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Matrix-independent B, Si and Fe isotope analyses by UV femtosecond laser ablation MC-ICP-MS with applications in marine geochemistry

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Ultrashort pulse laser ablation (LA) combined with ICP-MS offers significant advantages for metal and metalloid isotope analysis due to minimal thermal effects during ablation. Here, we employed a UV femtosecond LA system (Solstice, Spectra Physics) coupled with a MC-ICP-MS (Nu Plasma II, Nu Instruments) to develop analytical protocols for matrix-independent B, Si, and Fe isotopic ratio measurements at the micrometer scale [1; 2]. We demonstrate the accuracy of our approach across diverse reference materials, including silicates (MPI-DING glass series), carbonates (JCp-1), and Fe-rich mineral phases using non-matrix matched calibration without employing any correction and achieved a reproducibility of ±0.9‰ (2 SD) for B, ±0.20‰ (2 SD) for Si, and ±0.15‰ (2 SD) for Fe isotopes, respectively. These results confirm the absence of laser-induced or ICP-related matrix effects. To illustrate the method's potential for high-resolution isotope analysis in natural environments, we applied it to three case studies: (1) Investigations of B isotopes as a pH proxy in cold-water corals Desmophyllum dianthus from a Patagonian fjord revealed $\delta^{11}B$ values between 23.01‰ and 25.83‰ with minor intra-skeletal variability, corresponding to an internal pH up-regulation of 0.7–1.1 units relative to ambient seawater; (2) Measurements of Si isotopes in Devonian Lahn-Dill iron ore (Rhenish Massif) exhibited $\delta^{30}Si$ variations from –4.56‰ to –2.04‰ in microcrystalline quartz, which is consistent with the preservation of primary signatures reflecting strong kinetic effects during absorption of seawater Si onto Fe-(oxyhydr)oxides of hydrothermal origin; and (3) Fe isotopes in pyrite grains formed in coastal marine sediments of the Eastern Arabian Sea indicate complex formation histories shaped by micro-environmental conditions. These findings demonstrate the robustness and versatility of UV femtosecond LA for matrix-independent isotope analysis, expanding its applications in geochemistry and environmental sciences.

References:

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[2] Steinhoefel, Schmitt, Angerer, Kirnbauer & Klein (submitted), *Geochemistry, Geophysics, Geosystems (G3)*