with reduced melting features around the crater and on their walls compared to nanosecond craters. Ablated particles also display less melting effects in the femtosecond ablation case, and smaller sizes, easier to fully decompose in an ICP torch (Liu et al., 2004). Melting effects during ablation (Chenery et al., 1992) and incomplete decomposition of ablated particles in the Ar plasma of ICP-MS (Guillong et al., 2002) are the two main factors responsible for time-dependent chemical fractionation during nanosecond LA-ICP-MS analysis. Comparison of analytical data produced by nanosecond and femtosecond lasers under similar operating conditions show a significantly reduced chemical fractionation effect between elements of different volatilities during femtosecond laser ablation, thus leading to easier calibration. An other analytical benefit of femtosecond laser ablation is the production of more stable signals and of higher intensities for a given crater volume, which should result in decreased detection limits compared to nanosecond LA-ICP-MS. Uranium, thorium and lead analyses in glass, monazite and zircon were more accurate and precise by femtosecond LA-ICP-MS analysis, even when compared to the best analytical conditions for nanosecond laser ablation (Poitrasson et al., 2003). It was also found that femtosecond LA-ICP-MS calibration was less matrix-matched dependent, and therefore more versatile.

References

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196 nm femtosecond laser ablation: Applications to trace element and radiogenic isotope ratio determinations

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Laser ablation has been successfully applied to the determinations of trace element concentrations in a large variety of matrices and is widely used to determine Pb/U ratios in zircons and other minerals in geochronology. With increasing popularity of multiple-collector ICP-MS systems Laser ablation is now expected to provide highly precise data on radiogenic and stable isotope systems. The challenge arises from fundamental problems known from traditionally employed nanosecond Nd:YAG or Excimer laser systems such as “Elemental and isotopic fractionation” which make it difficult to achieve the precison needed for todays' applications.

In order to overcome these problems we employed a frequency-quadrupled femtosecond laser operating at a wavelength of 196 nm for our in-house built ablation system. Femtosecond laser pulses change the ablation process away from thermal ablation which provides significant advantages in terms of aerosol size, matrix dependency, transport efficiency, and stability. We investigated the potential of this laser by applying it to the Rb/Sr, U/Pb, Lu/Hf isotope systems as well as to trace element determinations performed using a Varian ICP-OES.

Our first results indicate that a precision close to that obtained by conventional ICP solution nebulization can be achieved for Sr and Hf isotope ratio determinations, and that no discrimination of volatile/refractory element pairs is observable within the precision of our measurements. It appears that the particle size of the aerosol produced during the ablation process is small so that “isotopic fractionation” produced from larger particles is therefore not observed. This allows the application of this system to stable metal isotope ratio determinations.

We will illustrate the potential of UV-fs-Laser ablation for the application of U/Pb dating of minerals and will discuss the differences to traditionally-employed nanosecond-based laser ablation.