Experimental investigation of the stability of Fe-rich carbonates in the lower mantle

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Carbonates are the main C-bearing minerals that are transported deep in the Earth's mantle via subduction of the oceanic lithosphere [1]. The fate of carbonates at mantle conditions plays a key role in the deep carbon cycle. Decarbonation, melting or reduction of carbonates will affect the extent and the way carbon is recycled into the deep Earth.

High-pressure high-temperature experiments were carried out up to 105 GPa and 2850 K on oxide assemblages of (Mg,Fe)O + CO_2. The presence of $Fe^{(II)}$ in starting materials induces redox reactions from which $Fe^{(II)}$ is oxidized and a part of the carbon is reduced. This leads to an assemblage of magnetite, diamonds, and carbonates or, pressure depending, their newly discovered $Fe^{(III)}$-bearing high-pressure polymorphs based on a silicate-like chemistry with tetrahedrally coordinated carbon [2]. Our results show the possibility for carbon to be recycled in the lowermost mantle and provide evidence of a possible coexistence of reduced and oxidized carbon at lower mantle conditions.

[1] Sleep, N. H., and K. Zahnle (2001) *J. Geophys. Res.-Planets* **106**(E1), 1373-1399. [2] Boulard *et al.* (2011) *PNAS*, **108**, 5184-5187.

Advances in high precision Ca isotope ratio measurements using TIMS

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Ca isotopes are used in various disciplines within Earth Sciences, e.g. paleoceanography, geochronology and biogeochemistry. Precise and reproducible measurements of Ca isotopes are among the most challenging measurements within TIMS. Most important factors influencing the precision and reproducibility are sample loading, choice of double spike, instrumental mass fractionation and mass spectrometer performance. Advances in mass spectrometry have been made with the introduction of the TRITON *Plus*.

The TRITON *Plus* has innovative features that enable high precision Ca isotope ratio measurements for all Ca isotope ratios. First of all, the TRITON *Plus* enables simultaneous collection of 40Ca up to 48Ca without zoom due to the extended mass dispersion. Also, the instrument can house different ohmic resistors (10^{10}, 10^{11} and 10^{12} Ohm). This is especially useful for isotope systems with a large dynamic range, such as Ca, where the abundance of the major isotope is almost 97%. If smaller samples are analysed, the low-noise 10^{12} Ohm amplifiers are advantageous, since they show up to a factor of 3 improvement in signal/noise ratio over the standard 10^{11} Ohm current amplifiers.

In this contribution, we present basic performance features for the TRITON *Plus* with regard to Ca isotope ratio measurements, as well as precision and reproducibility for different sample sizes.