Apatite composition effect on (U-Th)/He thermochronometer: a quantum point of view

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Periodic Density Functional Theory (DFT) calculations on apatite lattice have been performed to investigate the chemical composition effect on He diffusion and its impact on the (U-Th)/He thermochronometer. We determine the helium diffusion for a pure F-apatite lattice and for a lattice where a fluorine atom is substituted by a chlorine one. Two preferential diffusion directions in both structures have been identified, one along the fluorine atoms and the other one in the plane orthogonal to the later direction. A Nudged Elastic Band method (NEB) has been used to determine the activation energies between two He insertion sites, which range from 95,500 to 106,100 kJ/mol for the F-apatite and from 79,118 to 166,920 kJ/mol for the $Cl_{0.25}$-apatite. According to the energy barriers a small anisotropy is noticed in the case of the pure F-apatite and a more pronounced anisotropy in $Cl_{0.25}$-apatite. Consequently He diffuses preferentially in the plane in case of $Cl_{0.25}$-apatite while a 3 dimension (3D) diffusion process is observed in the pure F-apatite at low temperature.

In a second part, Kinetic Monte Carlo calculations have been performed to simulate the He 3D diffusion in the two-apatite lattices composition. From these calculations the Arrhenius law gives us access to the diffusion coefficient for infinite crystal such as:

$D\ (cm^2/s)=2.810^{-4}\ (cm^2/s)\ \exp(-98.94\ (kJ/mol) / RT)$ pure F-apatite

$D\ (cm^2/s)=3.010^{-4}\ (cm^2/s)\ \exp(-108.00\ (kJ/mol) / RT)$ $Cl_{0.25}$-apatite

He diffusion in F-apatite is significantly different that for the $Cl_{0.25}$-apatite, with calculated closure temperature of 41 to 71°C, for a 50 micron grain size and a cooling rate of 10°C/Ma. Then the closure temperature calculated from our DFT results is significantly different from the single existing DFT calculation[1], but is in good agreement with experimental results[2-3] in the case of F-apatite for non-damaged apatite[3]. On can conclude that (1) the apatite grain shape and size are important parameters, as even the slight anisotropic He behavior of the F-apatite has some impact on the He age. The use of the active radius[4] allows taking account of this behavior and will reduce the age dispersion. And (2) for high chlorine content (Ó25%), He diffusion behavior is significantly different compared to F-apatite and can explain some not understood He age variations.

References

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