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Solubility and trapping of helium in apatite

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Abstract

A fundamental but unquantified assumption in U-Th/He dating of apatite is that grains do not incorporate extraneous helium by solution or other processes, but large age dispersion seen in some samples suggests that this assumption might be violated. Our laboratory experiments show that helium solubility in apatite is quite low and unlikely to lead to age dispersion in most samples. However, in some samples highly variable and sometimes large helium uptake suggests that apatite grains can trap helium in microvoids that could be derived from fluid inclusions or other microstructures, a conclusion supported by crushing and step-heating experiments. The presence of such microvoids raises the possibility that closure and age systematics could be complicated either by trapping of internally generated radiogenic helium and/or alteration of helium diffusion kinetics by impeding diffusion.

Keywords: Helium; Apatite; Solubility; Diffusion; Thermochronology

1. INTRODUCTION

U-Th/He dating of apatite (Zeitler et al., 1987) has become a widely-used tool in studies of tectonic and surface processes because radiogenic ^{4}He diffusion remains significant at temperatures well below 100 °C. Considerable progress has been made in understanding the kinetics of helium diffusion (e.g., Farley, 2000; Shuster et al., 2006) as well as the systematics of the U-Th/He method (e.g. Ketcham et al., 2011; Brown et al., 2013). Lately, a considerable amount of work has been focused on understanding second-order age dispersion seen in many samples, especially those from slowly cooled rocks. Plausible explanations include grain-size effects (Farley, 2000), inadvertent analysis of crystal fragments (Brown et al., 2013), problems with the alpha-ejection correction related to U and Th zoning (Farley et al., 1996), external implantation of ^{4}He (Spiegel et al., 2009), presence of mineral inclusions (Farley, 2002), and in particular, the systematic alteration of diffusion behavior due to radiation-damage traps (Farley, 2000; Shuster et al., 2006). Nonetheless, for some samples showing dispersed ages these explanations still fall short.

As currently practiced the U-Th/He method assumes that helium solubility in apatite is sufficiently low that samples contain no initial ^{4}He, and violations of this assumption could be an additional source of age scatter. The assumption is rooted in the belief that helium solubility in apatite should be very low, as is true for the other noble gases in other minerals. The observation that many samples do give meaningful and replicable ages supports a low value for helium solubility. However, trapped ^{4}He could plausibly become an issue in some environments: although the

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concentration of helium in air is only about 5 ppm (Ozima and Podosek, 2002), concentrations in some crustal reservoirs like natural-gas accumulations are much higher (10's of ppm to several percent; Zartman et al., 1961), and in low-permeability metamorphic settings local ^{4}He partial pressures might become significant.

In this paper, we report our attempts to determine helium solubility in apatite and the implication of our results for apatite U-Th/He geochronology. Our work stemmed from a separate project on the effect that fission tracks have on helium diffusion. That project required that we anneal all radiation damage from samples before irradiating them to create induced fission tracks, but because such annealing outgasses all ^{4}He, we needed to return helium to samples which we attempted by soaking them at high partial pressures. Our trial runs on unirradiated samples thus provided us the opportunity to study helium solubility in apatite. One unexpected outcome of our work is that while the intrinsic solubility in apatite does appear to be very low ($<2.3 \times 10^{-11}$ mol/g-bar), even apparently "high-quality" crystals can incorporate significant amounts of helium in what we hypothesize to be fluid inclusions or other structures that represent microvoids, making the effective solubility much higher in some cases. This phenomenon in turn provides an additional explanation for U-Th/He age scatter as well as raising questions about the systematics of ^{4}He diffusion behavior during slow cooling.

