Ca isotopes and the rainfall limit of silicate weathering on Earth

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Arid (~20 mm rain y^{-1}) to extreme hyperarid (<2 mm rain y^{-1}) soils of the Atacama Desert reveal a threshold between limited silicate weathering and accumulation of soluble atmospheric salts. In the arid soil, silicate weathering has released 2.3 kmol Ca m^{-2}, and 1.9 kmol Ca m^{-2} is present as soluble carbonate and sulfate salts. The driest soil shows no evidence of silicate weathering, and has accumulated 3.1 kmol Ca m^{-2} (mainly as $CaSO_4$) from atmospheric deposition.

In the driest soil, Ca isotope values (vs. bulk Earth, $\delta^{44/40}Ca_E$) increase with depth and are inversely correlated with sulphate-$\delta^{34}S$ and $\delta^{18}O$ values, indicating fractionation with incremental downward transport. In the arid soil, $\delta^{44/40}Ca_E$ values ($\delta^{44/40}Ca_{E,total}$ = -0.62‰) are not decreased vs. inputs (-0.35‰) to the degree expected (-1.7‰) from sulfate-$\delta^{34}S$ values in the soil (14.3‰) vs. atmospheric deposition (5.7‰). This suggests retention of Ca from silicate weathering. At the same time, sulfate-$\delta^{18}O$ values (7-10‰) comparable with atmospheric deposition (8.6‰), and somewhat elevated soil $\Delta^{17}O$ values (+0.7‰), suggest a strengthened marine sulfate source in the past, with higher $\delta^{34}S$ values.

Low carbonate-$\delta^{44/40}Ca_E$ values in the arid soil (~-1‰) relative to sulfate-$\delta^{44/40}Ca_E$ (~-0.5‰) suggest fractionation with downward transport of $CaCO_3$ during wetter times in the past, followed by limited dissolution during precipitation of $CaSO_4$ minerals, which favors the lighter Ca isotope. $^{87}Sr/^{86}Sr$ ratios decrease in $CaCO_3$ below 1 m, indicating that the proportion of weathering derived Ca increases, and reflecting a time when wetter conditions prevailed.

Experimental determination of Ra partition coefficients for leucite, phlogopite, and feldspars, and a re-examination of ^{226}Ra-^{230}Th disequilibria

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^{226}Ra-^{230}Th disequilibrium is extensively used to date magmatic processes [1-6]. In most of the studies, the chemical behaviour of Ra was approximated by that of Ba, because Ra distribution coefficients were unavailable [1-5]. This experimental study determines D_{Ra} for the most common igneous minerals that incorporate Ra (e.g. leucite, K-feldspar, plagioclase, phlogopite), to quantify the fractionation of Ra/Ba and thus, to correctly calculate mineral ages and isochrons from Ra-Ba-Th measurements.

Different synthetic starting materials were used for each mineral to obtain crystals > 40 micron of the mineral of interest and crystal free melt pools > 200 micron of the silicate liquid. A few µl of ^{226}Ra solution were added such that the lower Ra-concentration was at least 1 ppm (detection limit of the LA-ICP-MS is ~ 0.01 fg). Partition coefficients for alkalis and the other earth alkalis were also determined to define Onuma type parabolas. The experiments were performed in an atmospheric furnace or in a piston cylinder apparatus at appropriate experimental conditions (P, T).

We found that D_{Ra} is generally different from D_{Ba}, Ra being compatible in leucite, K-feldpar and phlogopite, whereas it is incompatible in plagioclase. These results allow us to re-estimate the crystal ages of different magmatic sytems [1-6] using the appropriate value of D_{Ra}. The use of the correct D_{Ra}'s value results in a 2 to 10-fold change in the ages derived from minerals (plagioclase, leucite) in which the difference between D_{Ra} and D_{Ba} is high.

[1] Volpe & Hammond (1991) *EPSL* **107**, 475-486. [2] Volpe (1992) *JVGR* **53**, 227-238. [3] Reagan *et al.* (1992) *GCA* **56**, 1401-1407. [4] Schaefer *et al.* (1993) *GCA* **57**, 1215-1219. [5] Black *et al.* (1998) *JVGR* **82**, 97-111. [6] Cooper & Reid (2003) *EPSL* **213**, 149-167.