Mechanisms of argon release and rates of argon diffusion in hypogene and supergene alunites

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We investigate Ar release mechanisms in natural alunites through UHV prograde and retrograde heating experiments. We analysed masses of both coarsely crystalline (>0.5 mm) hypogene and finely crystalline (2-5 μm pseudo-cubes) supergene alunites crushed and sieved into various fragment sizes (200-500, 100-200, 50-100, 10-50, and < 10 μm) and irradiated in vacuum-sealed Si-capsules to quantify ^{39}Ar recoil losses. ^{40}Ar/^{39}Ar release spectra show that the amount of ^{39}Ar recoil lost during neutron irradiation, from the coarsest to the finest hypogene alunite fragments, is 0.10, 0.11, 0.15, 0.33 and 2.42%, where fragment size is inversely proportional to ^{39}Ar recoil loss. For supergene alunites, ^{39}Ar lost into the capsule, from largest to finest fragment sizes, is 1.05, 0.80, 0.90, 0.93 and 1.17%, respectively, showing that ^{39}Ar recoil loss is independent of fragment size. Coarsely-crystalline hypogene alunite ground to < 10 μm breaks into fine platelets with large surface areas, accounting for the larger (2.42%) recoil losses. In contrast, ^{39}Ar loss in supergene alunites appears to be controlled by the crystallite size (2-5 μm), not fragment size. Nevertheless, the small amounts (<2.42%) of ^{39}Ar lost during irradiation confirm that recoil is not a problem in alunite ^{40}Ar/^{39}Ar dating and diffusivity experiments. During heating, cumulative % ^{39}Ar release rises sharply at ~450 °C in hypogene and ~420 °C in supergene alunites, indicating that the Ar-hosting sites release gas at narrow temperature (T) ranges. ^{39}Ar release T in hypogene alunite increases with increasing fragment size. In supergene alunite, ^{39}Ar release T is independent of fragment size. Electron diffraction patterns in TEM vacuum-heating experiments reveal that single crystals of hypogene alunite transform into nanocrystalline aggregates at ~460 °C; supergene alunites undergo similar transformations at ~430 °C. Excellent match between the sharp rise in cumulative ^{39}Ar release and alunite recrystallization T suggests that argon isotopes are released mostly during and after phase transformation. Kinetic parameters derived from ^{39}Ar released below phase transformation reveal at least two diffusion domains in both supergene and hypogene alunites. Diffusion parameters derived for these distinct domains permit the reconstruction of thermal histories for the samples.