2. METHODS

2.1. Materials

Most of our experiments used aliquots of Durango apatite standard (Young et al., 1969), a fluorapatite with an unusual Th/U ratio of ~20 and a rather high effective uranium concentration (eU) of ~50 ppm (eU = U + 0.235Th). Durango apatite formed in a quickly cooled geological setting and bracketing ^{40}Ar/^{39}Ar ages establish its age as 31.44 ± 0.18 Ma (2σ) (McDowell et al., 2005). Optically clear fragments of Durango are commonly used as a laboratory standard and yield kinetic results consistent with volume-diffusion behavior that correspond to a slow-cooling closure temperature of ~70 °C (10 °C/m.y., 80 μm; Farley, 2000). The Durango working standard that we used in our experiments comprises ~180–250 μm internal fragments obtained from a large centimeter-sized gem-quality crystal. Some of our experiments also used aliquots of apatite grains taken from our archive of dated samples, and information about these can be found in the relevant data tables and references. Table 1 provides a summary of sample information and Table A4 provides U-Th/He analytical data for previously unpublished ages.

2.2. Solubility experiments

Apatite fractions from samples Durango, NC/MM-4a, and NC/SY-2AB were outgassed of their radiogenic ^{4}He by heating to ~450 °C for 24 h, and were then treated in two ways at very different helium partial pressures. Initial sample runs at relatively low partial pressures of 5–10 mbar (low P_{He}) were done at Lehigh University by flooding our helium extraction system with high-purity ^{4}He and measuring pressure using the extraction line's capacitance manometers (MKS model 627B; quoted accuracy of ±0.15%). For these runs, outgassed samples were placed in the crucible of a double-vacuum resistance furnace and heated to temperatures of between 200 and 900 °C while they were exposed to ^{4}He for durations of 0.2–32 h. When measurements showed that negligible helium was being taken up at these low pressures, we carried out additional high P_{He} "soaking" runs at Rensselaer Polytechnic University using a system in which outgassed samples in small quartz boats were heated in a cold-seal vessel pressurized with ~12 and 100 bar of pure helium gas, at temperatures around 650 °C and durations of ~930 to 1850 h. For all but a few of the low-P_{He} experiments, temperatures and durations of the runs were easily sufficient to allow complete equilibration of grain interiors by diffusion: using Durango-apatite kinetics of 33 kcal/mol and D_o/a2 of 50 (Farley, 2000), a large grain 100 μm in radius would be more than 99% equilibrated within 1 h at 650 °C, or 12 h 400 °C. We omit any data from the few trial runs that would not have equilibrated during soaking.

^{4}He contents for both single-grain and multi-grain apatite aliquots were measured using an all-metal extraction line that includes a sample dropper, the double-vacuum resistance furnace, capacitance manometers, SAES GP50 getter, and reference pipettes for ^{4}He concentration and ^{4}He/^{3}He discrimination. This line supplies gas to a Pfeiffer QMS 200 quadrupole mass spectrometer. Apatite samples were loaded in small Pt and later in Nb tubelets, placed into the sample dropper, pumped down and baked overnight at ~50 °C, then dropped into the furnace. Using this system, our observed precision on age for repeated analyses of Durango apatite is about 2.5% (1σ standard deviation), and our typical uncertainties for ^{4}He-abundance measurements are 1–2%. For the ^{4}He amounts reported in this paper, uncertainties for most analyses of low-P_{He} runs are about 25% (1σ), and for high-P_{He} runs 1–2%.

2.3. Crushing experiments

To gain insight into the locations of helium taken up by our samples, we performed a series of crushing analyses on weighed aliquots of previously outgassed and subsequently ^{4}He-soaked Durango fragments, as well as both ^{4}He-soaked and natural samples with varying geologic histories. Following crushing, a weighed subset of each aliquot was analyzed by heating to determine the amount of remaining ^{4}He. The crusher used a modified Varian all-metal mini valve in which a conical nose piece attached to the valve driver engages with the sample within a conical receptacle (Fig. A1); this device was fixed to the standard helium extraction line. When fully engaged, the crusher's nose piece left a dead volume in the receptacle, so in order to cause significant crushing to take place, it was necessary to process large ~2–10 mg aliquots containing hundreds of grains. As a result, it was not feasible to hand-pick grains using the criteria normally applied to dated samples, so in