

## ***In situ* Sr isotopic analysis of low Sr samples using LA-ICP-MS**

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### **New Technique**

We have developed a technique to determine <sup>87</sup>Sr/<sup>86</sup>Sr in geological samples having low Sr concentrations (30 – 400 µg/g). Because of its high sensitivity we used the single-collector sector-field ICP-MS Element 2, which was combined with a 193 nm Nd:YAG laser ablation system from New Wave.

Measurements were performed using spot sizes of 50 µm and the electrical scan mode of the ICP-MS. Various corrections were made for the determination of <sup>87</sup>Sr/<sup>86</sup>Sr: dead time correction of the ion counting system, blank, isobaric interference of Kr, possible interferences from doubly charged REE and Hf, isobaric interference of <sup>87</sup>Rb on <sup>87</sup>Sr (Rb/Sr should not exceed 0.1 for precise analysis), mass bias corrections for Sr and Rb.

### **Results**

The external precision (RSD) of our Sr isotope measurements ranges between about 0.04% (Sr = 400 µg/g) and 0.2% (Sr = 30 µg/g). The <sup>87</sup>Sr/<sup>86</sup>Sr ratios for the MPI-DING (KL2-G: 0.7036, ML3B-G: 0.7038, GOR128-G: 0.7076), USGS (BHVO-2G: 0.7035) and NIST (SRM 614: 0.7080) glasses agree within uncertainty limits with TIMS data.

### **Applications**

We have applied this technique for the *in situ* isotopic analysis of 100 – 300 µm glassy melt inclusions from one young Mauna Loa (Puu Wahi) basalt, ca. 200 – 500 µm x 100 µm large basaltic glass fragments from the submarine section of the Hawaii Scientific Drilling Project (HSDP) and small MORB glasses. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios of 150 melt inclusions are extremely variable (0.702 – 0.708). The highest ratios were found in ultra-depleted inclusions, where Sr is low (about 60 µg/g). The <sup>87</sup>Sr/<sup>86</sup>Sr values of 8 depleted MORB glasses (0.7022 ± 0.0004) and 8 HSDP Mauna Kea glasses (0.7036 ± 0.0003) are uniform within uncertainty limits.

## **Seawater dissolved Fe isotopes as a tracer of Fe sources to the ocean**

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Fe stable isotopes have been measured in seawater profiles from the San Pedro Basin and the North Atlantic near Bermuda. New methods allow us to measure seawater δ<sup>56</sup>Fe on 1 L samples with a precision of 0.05 ‰ to 0.13 ‰ (2σ) for seawater with 0.2 nM to 1 nM Fe, respectively. We have discovered significant variations in seawater δ<sup>56</sup>Fe and use this variability to trace different sources of Fe to the ocean.

Water column δ<sup>56</sup>Fe values in the San Pedro Basin range from -1.82 ‰ to 0.0 ‰. δ<sup>56</sup>Fe values are most negative in deep waters reflecting the input of isotopically light Fe(II) from the sediments. Paired measurements of dissolved and particulate δ<sup>56</sup>Fe allow us to constrain the processes which govern dissolved-particle interactions. The isotopic offset between these phases is inconsistent with either particle dissolution or equilibrium between dissolved-phase and particulate-phase Fe, but is consistent with a kinetic isotope effect during precipitation of Fe out of the dissolved phase. With a simple vertical model of Fe cycling in the deep San Pedro Basin we make quantitative predictions about the role of continental shelves in the global Fe cycle. Using this model we calculate Fe flux from San Pedro Basin sediments, δ<sup>56</sup>Fe of Fe released from the sediments, timescale of Fe precipitation in oxic seawater, and the isotope effect for precipitation.

In the North Atlantic near Bermuda, we find an average seawater δ<sup>56</sup>Fe of +0.3 ‰ in surface waters down to 1500 m, and at 4200 m. Heavier δ<sup>56</sup>Fe values are seen at 2000 m and 2500 m, with a maximum of +0.71 ‰ at 2500 m. We believe this relatively heavy δ<sup>56</sup>Fe value may be a signature for hydrothermal activity. A kinetic isotope effect during precipitation of hydrothermal Fe would leave hydrothermal plumes enriched in heavy isotopes. The height of the mid-Atlantic ridge is roughly consistent with maximum hydrothermal input between 2000 m to 3000 m. If the signal seen at Bermuda does have a hydrothermal origin, this suggests either extremely heavy (> 4 ‰) δ<sup>56</sup>Fe values in buoyant hydrothermal plumes or a large contribution of hydrothermal Fe to the waters near Bermuda at 2500 m (>10%).