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Variable helium diffusion characteristics in fluorite

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Abstract

Precise analysis of the diffusion characteristics of helium in fluorite is crucial for establishing the new fluorite (U–Th–Sm)/He thermochronometer (FHe), which potentially provides a powerful tool for dating ore deposits unsuitable for the application of conventional geochronometers. Incremental helium outgassing experiments performed on fluorites derived from a spectrum of geological environments suggest a thermally activated volume diffusion mechanism. The diffusion behaviour is highly variable and the parameters range between $\log D_0/a^2 = 0.30 \pm 0.27$–$7.27 \pm 0.46$ s^{-1} and $E_a = 96 \pm 3.5$–182 ± 3.8 kJ/mol. Despite the fact that the CaF_2 content of natural fluorites in most cases exceeds 99 weight percent, the closure temperature (T_c) of the fluorite (U–Th–Sm)/He thermochronometer as calculated from these diffusion parameters varies between 46 ± 14 °C and 169 ± 9 °C, considering a 125 μm fragment size. Here we establish that minor substitutions of calcium by rare earth elements and yttrium (REE + Y) and related charge compensation by sodium, fluorine, oxygen and/or vacancies in the fluorite crystal lattice have a significant impact on the diffusivity of helium in the mineral. With increasing REE + Y concentrations F vacancies are reduced and key diffusion pathways are narrowed. Consequently, a higher closure temperature is to be expected. An empirical case study confirms this variability: two fluorite samples from the same deposit (Horni Krupka, Czech Republic) with *ca.* 170 °C and *ca.* 43 °C T_c yield highly different (U–Th–Sm)/He ages of 290 ± 10 Ma and 79 ± 10 Ma, respectively. Accordingly, the fluorite sample with the high T_c could have quantitatively retained helium since the formation of the fluorite-bearing ores in the Permian, despite subsequent Mesozoic burial and associated regional hydrothermal heating. In contrast, the fluorite with the low T_c yields a Late Cretaceous age close to the apatite fission track (AFT) and apatite (U–Th)/He ages (AHe) from the same locality. Remarkably, thermal modelling of FHe yields comparable results to the well-established modelling based on AFT and AHe.

Keywords: Fluorite; Helium; Diffusion; Thermochronology

1. INTRODUCTION

(U–Th–Sm)/He thermochronology of accessory minerals like apatite and zircon can provide excellent constraints on low-temperature thermal histories. However, the use of this method is limited to rocks that contain these minerals. Especially in some ore deposits (e.g. greisens) apatite is often rare or lacking due to the typically low pH of the ore-bearing fluids. In contrast, fluorite is a common constituent in high- to low-temperature hydrothermal veins, in granites, pegmatites, carbonatites and alkaline intrusives, in stratabound deposits and in the cement of some clastic sediment. In particular, hydrothermal veins occur in a wide variety of geological settings, but such veins are often not

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well suited for apatite and zircon-based geochronology. The need to date the formation age of such ore deposits led to the development of isotopic techniques for fluorite geochronology using Sm/Nd (Chesley et al., 1991, 1994; Gigoux et al., 2015), and U–Th–Pb (Hofstra et al., 2000). Fluorite (U–Th–Sm)/He (FHe) thermochronology was introduced by Evans et al. (2005) and applied by Pi et al. (2005) and Siebel et al. (2009). A comprehensive dataset of FHe ages measured on samples from several ore deposits of the Erzgebirge (Germany/Czech Republic) along with FHe-based thermal modelling yielded constraints on the thermal history compatible with results from well-established thermochronometers such as apatite fission track and apatite (U–Th)/He (Wolff et al., 2015a,b).

The parameters controlling helium diffusion in fluorite, and thus the closure temperatures (T_c), are still under debate. Evans et al. (2005) published helium diffusion data on 200–350 μm diameter fragments of colourless fluorite. These measurements were accomplished by stepwise degassing between 215 °C and 335 °C. These authors suggested that volume diffusion is the dominant mechanism by which helium is released from fluorite. The observed deviation in the Arrhenius plot from linearity at higher temperatures was attributed to grain size effects, shape variability and/or defect/radiation damage density. The linear segment of their data yields an $E_a = 127.6$ kJ/mol and $\log D_0/a^2 = 4.9 \pm 0.6\ s^{-1}$ (at linearity of $R^2 = 0.9984$). These results correspond to a T_c of 60 °C ± 5 °C. In contrast, Peter W. Reiners' diffusion experiments (published in Pi et al., 2005) indicated a fluorite T_c of 200 °C. According to the empirical case study of Wolff et al. (2015a) the fluorite helium T_c is in the range of the thermal sensitivities of ZHe and AHe thermochronometers.

