Advances in analyses of radiogenic isotope by LA-MC-ICPMS: The importance of mass bias and interference correction

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Isotope analysis by laser ablation sector-field ICP mass spectrometry (LA-SF-ICPMS) becomes increasingly important to study magmatic, metamorphic, and sedimentary processes. The information gained can be, for instance, crucial for a better understanding of the timing and genesis of magmatic and sedimentary rocks, the formation of ore deposits, and the evolution of the continental crust. Due to disturbance of the isotope system by alteration and partial recrystallization the initial isotope composition is often preserved only in single growth domains of minerals.

Developments in LA-SF-ICPMS over the last years make it now possible to analysis precisely the isotopic composition of Sr, Nd, Hf, and U-Th-Pb with a spatial resolution of down to 30 to 5μm, depending on elemental concentration. Hence, a very sensitive detection system coupled to powerful Laser with short wave length and high resolution imaging system is crucial for this type of analyses.

Beside high background (e.g., gas blank), matrix effects, and mass bias correction, the precision and accuracy of these isotope analyses often strongly suffers from isobaric and molecular interferences on the relevant masses. Although these interferences in question can be usually monitored simultaneously on a different mass, the interference correction is hampered by prediction of the mass discrimination behaviour of this isotope pair.

Data will be shown that the discrimination of the lighter isotopes in the plasma interface of the ICP-MS is dependent on element and on the matrix. With examples from the different isotope system, analytical protocols will be discussed to overcome this problem. The results of recent studies performed in our lab demonstrate that LA-MC-ICPMS analyses of ^{87}Sr/^{86}Sr (e.g., plagioclase, titanite, apatite, monazite, xenotime, pyrochlor, perovskite), ^{143}Nd/^{144}Nd (e.g., titanite, monazite, apatite, pyrochlor, perovskite, garnet) and ^{176}Hf/^{177}Hf (e.g., zircon, zirconolite, baddeleyite) isotopes can be precise and accurate to about 0.01% or better, despite of 10 to >50% interference on the relevant isotope ratio. Providing that between different phases the range in the mother-daughter isotope ratio is sufficient large enough, it is even possible to obtain geologically meaningful isochrones in the Rb-Sr and Sm-Nd system by LA-MC-ICPMS analyses.

Geochemical signatures of thermochemical sulfate reduction – Ketones and sulphur species

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Thermochemical sulfate reduction (TSR) is defined as the abiological, thermally-driven reduction of sulfate with H_2S and CO_2 as major reaction products. The reaction can proceed at temperatures above 120°C when sulfate as well as reducing agents, such as e.g. hydrocarbons or ferrous iron, are present. In spite of its great importance for hydrocarbon reservoir alteration and sulfide ore formation, the TSR process is not adequately understood. In this study we present findings from laboratory experiments that lead to an improved description of the geochemical signature of TSR and thus to a better understanding of TSR reaction mechanisms. A major goal was to identify key chemical compounds that play an important role during TSR.

Experiments were performed in sealed gold capsules, at 300°C and 350°C, 350 bar, for a duration of 24 - 336 h. A redox-mineral buffer, consisting of pyrite (FeS_2), pyrrhotite (FeS) and magnetite (Fe_3O_4) was used to constrain the redox conditions during the experiments. Na_2SO_4, dissolved in water, was used as sulphate source and C_8H_{18} as model hydrocarbon (= reducing agent). Furthermore, the influence of elemental sulphur on the TSR reaction was investigated. After the experiments the products were analyzed by different gas chromatographic techniques. In addition to CO_2 and hydrocarbons, we focused on the analysis of ketones and organosulphur compounds.

In general, a higher reaction rate was found at 350°C compared to 300°C. Concurrent processes in the degradation of octane under the experimental P-T conditions comprise cracking and TSR reactions. A pronounced influence of TSR was indicated by the formation of CO_2, ketones, aromatics and organosulphur compounds. The experiments with elemental sulphur showed the highest yields of TSR products. The analytical data suggest that the oxidation of carbon proceeds via one or more intermediate reaction steps with metastable oxygenated or sulfurized compounds, e.g. the formation of ketones.