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The evolution of K/Ca in the upper continental crust constrained from Ca isotopic measurements of glacial diamictites.

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Glacial diamictites form by physical weathering of bedrock under cold and arid conditions minimizing syn-depositional chemical weathering. Post-deposition weathering signatures [1] are absent (except two samples) and hence the chemical weathering signatures observed in these samples are representative of the crust they sampled. Glacial diamictite composites from four major pre-Cenozoic glacial events - Mesoarchean (2.9 Ga, n=2), Paleoproterozoic (2.4-2.2 Ga, n=6), Neoproterozoic (0.75-0.58 Ga, n=9) and Paleozoic (0.45- 0.30 Ga; n=1), have been analysed for their stable calcium isotopic compositions ($d^{44/40}Ca$, $d^{44/42}Ca$) using a double spike (DS, ^{43}Ca – ^{48}Ca)-thermal ionization mass spectrometry (TIMS, Thermo Triton Plus) technique [2] at the Centre for Earth Sciences, IISc, Bangalore. Subsequently, $\varepsilon_{40/44Ca}$ has been calculated from the measured $\delta^{44/40}Ca$ and $\delta^{44/42}Ca$ assuming equilibrium mass-dependent fractionation using the following relationship:

$\varepsilon_{40/44Ca} = [\ (^{40}Ca/^{44}Ca)_{sample} / (^{40}Ca/^{44}Ca)_{SRM915a} - 1] * 10^4$.

The values of $\varepsilon_{40/44Ca}$ reflect the degree of radiogenic ingrowth of ^{40}Ca due to the decay of ^{40}K. The values of $(K/Ca)_{time-integrated}$ and $(K/Ca)_{protolithÂ}$, calculated from $\varepsilon_{40/44Ca}$, when compared with the measured K/Ca in these samples, reveal K loss due to chemical weathering in the upper crust. The observation is consistent with higher solubility of K compared to Ca as indicated by its high seawater upper crust partitioning ratio and relatively long residence time [3]. In plots of $(K/Ca)_{time-integrated}$ and $(K/Ca)_{protolith}$ versus $(K/Ca)_{measured}$, the majority of the diamictite composites show depletion in K, with some samples having lost up to 99 percent of their original K. Potassium is the most abundant heat producing element in the upper crust and the loss of K from the lower crust [4] and the upper crust through chemical weathering has implications for heat flow in the continental crust.

[1] Li et al. (2016) *Geochimica et Cosmochimica Acta* 176 : 96-117. [2] Mondal and Chakrabarti (2018) *Journal of Analytical Atomic Spectrometry* 33.1 : 141-150.; [3] Taylor and McLennan (1985); [4] Antonelli et al. (2019) *Geochemical perspectives letters* 9 : 43-48.