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Influence of vacancy damage on He diffusion in apatite, investigated at atomic to mineralogical scales

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Abstract

Helium diffusion in U–Th-rich minerals, especially apatite, is considered as strongly impacted by damage, even at low U–Th content. To get direct evidence and better understand the impact of damage on He diffusion, we conducted a study on vacancy damage in apatite, at nanometric to atomic scales, using different methodologies. Firstly, damage was created on apatite crystals by He implantation at different He fluences ranging from 2×10^{15} to 1×10^{17} He/cm^2, corresponding to atomic displacement ranging from 12 to more than 100% of the total structure in the first 200 nm below the surface. Transmission Electron Microscopy (TEM) was used to image the damage structure, for the lowest He fluence. TEM images present no visible damage zone at nano-scale, implying that the created damage corresponds well to Frenkel defects (vacancies and interstitials). Secondly, diffusion experiments were performed on those samples by mapping He concentration vs. depth profiles using Elastic Recoil Detection Analysis (ERDA). After measurement of implanted-He profiles and He concentrations, the samples were heated in order to diffuse the implanted profile during 15–45 h at temperatures from 145 to 250 °C. The obtained He vs. depth heated profiles and He concentrations reveal the impact of damage on He diffusivity. The results can only be explained by a model where diffusion depends on damage dose, taking into account He trapping in vacancies and damage interconnectivity at higher damage dose. Thirdly, Density Functional Theory (DFT) calculations were performed to simulate a vacancy in a F-apatite crystal. The structure becomes slightly deformed by the vacancy and the insertion energy of a He atom in the vacancy is lower than for an usual insertion site. Accordingly, the additional energy for a He atom to jump out of the vacancy is $\Delta E_a \approx 30$–40 kJ/mol, in good agreement with published estimates. This calculation thus shows that small modifications of the structure due to the presence of vacancies efficiently trap He atoms, thus reducing diffusivity. Finally, for apatite crystal having vacancy-type damage, we propose a He diffusion model able to reproduce well He diffusion data obtained on irradiated samples. We anticipate that, for natural apatite, the recoil-damage that corresponds to vacancy clustering, would have a higher trapping power with $\Delta E_a > 50$ kJ/mol.

Keywords: Thermochronology; (U-Th)/He; Vacancy; Damage; Diffusion; Quantum calculation; ERDA; TEM; Apatite

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1. INTRODUCTION

The apatite (U–Th)/He (AHe) thermochronometer is widely used to quantify burial and exhumation in different geological contexts (*e.g.*, Reiners and Brandon, 2006; Gautheron et al., 2013a; Herman et al., 2013). However, AHe age interpretation is strongly dependent on knowledge of helium diffusion in apatite, which is grain-dependent. Damage associated to U–Th–Sm decay (alpha and recoil damage) has been suggested as the main parameter influencing He diffusion, as it can offer traps for He atoms (Green and Duddy, 2006; Shuster et al., 2006) even at low dose (*e.g.,* Valla et al., 2012). Indeed, crystals naturally contain vacancies and, at a lower extent, Frenkel-pair defects (White et al., 2005; Jay et al., 2015), as well as defects that can also be created by nuclear processes: α-emission, U–Th recoil, U spontaneous fission (*e.g.*, Fleisher and Price, 1964; Naeser, 1967; Ewing et al., 1995; Weber et al., 1998). Damage is initiated by collisions of the emitted fast particle with atoms of the medium, knocking them out of their sites and producing Frenkel pairs, *i.e.*, vacancy + interstitial. For highly ionizing particles, like fission fragments, the collided electrons are also responsible for damage production by break up of their links in an insulator medium such as apatite, where the electrons may take a long time before getting back to their original position. However, this electronic mechanism is negligible in the case of alpha particles and their associated recoils. After this initialization step, damage may evolve, either by partially self-annealing when interstitial atoms reach vacancies, or by clustering leading to metamictization. Using codes simulating the penetration of ions into matter (SRIM: Ziegler et al., 1985; Ziegler, 2008), or computer simulation (*e.g.*, Trachenko et al., 2002; Devanathan et al., 2006; Jay et al., 2015 for some picoseconds), one can describe the number of bonds broken during damage creation, as well as the size and topology of damage for U–Th rich minerals such as apatite and also zircon, a mineral richer in U and Th than apatite. However, one should have in mind that those codes ignore the electronic contribution, and for some the self-annealing effects. They only simulate the vacancies and interstitials produced by atom collisions. Alpha particles are stopped at a distance of about 10 μm and produce mostly vacancies and interstitials at the end of this range, whereas U–Th recoils create far more damage than alpha particles, even if their energy is lower (typical range is 50 nm). However, the actual damage topology, except for fission tracks, is difficult to access because of their nanometer-scale and possible annealing.

