Constraints on Ca diffusion in Archean biotite from southwest Greenland using coupled $^{40}Ar/^{39}Ar$ and in situ K-Ca dating

MIGUEL F. CRUZ[1], MARTY J. GROVE[2], KRISTOFFER SZILAS[2]

[1] Department of Geological Sciences, Stanford University, 450 Serra Mall, Stanford CA 94305, mfcruz@stanford.edu

[2] Department of Geological Sciences, Stanford University, 450 Serra Mall, Stanford CA 94305, mjgrove@stanford.edu

[3] Geological Survey of Denmark and Greenland, Øster Voldgade 10, 1350 Copenhagen K, Denmark, ksz@geus.dk

For old, K-rich, Ca-poor minerals, K-Ca dating can yield geologically meaningful information. However, quantitative interpretation of K-Ca ages requires knowledge of the Ca diffusion properties of the minerals being dated. Ca diffusion in biotite has proved difficult to measure. We have focused on measuring the relative retentivity of Ar and Ca within natural Archean biotites from southwest Greenland, using $^{40}Ar/^{39}Ar$ and 'double-plus' ion microprobe in situ K-Ca dating methods. $^{40}Ar/^{39}Ar$ analysis by incremental heating reveals that biotites from seven of 22 samples cluster tightly at 2963 ± 25 Ma. In contrast, ion microprobe K-Ca ages are much younger, averaging 1148 ± 325 Ma. Thus, significant Ca loss occurred while Ar was retained, i.e., below the ca. 350-400 °C closure temperature for Ar retention in biotite. This suggests that Ca diffuses faster than Ar in biotite at low temperatures.

Ca diffusion rates in biotite can be quantified via numerical interpretation of the contrast between $^{40}Ar/^{39}Ar$ and K-Ca ages. We explored cooling histories ranging from slow, steady cooling to transient heating events at 1100 Ma that could reasonably be ascribed to a Grenville thermal overprint for which regional evidence exists. We systematically adjusted temperatures and diffusion properties in a manner consistent with previous measurements on Ar diffusion in phlogopite (E_a = 57.9 kcal/mol; D_0 = 0.75 cm^2/s; Giletti, 1974) and divalent cation diffusion in silicates (see Brady and Cherniak, 2010) to cause up to 99% Ca loss with less than 10% Ar loss at 1100 Ma. From this we estimate $E_a \sim$ 20-30 kcal/mol and $D_0 \sim 10^{-11}$-10^{-8} cm^2/s. The much lower E_a value for Ca relative to Ar means that Ca diffuses more slowly than Ar above 500-600 °C, but faster at lower temperatures.