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Mechanisms of radon loss from zircon: Microstructural controls on emanation and diffusion

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Abstract

Understanding how radon escapes from minerals is important for many fields in Earth science, yet few studies have focused on the mechanisms for radon escape. We measured radon emanation rate and radon loss upon heating for crushed aliquots of three large zircon crystals from three localities: Mud Tank (Australia), Bancroft (Canada), and Malawi (Africa). Our study, in conjunction with published data, shows that the room temperature radon emanation coefficient (REC) varies over 5 orders of magnitude in zircon. For low U zircon, Mud Tank, there are variations in REC that appear to be related to annealing at different temperatures, possibly due to annealing of fission tracks, however, all REC values for Mud Tank zircon are within error of one another. Bancroft and Malawi zircons have higher U content and do not show any systematic relationship of REC to annealing temperature. Results from Mud Tank zircon suggest that partial annealing of fission tracks decreases REC, but when all fission tracks are annealed REC reaches a maximum. REC in zircons with high U content, Bancroft and Malawi, is slightly higher than in zircon with lower U, although results are within error. Results of measurements of radon loss upon heating suggest that radon diffusion is slow, ~30% of the radon is lost during heating at 975 °C for 48 h. Samples heated a second time yield less fractional radon loss, ~10%, suggesting that diffusion parameters are changed during heating at temperatures ⩾975 °C, which is likely the result of annealing of radiation damage. Diffusion parameters calculated from the fractional loss experiments reflect diffusion in highly radiation damaged or metamict zircons. Our results indicate that internal microstructures in zircon, such as fission tracks and alpha-radiation damage, influence radon escape for diffusion and recoil mechanisms, and hence if these effects can be further characterized, measurements of ^{222}Rn escape have the potential to be useful for probing the internal structure of zircon, and other U-bearing minerals.

Keywords: Radon emanation; Zircon; Geochronology; Diffusion kinetics

1. INTRODUCTION

Investigations of radon emanation rates have implications for many fields in Earth and atmospheric sciences. Concentrations of radon in air and water have been utilized as tracers for locating subsurface uranium deposits (e.g., Levinson et al., 1982), predicting earthquakes (e.g., Fleischer and Mogrocampero, 1985; Igarashi et al., 1995; Whitehead and Lyon, 1999), identifying subsurface hydrocarbon deposits (Fleischer and Turner, 1984), and sources of air masses (Turekian et al., 1977). In particular, ^{222}Rn and its progeny have been widely utilized as tracers to quantify atmospheric processes including source tracking and transport (within and between the troposphere and stratosphere), time scales for air mass stability and vertical movement, removal rates and residence times of aerosols, sources of continental dust in an air mass, and gas exchange studies at air-sea interfaces, etc (e.g., Rama, 1969; Broecker

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and Peng, 1974; Turekian et al., 1977; Lambert et al., 1982; Liu et al., 1984; Kritz et al., 1993; Zahorowski et al., 2004; Baskaran, 2011; Chambers et al., 2014). Mobility of radon from subsurface rocks and soils to surface air and its entry into homes has been a serious public health concern for several decades. Radon, along with its progeny, accounts for over half of a typical individual's exposure to natural radiation in the environment (NCRPM, 1987; Greeman and Rose, 1996). Thus, understanding the mechanisms by which radon is released from materials is important for a wide range of applications.

Radon-222, the longest-lived radon isotope ($T_{1/2} = 3.82$ d) and heaviest of all the noble gases, is an intermediate daughter product in the decay of ^{238}U to ^{206}Pb, thus its escape from rocks and minerals over extended periods of time could significantly alter their U–Pb and U–He chronological clocks (e.g., Heaman and LeCheminant, 2000; Corfu, 2012). When an atom of ^{226}Ra undergoes alpha decay, the daughter nuclide, ^{222}Rn, undergoes recoil with a kinetic energy of ~100 keV, resulting in displacement from its original location (Tanner, 1978). These recoiled atoms can be ejected from a mineral grain into surrounding aqueous solution, embedded into adjacent mineral grains, or released into air space (Tanner, 1978) (Fig. 1). Internal defects in the crystal lattice, caused primarily by alpha and fission tracks, can create conduits through which radon may escape.

