

# **Determination of Ti isotopes in rutiles with high spatial resolution by femtosecond laser ablation multi- collector inductively coupled plasma mass spectrometry**

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Crystallization of Fe-Ti oxides can induce significant Ti isotope fractionation during magmatic differentiation. As such, rutile (TiO<sub>2</sub>), a common Ti-rich mineral present in igneous, metamorphic, and sedimentary rocks, can serve as potentially powerful tracer of the geologic processes. Here, we establish a method for *in situ* analysis of stable Ti isotope ratios in natural rutile (TiO<sub>2</sub>) by femtosecond laser ablation multi-collector inductively coupled plasma mass spectrometry (fs-LA-MC-ICP-MS). Using a high sensitivity cone combination (Standard sampler cone + X skimmer cone) to increase the Ti signals allows for high spatial resolution. Our results show that changing laser parameters (e.g., spot size and laser fluence) between samples and references can cause bias towards higher  $\delta^{49}\text{Ti}$  values of 0.16‰ to 0.59‰ under dry plasma conditions, which can be suppressed by using wet plasma conditions instead. After optimization our approach provides accurate  $\delta^{49}\text{Ti}$  results at a precision of  $\pm 0.1\text{‰}$  with a spatial resolution of only  $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m} \times 4\text{ }\mu\text{m}$ . Long-term reproducibility established by measurements of USA75 rutile is  $\pm 0.13\text{‰}$  in  $\delta^{49}\text{Ti}$  for our fs-LA-MC-ICP-MS approach. Measurement of nine natural rutile crystals by both solution MC-ICP-MS and fs-LA-MC-ICP-MS provide consistent  $\delta^{49}\text{Ti}$  values, thus confirming the accuracy of our fs-LA-MC-ICP-MS method. The  $\delta^{49}\text{Ti}$  of the nine rutiles vary by  $\sim 2.9\text{‰}$ , reinforcing the idea that Ti isotopes in rutile may be a powerful geochemical tracer. Long-term characterization shows that rutile USA75 can be used as a reference material for future *in situ* Ti isotope ratio measurements.