



New developments for the in situ-analysis of non-traditional isotopes

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While the measurements of precise (50-100ppm precision) ratios for the non-traditional isotopes by MC-ICP-MS is now almost routine, the extraction of such isotope information from solids at high spatial resolution by SIMS and nanosecond laser ablation has been plagued by intrinsic physical limitations posed by matrix effects and matrix-induced irregular ablation and ionisation. We have overcome these limitations by coupling a UV (266 or 196nm) all solid-state femtosecond laser to our Thermo Neptune ICP-MS. The advantages of the generated ultra-short pulses over those produced by nanosecond lasers used to date (excimer and solid-state) are a sampling area that is not heated to beyond that illuminated by the laser beam, thereby minimising thermal effects; a much higher energy deposited per pulse resulting in much smaller particle size. Both result in a higher sensitivity, much reduced matrix effects, and stability in the isotope mass bias produced by the ICP source.

We can now measure stable Fe isotopes at a spatial resolution of 25 micrometers on metal, oxides, carbonates, sulfides and silicates. All these matrices are bracketed against a metal standard; the mass bias is independent of the sample matrix. Intensity matching is done by adjusting the repetition rate of the laser according to Fe concentration in the sample. For example, individual magnetite grains and associated siderite and sulfides can be measured in polished BIF samples. Similarly, we routinely measure stable Si isotopes in elemental Si, Si oxide and silicates, and even from Si-rich solutions. For example, Si isotope variations within individual sponge needles can be resolved. The long-term reproducibility in isotope ratios is 0.1 to 0.2 permil. Although such systems are not yet commercially available, they still carry perhaps the greatest

promise for future stable isotope work, given their robustness and ease of analysis when compared to other techniques.