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Trapping of helium in nano-bubbles in euxenite: Positive identification and implications

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ABSTRACT

The (Y,REE,U,Th)–(Nb,Ta,Ti) oxides, like euxenite, fergusonite, pyrochlore, zirconolite, are known to contain nanometric spherical cavities or bubbles, interpreted to contain radiogenic helium. *In-situ* analyses by Scanning Transmission Electron Microscopy (STEM) coupled with Electron Energy Loss Spectroscopy (EELS) inside nano-bubbles from an euxenite crystal, sampled in its host c. 920 Ma old pegmatite in Norway, deliver, for the first time, a positive identification of helium and an estimation of helium pressure in such bubbles. The chemically unaltered euxenite crystal proves amorphous and homogeneously speckled with bubbles ranging from 5 to 68 nm in diameter, around a log-normal distribution centered at 19 nm. The euxenite contains 9.87 wt% UO_2 and 3.15 wt% ThO_2. It accumulated a theoretical alpha-decay dose of 3.46×10^{20} α/g (i.e. 170 He/nm^3), at a dose rate of 11 926 α/g/s. This corresponds to production of 0.23 wt% He. The density of helium inside the bubbles, estimated from EELS data, ranges from 2 to 45 He/nm^3, leading to a pressure of 8 to 500 MPa. The proportion of produced helium trapped in bubbles is about 10%. Helium bubbles clearly influence helium diffusion. They may contribute to the swelling of euxenite during amorphization and to the fracturing of the host rock. Our results suggest that dose, dose rate and structural state seem to be important parameters for the nucleation, growth and coalescence of helium bubbles but also demonstrate the crucial need of experimental studies to be able to develop a predictive model of the long term behavior of materials in response to helium irradiation. Furthermore, chemical alteration of euxenite, here materialized by fluid driven dissolution–precipitation towards silica bearing euxenite, removes the bubbles and mobilizes helium into the rock via cracks and grain boundaries. It is then suggested that helium-rich fluid released from such U–Th rich sources may percolate into surrounding rock units, inducing perturbation of the (U–Th)/He systematics of apatite and zircon in these units.

1. Introduction

Radioactive uranium-thorium minerals like zircon, monazite, pyrochlore, zirconolite, have been extensively studied in the context of immobilization of high-level nuclear waste and as support minerals for (U–Th)/He and U–Th–Pb geochronology (see review in Weber et al., 1998; Ewing et al., 2000). Radiation damage resulting from alpha-decay from U and Th chains critically affects the long term behavior of minerals. It is caused by both ejection of recoil-nuclei and alpha particles, causing fundamental modifications in physical and chemical properties of minerals. In particular, amorphization is essentially induced by recoil-nuclei and results from the accumulation of thousands of atomic displacements within collision cascades (Weber et al., 1998; Ewing et al., 2000). It principally contributes to macroscopic swelling of the mineral, as high as 18% for zircon (Holland and Gottfried, 1955). Swelling in response to amorphization may also induce cracks within metamict minerals; this is particularly well-known for zircon crystals (e.g. Chakoumakos et al., 1987; Lee and Tromp, 1995). It may also induce cracking in surrounding minerals or the host rock. This process has been less described (Seydoux-Guillaume et al., 2009; Montel and Giot, 2013), although

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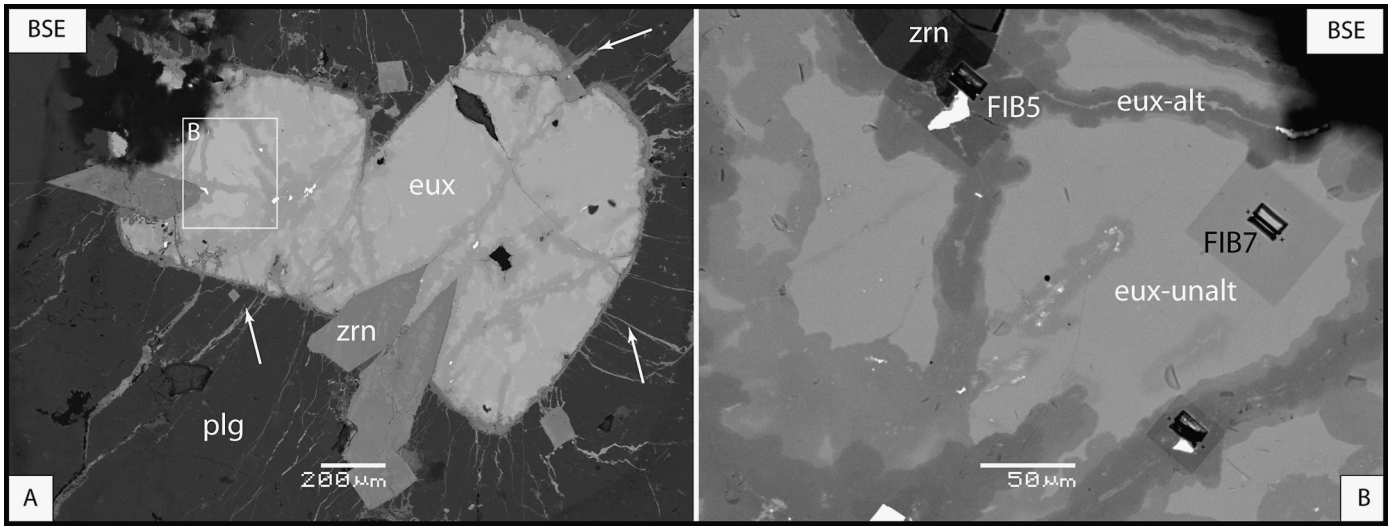

