New possibilities for the *in situ* measurement of δ^{34} S and δ^{33} S by laser ablation multiple collector ICP-MS

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High precision sulfur isotope data provide key constraints on the sulphur cycle relevent for studies of microbial life, the origin of ore deposits and can be linked to planetary-scale tectonic and atmospheric processes. Unfortunately existing measurement techniques (e.g. laser fluorination GS-MS, SIMS) are not widely available, require extensive sample handling and can suffer from matrix effects. We have developed a new technique that employs laser ablation MC-ICP-MS for direct microanalysis on a scale <150 μ m. Our new technique provides access to ³³S as well as ³²S and ³⁴S for the measurement of mass-independent fractionation.

Our method has been tested on two different sets of instrumentation, both of which give comparable results. There were two major aspects to our method development: (1) the avoidance of spectroscopic interference from O_2^+ , NO⁺ and OOH⁺ and (2) a two-stage correction for mass bias. The levels of interference and mass bias, common to all isotope systems analysed by MC-ICP-MS, are extreme in the case of S isotopes. In the first set of experiments, interferences were attenuated in a hexapole colision and reaction cell and mass bias was normalized using the exponential law against the NIST SRM 975a Cl isotopic standard. The second instrumental set-up avoided intereferences using intermediate mass resolution (m/ Δ m =5000) with normalization against the IRMM-018 Si isotopic standard. A second linear interpolation correction was carried out in both sets of experiments against external pressed pellet standards made from the IAEA-S series AgS reference materials. Mean $\delta^{34}S_{V\text{-}CDT}$ and $\delta^{33}S_{V\text{-}CDT}$ showed excellent agreement (within analytical error, typically 0.6 and 1.5 % respectively) against reference data. Matrix effects led to consistent deviations in accuracy of up to 3 % when calibrating elemental sulphur or sulphate against sulphide standards. This new method opens up exciting possibilities for tracing metabolic sulphate reduction in small inclusions and minerals preserved in early Archaean rocks. We present preliminary data for sulphide and sulphate minerals collected from the Pilbara block, NW Australia.