All of the above listed diffusion experiments are based on only very few data sets and the chemical composition of the studied specimens or other crystallographic characteristics were not reported. Yet, fluorite is famous for its broad variety in colour which results mainly from radioactive irradiation and the degree of substitution of calcium and fluorine in the crystal lattice, leading Evans et al. (2005) to suggest that variations in mineral colours may correlate with the diffusion characteristics of fluorite. However, the relation between colour and real structure (i.e. substitution of formula elements, vacancies, etc.) remains ambiguous (e.g. Dill and Weber, 2010). In order to shed light on this situation, we performed a detailed study on helium diffusion in fluorite using highly diverse samples derived from a variety of geological settings with variable genesis, precipitation temperatures, colours, habits and REE distribution patterns. The associated differences in T_c were constrained in a case study where distinct FHe ages from natural fluorites from one deposit with differing T_c could be compared.

2. SAMPLE SELECTION

Using the (U–Th–Sm)/He method, we have dated over 660 fluorite crystal aliquots from 112 samples originating from 58 localities (Wolff et al., 2015a). Sample selection for diffusion experiments was based on this data set because proper test material needs to be homogeneous, free of inclusions, and should contain sufficient helium to allow multi-step degassing experiments. Decrepitation experiments were performed on 7 samples, whereas diffusion experiments were performed on 34 aliquots from 14 samples (Table 1). Beyond 'near stoichiometric' fluorites, we performed diffusion experiments on samples with unusual compositions including Y-rich fluorite (sample K2), brownish, thorium-rich fluorite (SD1001), "black" (dark pink), stink-fluorite (RW-5-11), and sodium-and REE-rich green fluorite (HK13). Most of the samples were characterised in detail in earlier studies, e.g. fluorites from tin and polymetallic deposits in the Erzgebirge (Zinnwald, Horni Krupka, Sadisdorf, and Lauta; see Kempe et al. (2002), Wolff et al. (2015a)), from Usakos, Namibia (Bühn et al., 2002, 2003), from the giant Be-deposit Ermakovka, Transbaikalia (Kempe and Götze, 2002), and from the W-deposit of Kyzyltau, Mongolian Altai (Kempe and Belyatsky, 2000). Samples from inaccessible mining sites in the Erzgebirge could be obtained from the mineral collection of the Technische Universität Berkakademie Freiberg.

3. METHODS

3.1. Mineral chemistry

The concentrations of 27 cations were determined on same aliquots previously used for diffusion experiments and age dating. The dissolved fluorite aliquots were analysed using externally calibrated solution ICP-MS analyses (see data in Electronic Appendix EA1). The chemical composition was determined on inclusion free crystal fragments of *ca.* 13–338 μg (average 72 μg). The sensitivity and resolution of this technique is between classical wet chemical analyses performed on powdered samples consisting of several hundred mg and the laser ablation technique that consumes less volume, but has considerably higher uncertainty. Additionally, the laser ablation method is typically not viable for fluorite because of the low adsorption of UV light in the mineral, frequent fragmentation and small explosions that occur during ablation.

We also investigated whether variations in trace levels of anions might influence He diffusion rates in fluorite. The CAMECA 1280-HR instrument at the Helmholtz-Zentrum Potsdam was used to establish variations in the C, O, P, S and Cl contents of six samples with variable REE, Y, and Na composition. Due to the lack of a suitable fluorite reference material, it was only possible to determine the relative abundances of these anionic species between the samples and the inter- and intra-crystalline variability of their concentrations within a single sample. By normalising to the observed $^{19}F^-$ count rate, our method was able to establish the relative concentrations of these trace elements over a range exceeding 10^5. The spot size diameter for a single analysis was roughly 10 μm with a total sampling mass in the low nano-gram range (for analytical parameters see EA2).