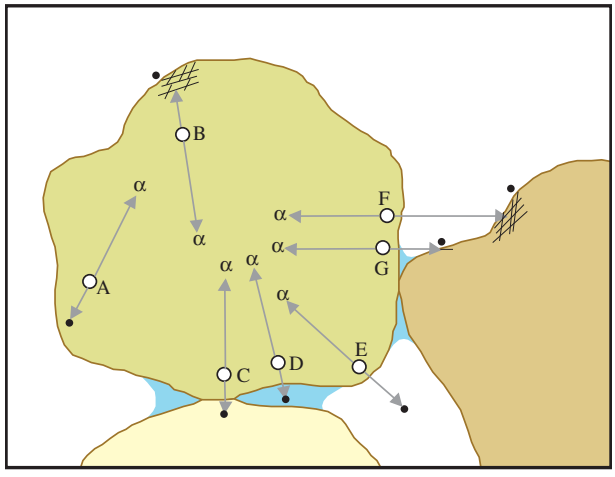

Fig. 1. The fate of ^{222}Rn after recoil includes several possibilities, not all of which include escape or emanation. Open circles represent a ^{226}Ra atom undergoing alpha decay to produce ^{222}Rn, represented by filled circles. (A) Radon is produced in the interior of the grain, beyond the recoil distance, and remains inside the grain. (B) Radon is produced at depth as in (A), but its pathway intersects an internal network of passageways, which arise from internal defects such as fission tracks, allowing the radon to escape. (C) ^{222}Rn exits the source grain, but its energy allows it to travel into an adjacent grain. (D) ^{222}Rn escapes the grain and is stopped by water surrounding the grain, or within pore space. (E) ^{222}Rn escapes the grain into the air, or open pore space. (F) ^{222}Rn is implanted into a neighboring grain, however an internal network of pathways allows the radon to escape. (G) ^{222}Rn implants in neighboring grain, and escapes back through the recoil pathway (adapted from Tanner, 1978).

Based on measurements of ^{222}Rn released from a suite of samples that included saprolite, zircon-monazite mixture, and monazite sand, Rama and Moore (1984) hypothesized that there is an internal network of nanopores that allows Rn to escape. The fractional release of radon may thus yield information on the internal microstructure of minerals.

Zircon is a commonly occurring accessory mineral found in a variety of rock types, and is widely utilized for geochrological studies due to its low common Pb, high crystallization temperature, and stability in weathering environments. In this study, we investigate the ^{222}Rn emanation rates for three zircon samples collected from 3 localities: Mud Tank (Harts Range, Australia), Bancroft (Bancroft, Ontario, Canada), and Malawi (Mount Malosa pegmatite, Malawi, Africa). We measured room temperature radon emanation after annealing at various temperatures in order to investigate the effects of microstructure on ^{222}Rn emanation. In addition, we measured ^{222}Rn loss upon heating to investigate the potential for ^{222}Rn diffusion at high temperatures. These results are important for understanding the mechanics of ^{222}Rn loss from zircon, and have potential implications for U–Pb and U–Th–He geochronology.

2. MATERIALS AND METHODS

We selected three large (~100 g) single crystal zircon samples from three localities (Mud Tank (~732 Ma U–Pb (Black and Gulson, 1978)), Malawi (~730 Ma U–Pb (Ashwal et al., 2007)), and Bancroft (~1050 Ma U–Pb (Nasdala et al., 2010)) that have different ^{238}U concentrations. The zircons were crushed and separated into five grain-size fractions (>500 μm, 250–500 μm, 125–250 μm, 63–125 μm, and <63 μm). After sieving, the grains were run through a Frantz magnetic separator to remove obvious iron impurities.

2.1. ^{226}Ra activity

It is necessary to measure ^{226}Ra activity in order to determine how much of the total ^{222}Rn produced is escaping the grain. Activity of ^{226}Ra was measured using gamma-ray spectrometry. ^{226}Ra was measured using two gamma energies: 352 keV from ^{214}Pb and 609 keV from ^{214}Bi (Porcelli and Baskaran, 2011). For all samples, ^{226}Ra and ^{238}U, as well as ^{228}Ra and ^{232}Th are assumed to be in secular equilibrium, so ^{238}U and ^{232}Th concentrations can be determined from the ^{226}Ra and ^{228}Ra activities. Approximately 0.5 g of each size fraction, weighed to a precision of 0.1 mg, was placed in 10 ml graduated (1–10 ml) counting vials (volume of the sample in the vial is ~0.5 ml) and counted in a high-purity germanium well detector coupled to a Canberra DSA multichannel analyzer. The detector was calibrated with IAEA solid standards (RGU-1 for ^{226}Ra and RGTh-1 for ^{228}Ra) in the same size and shaped vial, using standard volumes from 1 to 10 ml by obtaining disintegration per minute (dpm)/-counts per minute (cpm) ratios. The dpm/cpm ratio remains the same for standards with volumes less than 1-ml. The self-absorption corrections at the energies of interest are negligible, and both 352 keV and 609 keV lines