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Calcium isotopes in a proglacial weathering environment: Damma glacier, Switzerland

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Calcium is a key element in global biogeochemical cycles. It is an essential nutrient and the dissolution of Ca from silicate minerals is intimately linked to the global carbon cycle. Yet relatively few studies have utilized the potential of stable Ca isotopes to directly investigate (as opposed to using Sr isotopes) processes affecting Ca during initial weathering and subsequent cycling within the ecosystem.

The Damma glacier fieldsite (Central Swiss Alps) provides an ideal opportunity to study the early stages of silicate weathering processes and is the site of a larger multidisciplinary research project (BigLink). The catchment is underlain by Central Aar granite, which does not contain detectable carbonates. The Damma is a small, glacial catchment (10.7 km^2) where the glacier has retreatred since 1850 creating a 1.5 km long chronosequence which spans approximately 150 years of soil development and exhibits a strong vegetation gradient along its length.

In order to investigate the biogeochemical Ca cycle in the forefield, extensive sampling of the main reservoirs of Ca was undertaken. Soil samples from two different depths (0-5 and 5-10 cm) were collected at 23 randomly selected sites across the forefield in addition to six bulk rock samples. To further investigate potential fractionation between different soil pools, sequential extractions were performed. Stream water was collected at three different locations in the forefield on a biweekly basis throughout the sampling season, in addition to precipitation (snow and rain) and porewater samples. To investigate the effect of biological cycling on Ca, leaves from *Rhododendron ferrugineum* were also analysed. Analyses of all samples were performed using a Triton TIMS with a ^{43}Ca-^{46}Ca double spike, after a 4-step chromatographic separation procedure.

During this very early stage of weathering, the young soils which have formed were isotopically identical in $\delta^{44/42}$Ca to the rock from which they were derived, indicating that primary dissolution of the bulk rock does not strongly fractionate Ca isotopes. This is further corroborated by the analyses of the streamwaters which were within error of the average soil. Only one time point, coinciding with the end of the main snow melt period, was significantly different in $\delta^{44/42}$Ca from bulk rock. The only Ca pool which was significantly fractionated from bulk rock was vegetation, which exhibited an enrichment of light Ca isotopes.

Significant calcium isotope fractionation between bulk rock and soils is likely to only occur where the soils are no longer buffered by primary mineral dissolution and secondary processes such as biological cycling and secondary mineral precipitation become dominant.