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Depth profiling by femtosecond-LA-(MC-)ICP-MS for the investigation of chemical and isotopic diffusion profiles with high spatial resolution

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Femtosecond laser ablation coupled to MC-ICP-MS has been proven to be a powerful means to analyze isotope ratios of "non-traditional" stable isotope systems with high spatial resolution *and* high precision and accuracy. The technique has been successfully applied e.g. to investigate diffusion-generated Li- and Fe-Mg isotopic zoning in magmatic olivine crystals. However, due to the typically used spot size of the laser (~20-30 µm), the spatial resolution is limited to diffusion profiles with length scales of >50 µm. Here, we present a novel sampling technique employing a fs-LA system (*Solstice*, Spectra Physics) that is equipped with a CNC-controlled laser stage, using the open-source software Linux-CNC operating in real-time. This set up allows to perform depth profile analyses of major and trace elements as well as metal stable isotope variations (Li-Mg-Fe) in olivine crystals and in experimental diffusion couples with a depth resolution of ~1 µm.

Samples are ablated in circular patterns with diameters of 100-200 µm. Depending on the scan speed and the repetition rate of the laser (typically between 20 and 60 Hz), each ablated sample layer is between 300 nm and 2.5 µm thick. The integrated signal of one ablated layer represents one data point of the depth profile. The total depth of the profile can be controlled by the number of ablated layers (typically 15-25 layers). We have tested this technique by analyzing chemical diffusion profiles in olivine crystal cubes which are compared to "horizontal" profile data acquired by electron microprobe analyses. Furthermore, Fe-Mg isotopic depth profiles were analyzed in a diffusion couple consisting of a ^{25}Mg- and ^{57}Fe-doped olivine thin film (~1 µm thick) in contact with a natural olivine crystal cube, which was prepared using pulsed laser deposition. Our results indicate (i) that concentration data acquired by LA depth profiling match well with electron microprobe data, (ii) that precise and accurate δ^{25}Mg, δ^{26}Mg, δ^{56}Fe and δ^{57}Fe data can be obtained (i.e. precision and accuracy are ≤0.10‰ and ≤0.15‰, respectively, for both δ^{26}Mg and δ^{56}Fe), and (iii) that potential top-to-bottom contamination during depth profiling of isotope ratios can be avoided.