



Diffusion of helium in carbonates: Effects of mineral structure and composition

D.J. Cherniak^{a,*}, W. Amidon^b, D. Hobbs^b, E.B. Watson^a

^a Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

^b Geology Department, Middlebury College, Middlebury, VT 05753, USA

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Abstract

Diffusion of helium has been characterized in four carbonates: calcite, dolomite, magnesite, and aragonite. Cleaved or oriented and polished slabs of carbonate minerals were implanted with 100 keV or 3 MeV ^3He at doses of $5 \times 10^{15} \text{ } ^3\text{He}/\text{cm}^2$ and $1 \times 10^{16} \text{ } ^3\text{He}/\text{cm}^2$, respectively, and annealed in 1-atm furnaces. ^3He distributions following diffusion experiments were measured with nuclear reaction analysis using the reaction $^3\text{He}(d,p)^4\text{He}$.

Our results show that He diffusion in calcite is the fastest among the carbonates studied, with diffusivities progressively slower in magnesite, dolomite and aragonite. In the case of the isomorphous trigonal carbonates (calcite, dolomite, magnesite), these observations are broadly consistent with predictions based on lattice characteristics such as unit cell size and inter-atomic apertures, with diffusivities faster in more open carbonate structures. Dolomite is an exception to this trend, suggesting that its unique ordered R3 crystal structure may play a role in slowing helium diffusion. Diffusion is anisotropic in all of the trigonal carbonates, and is typically slowest for diffusion along the c direction, and faster for diffusion normal to c and in directions normal to cleavage surfaces. The patterns of diffusional anisotropy are predicted to first order by the size of limiting inter-atomic apertures along any given crystallographic direction, providing additional support to the concept of modeling crystal lattices as “molecular sieves” with regard to diffusion of helium.

When the effects of anisotropy and diffusion domain size are considered, our results are in reasonable agreement with previous results from bulk degassing of natural samples. Modeling of helium diffusive loss shows that calcite and magnesite are unlikely to be retentive of helium on the Earth’s surface for typical grain sizes and time/temperature conditions. Dolomite and aragonite may be retentive under cooler conditions, but because helium retention is strongly dependent on diffusion domain size, general predictions are difficult given the structural complexities of natural samples. Our axis-specific diffusion measurements across a range of carbonate compositions, evaluated through direct profiling, offer important constraints for modeling helium mobility in carbonates, and for understanding the influence of the complexities of carbonate structures on He outgassing patterns.

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1. INTRODUCTION

Understanding diffusion of noble gases in minerals is of broad importance in the earth sciences. For example,

helium thermochronology has advanced the field of tectonics by providing information on cooling and exhumation of rocks from shallow depths. Inferring cooling histories depends on precise knowledge of helium diffusion systematics in a range of minerals. Mineral phases with sufficiently fast diffusion kinetics to be sensitive to low temperatures, such as apatite, are especially useful. Noble gas cosmogenic dating has also become an increasingly important tool in

* Corresponding author. Tel.: +1 518 276 8827.
E-mail address: chernd@rpi.edu (D.J. Cherniak).

geomorphology, and requires that noble gases be quantitatively retained in minerals at Earth surface conditions. It has recently been proposed that cosmogenic ^3He inventories in minerals with very low closure temperatures could be used to reconstruct temperature variations in Earth's atmosphere (Tremblay et al., 2014). In addition, noble gases are commonly used to constrain the long term evolution of Earth's mantle and atmosphere, with diffusion kinetics placing first order constraints on these processes (Albarède, 2008; Jackson et al., 2009).

Diffusion of helium in carbonate minerals is of particular interest due to their ubiquity, large grain size, and potential use as very low temperature thermochronometers. Early studies approached the problem by computing (U-Th)/He ages on carbonate rocks of known age (Fanale and Kulp, 1961). The resulting ages were higher than expected for marble, which suggested He retention, but were lower than expected for low temperature and biogenic calcite, suggesting diffusive loss of helium. Subsequent studies on aragonite suggest it is retentive, based on good agreement between (U-Th)/He and U-series ages of a suite of fossil corals, although certain samples appeared to have He deficits up to 30% of their expected value. (Fanale and Schaeffer, 1965; Bender, 1973; Bender et al., 1973).

