In-situ apatite Ca isotope analysis: A potential new tool to decipher crust formation

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Calcium (Ca) is the fifth most abundant element in the Earth's crust and its isotopes fractionate during a range of geological and biological processes. Applications of stable and radiogenic Ca isotopes within the Earth Sciences are versatile: For instance, Ca isotopes have been deployed to elucidate magma sources and understand processes involved in the formation of continental crust. Furthermore, Ca isotopes trace the recycling of carbonates, and thus Ca sources, into otherwise inaccessible regions of the solid Earth, and track changes in seawater chemistry and climate perturbations over geologic timescales. However, to date the measurement of Ca isotopes predominantly relies on solution techniques (e.g., TIMS or MC-ICPMS) requiring digestion of the sample in acid and complex chromatography procedures prior to analyses.

This study assesses the feasibility of in situ analysis of stable Ca isotopes from apatite, a ubiquitous mineral in a wide range of rock types. Apatite allows the direct link of Ca isotopes to other isotopic signatures (e.g., Sr and O) and age information (e.g., through U-Pb, Lu-Hf geochronology). Measurement of stable Ca isotopes in apatite on the (inter-) grain scale provides a promising tool to enhance our understanding of stable Ca isotope fractionation during magmatic and metamorphic processes and track Ca sources in crustal rocks through deep time.

Here we report the results of in situ Ca isotope analysis (including ⁴⁰Ca, ⁴²Ca, and ⁴⁴Ca) in apatite via secondary ion mass spectrometry. We test two different analytical setups involving the measurement of singly and doubly charged Ca ions, and assess protocols for interference and matrix corrections. In situ results are validated through comparison with thermal ionization mass spectrometry (TIMS) equipped with ATONA signal amplification system for low-level Ca isotope ratio measurements via double-spike approach.