So, the impact of damage on He diffusion has only been evocated using indirect evidence, particularly for apatite (Shuster et al., 2006; Shuster and Farley, 2009) and zircon (*e.g.*, Ketcham et al., 2013; Guenthner et al., 2013). For the apatite structure, no clear model exists of damage topology (size, shape, interconnection), even if some important studies have been conducted on damage (Soulet et al., 2001a,b; Shuster and Farley, 2009; Jay et al., 2015). Jay et al. (2015) have shown, that for recoil damage, many phosphate groups may move or rotate from their original lattice positions, and that a large fraction remains intact. On the contrary, for zircon, numerous studies on damage topology exist. It has been recognized that the defects caused by recoil are densely clustered and, as opposed to the single structure vacancies characteristic of alpha impact (*e.g.*, Trachenko et al., 2003; Devanathan et al., 2006), create amorphous cores that can be observed at atomic scale on Transmission Electron Microscopy (TEM) images (Ewing et al., 2003).

With respect to diffusion processes, such damage is believed to generate traps for He atoms, meaning that helium atoms need some supplementary energy, ΔE_a (Shuster et al., 2006), to be added to the inter-site He activation energy, to jump out of a damage site. Based on this trapping hypothesis, He diffusion models for apatite, which take care of damage and their annealing upon heating, have been worked out (Flowers et al., 2009; Gautheron et al., 2009). It has also been inferred that the damage-annealing rate in apatite is chemistry dependent, similarly to fission tracks (Gautheron et al., 2013b). Consequently, in apatite, the He diffusion coefficient decreases with increasing number of traps, and the closure temperature (T_c) increases accordingly. However, no direct evidence of damage impact on He diffusion exists, except for the Shuster and Farley (2009) study. For zircon, at high damage density, Ketcham et al. (2013) inferred that the recoil damage sites interconnect, thus facilitating He leak through the surface. Guenthner et al. (2013) also suggested that the He diffusion coefficient decreases with increasing number of defects (T_c increases) up to the first percolation point, at a dose of $\sim 2 \times 10^{18}$ alpha/g, then He diffusion increases again (T_c decreases) when amorphous domains connect together at higher damage dose (Ketcham et al., 2013). However, such damage interconnection behavior has not yet been identified for apatite.

In this study, we used different methods from atomic to nanometer scales, to get insight into vacancy damage structure and its impact on He diffusion in apatite crystals. Direct evidence of damage effects serves as both a validation of previous bulk diffusion experiments, and as a mean of exploring processes that modify diffusivity. First of all, we create alpha-type damage (*i.e.*, vacancies and interstitials) in apatite crystals by He implantation at different doses, and generate TEM images of an irradiated sample to visualize the structural damage. In short, the purpose of helium implantation is twofold: (i) creation of a concentration profile to probe helium diffusion, and (ii) production of damage to quantify its impact on diffusion. Secondly, we use the Elastic Recoil Detection Analysis (ERDA) method on apatite crystals bearing implanted helium in a ~200 nm depth layer close to the surface (*e.g.*, Ouchani et al., 1998; Cherniak et al., 2010) to map the helium concentration profile with depth and see how this profile evolves by diffusion. This method, using an accelerator-ion beam, is similar to the one used in Cherniak et al. (2009) and Cherniak and Watson (2011) for He diffusion in apatite, zircon, titanite and rutile. The main difference is that ERDA allows direct imaging of the shape of the He implanted profile and of the He content, after the implantation and heating sequence (see Cherniak et al., 2010 for analytical differences). Thirdly, we use Density Functional Theory (DFT) calculations for