Fig. 1. Back Scattered Electron (BSE) images. (A) View of euxenite (eux) crystals included in plagioclase (plg). Note the presence of zircon (zrn) crystals and intense radial fracturing (arrows) around these radioactive phases. (B) Detail from (A) showing location of two Focused Ion Beam (FIB) foils prepared from one pristine domain (eux unalt) in the center of the crystal (FIB7) characterized by bright BSE contrast and from an altered domain (eux-alt; darker BSE contrast) across the grain boundary of the crystal (FIB5).

it has significant consequences on chemical transfer (e.g. U, Pb mobility) mediated by fluid through cracks within rocks. Some examples have been described for zircon within plagioclase and xenotime (Seydoux-Guillaume et al., 2015), urano-thorianite within diopside (Seydoux-Guillaume et al., 2009), thorite in monazite (Seydoux-Guillaume et al., 2007, 2012), monazite in plagioclase, cordierite and quartz (Procházka et al., 2011) and euxenite within plagioclase (this study; Seydoux-Guillaume et al., 2015; Duran et al., 2016).

The role of helium resulting from alpha particle production, was much less studied. Nasdala et al. (2001, 2006) demonstrated that radiohalos commonly observed in biotite or cordierite around radioactive minerals are created by α particles and correspond only to modification of optical properties of the host mineral. The width and intensity of the radiohalos correlate positively with the energy of the α particles. Seydoux-Guillaume et al. (2009) demonstrated that radiohalos are a point of chemical and mechanical weakness in a rock and probably a starting point for alteration. In the context of immobilization of high-level nuclear waste, it is essential to understand the behavior and fate of helium, especially its migration as a function of time. In U–Th-minerals, helium may (1) accumulate within the lattice at interstitial position, (2) diffuse out of the crystal or (3) be trapped within defects (e.g. vacancies, dislocations, voids or fluid inclusions). Accumulation of helium may therefore contribute to swelling and affect physical properties of the solid (Weber et al., 1998). Studying the localization of helium in U–Th-minerals helps to evaluate its long-term behavior. In particular some authors have described, by using a Transmission Electron Microscope (TEM), the presence of spherical nano-cavities inside highly radioactive minerals and have proposed they may correspond to helium bubbles. They have nucleated and grown as a result of accumulation of radiogenic helium. This interpretation has been proposed for the first time by Headley et al. (1981) describing cavities in Nb–Ta–Ti-oxides (amorphous euxenite crystals) and has been reiterated by others for zirconolite (Lumpkin et al., 1986; Ewing and Headley, 1983), uraninite (Janeczek and Ewing, 1991; Roudil et al., 2008) and fergusonite (Gieré et al., 2009; Ruschel et al., 2010). Helium measurements by desorption experiments in uraninite crystallized some 320 Ma ago in Pen Ar Ran (France), have indirectly shown that such nano-cavities contain helium (Roudil et al., 2008). However, up to now, no direct demonstration has been made that such nano-cavities correspond to helium bubbles and that they are still filled with helium today.

In the present study, we fill this gap, focusing on some euxenite crystals from Norway, formed ca. 920 Ma ago. Analyses by spatially-resolved Electron Energy Loss Spectroscopy (EELS) of these nano-cavities, provide a positive, *in-situ* measurement of helium. Implications of this discovery are discussed.

2. Sample and analytical details

The sample comes from a pegmatite of the ca. 920 Ma Evje-Iveland rare-metal-rich pegmatite field in South-Norway (UTM coordinates: 32V 0436180-6484805) (Scherer et al., 2001; Larsen et al., 2004; Müller et al., 2015). In the present study, we exclusively focus on euxenite, $[(Ca,Fe,Y,REE,Th,U)(Ti,Nb)_2O_6]$, orthorhombic with Pcan space group. In the sample, millimeter-scale euxenite crystals are included in plagioclase matrix and associated with zircon, monazite, and xenotime (Seydoux-Guillaume et al., 2015; Duran et al., 2016). Euxenite contains ca. 10 wt% UO_2 and 3 wt% ThO_2 but depending on its alteration degree (gray patches in euxenite in Fig. 1A and B) its composition is in the range of 8.0–14.4 wt.% UO_2, 2.0–4.3 wt.% ThO_2, 19.1–24.9 wt.% TiO_2, 18.6–28.3 wt.% Nb_2O_5, 1.1–2.4 wt.% Ta_2O_5, 6.7–14.7 wt.% Y_2O_3 and 7.6–13.0 wt.% REE. Many cracks are observed between euxenite and zircon crystals through the feldspar matrix. These cracks are filled with various microphases, containing elements like Nb, Ti, Ca, Fe and U, presumably coming from the alteration of euxenite (Fig. 1A; Seydoux-Guillaume et al., 2015; Duran et al., 2016). Formation of cracks is a direct consequence of swelling of euxenite structure in response to amorphization (Chakoumakos et al., 1987; Lee and Tromp, 1995; Seydoux-Guillaume et al., 2009; Montel and Giot, 2013). Euxenite crystals are partially altered into a silica-bearing euxenite (gray patches in euxenite in Fig. 1A and B) and into pyrochlore (dark rims around euxenite in Fig. 1A). This pattern is interpreted as evidence of alteration at low temperature in the presence of a fluid phase (Seydoux-Guillaume et al., 2015; Duran et al., 2016).

Two Focused Ion Beam (FIB) foils, less than 100 nm thick, were prepared (method descriptions in Deschanels et al., 2014) from one euxenite crystal exposed in a polished thin section (Fig. 1B). The first one targets a pristine domain (not affected by silica enrichment) in the center of the crystal, characterized by bright Back