More recent work by Copeland et al. (2007) directly evaluates ^4He diffusion kinetics by soaking a variety of carbonates in pressurized ^4He gas and undertaking bulk step-heating experiments. The measured diffusion parameters predict closure temperatures from ~ 54 to 90°C . However, Arrhenius relationships suggest multi-diffusion domain (MDD) behavior, making it difficult to make broad predictions about bulk He retention in natural samples. This complexity is underscored by (U-Th)/He ages reported on a suite of known-age samples, several of which yield anomalously young ages. In contrast to the MDD behavior observed for some carbonates, Copeland et al. (2007, 2015) find step-heating results for crinoid columnals that suggest He diffusion from a single domain is dominant in these samples. They suggest that the biotic origin of these samples produces a more uniform microstructure in the carbonate, which develops into large effective He diffusion domains upon heating.

A scatter of (U-Th)/He cooling ages was also observed by Cros et al. (2014) on a set of Eocene-aged calcite samples, which ranged in age from ~ 2 to 35 Myr despite being collected from the same sample location. Helium retention varied with the type of calcite, and step-degassing experiments suggest this variability can be attributed to MDD behavior. Further, a recent study by Amidon et al. (2015) also documents MDD behavior for bulk degassing of ^3He in a set of proton-irradiated calcite samples. Comparison of observed kinetic parameters with cosmogenic ^3He inventories in a variety of natural samples leads these authors to propose that opaque natural calcite may have slower diffusion kinetics than gem-quality calcite due to imperfections in the crystal lattice and/or the presence of inclusions that might disrupt diffusive pathways. In summary, diffusion of helium in carbonate minerals is complex and may be controlled by both lattice-scale crystal defects and the presence of larger scale diffusion domains. Previous work

suggests that aragonite may be more retentive than calcite, presumably due to its different mineral structure.

One limitation of previous bulk degassing experiments is the ambiguity in distinguishing between the controls of diffusion kinetics and diffusion domain size, as well as anisotropy of diffusion, on the observed Arrhenius plots. This study attempts to clarify these effects by determining diffusion kinetics by direct depth profiling in gem-quality carbonates. We utilize a technique which involves implantation of ^3He atoms followed by isothermal heating, and then measurement of the relaxed ^3He profile using nuclear reaction analysis (NRA) with the reaction $^3\text{He}(d,p)^4\text{He}$ (Cherniak et al., 2009). Similar experimental and analytical procedures have been used previously to characterize diffusion in a variety of minerals, including zircon and apatite (Cherniak et al., 2009), titanite and rutile (Cherniak and Watson, 2011) olivine (Cherniak and Watson (2012), and monazite (Cherniak and Watson, 2013).

This approach allows diffusion kinetics to be determined over spatial scales that are likely to be smaller than the dominant diffusion domains in carbonate minerals, and is less sensitive to bulk heterogeneities in the crystal lattice, permitting measurement of lattice diffusion without the overprint of MDD behavior or fast path diffusion that might affect He release patterns in bulk degassing experiments. Further, because diffusion is effectively measured in one direction on each sample, axis-specific diffusion kinetic parameters can be determined, which can be used to assess diffusional anisotropy (e.g., Cherniak et al., 2009; Cherniak and Watson, 2011) and model it in natural systems.

2. EXPERIMENTAL PROCEDURE

2.1. Sample preparation

Gem-quality samples were selected for each of the four major carbonate minerals – calcite, dolomite, magnesite and aragonite – to investigate the effects of differences in composition and structure on He diffusion. A synthetic calcite sample was obtained from Commercial Crystal Labs, the same material used by Copeland et al. (2007) and Arvidson et al. (2003). A dolomite specimen from Styria, Austria was obtained from the Smithsonian collection (USNM # R12596). A sample of magnesite was purchased from the Brumado district in Brazil, presumably equivalent to specimen #R050443 in the RRUFF database (<http://rruff.info/>). A specimen of aragonite was used from the Tazoutu Mine in Sefrou Province, Morocco. Prior to diffusion measurements, samples were analyzed for bulk composition via ICP-AES and mineralogy via XRD. Trace and minor element compositions are presented in [Supplementary Table 1](#). Samples, selected to be optically clear and free of inclusions, were oriented, and cleaved or cut in sections a few mm on a side and 0.5–1 mm thick. Orientations were chosen to measure diffusion parallel and normal to *c* in all of the carbonates, and normal to cleavage surfaces for calcite, dolomite and magnesite. Samples with faces along cleavage surfaces were prepared

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