

Fingerprinting early continental evolution using Ca isotopes

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Questions concerning the formation of the earliest continental crust and its characteristics are highly debated but remain unclear. Does the scarcity of Archaean crust reflect a continuous growth of continental crust with time or very effective destruction? Do different geochemical characteristics mirror different crustal provinces and hence different mechanisms of crust formation? The K-Ca isotope system is highly suitable to address these problems due to: *i*) the short half-life of ^{40}K , decaying to ^{40}Ca , compared to the age of the Earth results in non-linear growth of ^{40}Ca , *ii*) the Ca isotopic composition of the mantle remains effectively constant because of its very low K/Ca ratio, and *iii*) K and Ca are strongly fractionated during crust formation processes.

We analysed ~3.6 Ga old felsic and mafic rocks from different Archaean Cratons. The Ca isotopic compositions of plagioclase and titanite separates in addition to the whole rocks were measured using the Finnigan-Triton TIMS. Ca is a major component in plagioclase and titanite, which are also characterised by low K/Ca. Therefore, both minerals should reflect the initial Ca isotopic composition of the source. The Ca isotope data show a clear distinction of the different Archaean provinces. TTGs from Zimbabwe show a Ca isotopic composition indistinguishable from our measured MORB value. Greenland samples, however, yield evolved radiogenic signatures of $\epsilon_{\text{Ca}} \approx +3$. The Akilia gabbros and the Itsaq gneisses show the same range of radiogenic ϵ_{Ca} values and plot on or above a single stage crustal evolution curve starting 4.5 Ga ago with a K/Ca ratio of 0.35.

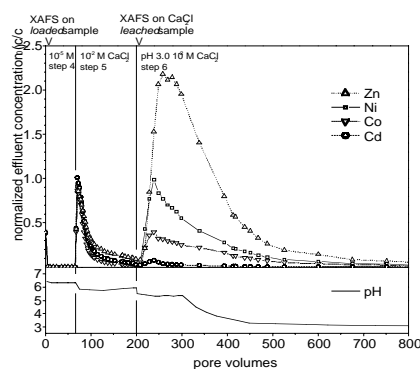
Due to the fact that most Archaean rocks underwent metamorphism and alteration, the interpretation of back-corrected initial isotope values requires great care. A less radiogenic titanite compared to the corresponding plagioclase in the Zimbabwe samples indicates that the Ca isotopic composition of plagioclase might in some cases reflect a mixture of original, initial value and a ratio that evolved in the whole rock. It might also suggest that titanite more likely exhibits the pristine ratios and, therefore, more titanites will be analysed. However, exchange of the isotope signature due to recrystallisation during later thermal events can not explain the same back-corrected ϵ_{Ca} values obtained from different lithologies such as in Greenland. Felsic and mafic rocks have different K/Ca ratios and, thus, should yield different isotopic compositions. Only a very K-enriched crustal precursor comparable with the K-fraction of lunar KREEP basalts formed > 3.9 Ga ago can account for such radiogenic values up to $+3 \epsilon_{\text{Ca}}$.

Formation and dissolution of Zn-precipitates during reactive transport in a circum-neutral soil

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Recent spectroscopic studies have demonstrated the formation of layered double hydroxides (LDH) and phyllosilicates upon sorption of Zn^{2+} , Ni^{2+} , and Co^{2+} to clay minerals and aluminum oxides at neutral to alkaline pH, and at relatively high initial metal concentrations (~1 mM). The intention of the present study was to investigate, whether such phases also form in soil under slightly acidic conditions (pH~6.5) and at lower metal concentrations. Columns packed with a loamy soil were percolated with aqueous solutions containing 0.1 mM to 0.2 mM ZnCl_2 , NiCl_2 , CoCl_2 , and CdCl_2 in a 10 mM CaCl_2 background at pH 6.5. Metal breakthrough curves indicated a rapid initial sorption step, resulting in retarded breakthrough fronts, followed by further slow metal retention during the entire loading period of 42 days (~7000 pore volumes). Total metal sorption and the contribution of slow sorption processes decreased in the order $\text{Zn} > \text{Ni} > \text{Co} > \text{Cd}$. Leaching the reacted soil with 10 mM CaCl_2 at pH 6.5 remobilized 8% of the total retained Zn, 15% of Ni, 21% of Co and 77% of Cd (Fig. 1, 70-200 pore volumes). Leaching with acidified influent (pH 3.0) remobilized most of the remaining metals (Fig. 1, 200-800 pore volumes). Analysis of soil samples from the column experiments by X-ray absorption fine-structure (XAFS) spectroscopy showed that slow Zn sorption was due to formation of an Zn-LDH solid phase. Although Ni,



Co and Cd concentrations were too low for XAFS analysis, their leaching patterns suggest that part of Ni and Co were also incorporated in solid phases, while most Cd remained as exchangeable sorption complex. A small but significant percentage of the sorbed metals (2% to 5%) remained in the soil even after leaching with more than 3000 pore volumes at pH 3.0, which may suggest micropore diffusion or precipitation of more stable mineral phases.