Calcium isotopic ($\delta^{44/40}Ca$) compositions of pedogenic carbonates from south India: links with paleo weathering

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Transfer of calcium from continent to the ocean through carbonate and silicate weathering and subsequent precipitation in oceanic sediments play a major role in atmospheric CO_2 regulation over geological timescales. However, calcium can be temporarily trapped as pedogenic carbonates in arid and semi-arid environments, i.e., in areas receiving mean annual rainfall (MAR) below 700 mm [1 and references therein]. These carbonates constitute potential proxies for paleoclimatic studies but may have experienced complex dissolution/growth phases that need to be identified.

Carbonate nodules were collected in the forested tropical watershed of Mule Hole in Southern India. These carbonates formed ~1.3-60 kyr ago as determined using using U-Th method [1]. Present day MAR at Mule Hole is 1100 mm which is unfavorable for pedogenic carbonate formation. One goal of this study was to understand the dynamics of nodule formation using calcium isotopic signatures of calcite.

The carbonate fraction of pedogenic nodules was dissolved in 6N HCl. Calcium was separated from the matrix by column chromatography. Isotopic ($\delta^{44/40}Ca$) measurements were performed using a ^{43}Ca-^{48}Ca double spike technique with a Thermo Triton Plus TIMS at the Centre for Earth Sciences, Indian Institute of Science, Bangalore. External reproducibility of the measurements is better than ±0.08‰, estimated by multiple measurements of NIST standards SRM915a and SRM915b and seawater (NASS6). $\delta^{44/40}Ca_{SRM915a}$ of carbonate fractions range from -0.01 to +0.72 ‰. The $\delta^{44/40}Ca$ of the nodules are inversely correlated with Al and Mg concentrations suggesting binary mixing between carbonate-rich and smectite-rich end-members. Older samples which experienced several dissolutions and regrowth show enrichments in heavy Ca isotopes. Calcium isotopic compositions of pedogenic carbonate can be used to understand the links between paleo-weathering and paleo-climatic conditions.

[1] Violette et al., 2010, Geochim. Cosmochim Acta, 74(24), 7059-7085.