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Femtosecond laser ablation – ICP mass spectrometry: a powerful high-resolution method for in-situ trace element and isotope ratio measurements in climate geochemistry

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Highly resolved in-situ analyses in the nm - µm range play an increasing role in many fields of geosciences, such as in climate geochemistry. To perform such analyses in our laboratory, we use laser ablation (LA)-(MC)-ICPMS with a 200 nm wavelength fs laser (NWR Femto-200) for trace element and isotope ratio measurements, optionally combined with a sensitive single-collector sector-field (Element2) and a multi-collector (Nu Plasma) ICP mass spectrometer, respectively. An advantage of fs over ns LA is that non-matrix matched calibration with certified silicate reference glasses can be performed [1]. Special settings have to be applied for highly resolved measurements, such as low fluence (0.1 J cm^{-2}), small spot size (10 µm), low pulse repetition rate (5 Hz), fast scan speed (e.g., 80 µm s^{-1}) for the laser, medium mass resolution (2000), and fast or simultaneous ion beam measurements using the single collector and the multi-collector ICPMS, respectively.

In-situ high-resolution fs LA-ICPMS trace element measurements have been performed for the investigation of archives of past environments, such as stalagmites, ostracods, foraminifera, shells, rock varnish, and glass sponges. We recently investigated 5 – 50 µm layers of varnish on terrestrial rock surfaces from different deserts worldwide and on meteorites with known terrestrial ages fallen in deserts. It was possible to measure Mn/Fe ratios with a precision (RSD) of better than 8 % at a resolution of 10 nm [2]. Significant variations are probably caused by microlamination of Mn- and Fe-rich layers, where low and high Mn/Fe ratios can be related to dry and wet climates [3]. To study major and trace element concentrations from the surface of the varnish to the bulk meteorite, we generated < 1 µm deep lines using a fast scan speed. The fs laser allows the determination of trace elements in 1 µm layers of ca. 5 µm thick ostracod valves to study their element distribution. Strontium and Mg are homogeneously distributed, and Cu and the REEs are concentrated on the surface of the ostracod shell. Trace element ratios, such as Mg/Ca and Sr/Ca, can be related to paleohydrochemical processes. Femtosecond LA-ICPMS Si isotope ratio measurements have been conducted on giant spicules of the long-living glass sponge *Monorhaphis chuni*. The determination of δ^{30}Si from the rim to the center of co-axial cross sections provides detailed information about the temporal Si content trend of the seawater. Si isotope ratios can be determined by LA-MC-ICP-MS with a long-term repeatability (2 RSD) of about 0.2 ‰ [4].

High spatial and depth resolution measurements are extremely useful to unravel the paleoclimate at high temporal resolution and other geochemical problems. The development of new, almost matrix independent LA systems with short wavelengths and short pulse lengths allow to perform precise and accurate microanalyses [1].

References:

[1] Jochum KP et al. (2014) Geostand. Geoanal. Res. 38:265-292
[2] Jochum KP et al. (2015) AGU Fall Meeting, abstract
[3] Liu T and Broecker WS (2013) Geomorphology 187:38-60
[4] Schuessler JA and von Blanckenburg F (2014) Spectrochim. Acta Part B 98:1-18