Light noble gas dissolution into ring structure-bearing materials and lattice influences on noble gas recycling

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Version: Accepted Manuscript

Link(s) to article on publisher’s website:
http://dx.doi.org/doi:10.1016/j.gca.2015.02.036

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Title: Light noble gas dissolution into ring structure-bearing materials and lattice influences on noble gas recycling

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Abstract: Light noble gas (He-Ne-Ar) solubility has been experimentally determined in a range of materials with six-member, tetrahedral ring structures: beryl, cordierite, tourmaline, antigorite, muscovite, F-phlogopite, actinolite, and pargasite. Helium solubility in these materials is relatively high, 4×10^{-10} - 3×10^{-7} mol g^{-1} bar^{-1}, which is ~100 to 100,000× greater than He solubility in olivine, pyroxene, or spinel. Helium solubility broadly correlates with the topology of ring structures within different minerals. Distinctive He-Ne-Ar solubility patterns are associated with the different ring structure topologies. Combined, these observations suggest ring structures have a strong influence on noble gas solubility in materials and could facilitate the recycling of noble gases into the mantle. Measurements of Ne and Ar solubility in antigorite, however, are highly variable and correlated with each other, suggesting multiple factors contribute the solubility of noble gases in serpentine-rich materials.

1.0 Introduction
Earth’s mantle and atmosphere are distinct in both their elemental and isotopic noble gas compositions (Lupton and Craig, 1975; Staudacher and Allègre, 1988; Sarda et al., 1985; Sarda et al., 1988; Moreira et al., 1998; Holland and Ballentine, 2006, Holland et al., 2009; Mukhopadhyay, 2012). Isotopic heterogeneity between the atmosphere and mantle exists for long-lived radiogenic systems, short-lived radiogenic systems, and non-radiogenic systems. However, it is well-established that oceanic sediments and uppermost oceanic crust contain relatively high concentrations of seawater-derived noble gases, which are delivered to subduction zones (Matsuda and Nagao, 1986; Staudacher and Allègre, 1988). To maintain the distinct compositions of noble gases in the atmosphere and mantle, it has been argued that devolatilization of subducted material is sufficiently efficient that subduction zones provide a near-complete barrier to noble gas recycling (Staudacher and Allègre, 1988).

The model of an efficient barrier to noble gas recycling has since been challenged by a diverse set of observations. Measurements of hydrated mantle sections of exhumed slabs (serpentinites) demonstrate deeper, and harder to devolatilize, horizons of the slab are capable of hosting large quantities of seawater-derived noble gases (Kendrick et al., 2011, Kendrick et al., 2013). Peridotitic rocks exhumed from the mantle wedge contain noble gases with elemental ratios most consistent with a seawater origin (Sumino et al., 2010). Samples of metasomatized subcontinental lithospheric mantle also show evidence for atmospheric Ar-rich fluids (Nagao and Takahashi, 1993; Matsumoto et al., 2001; Matsumoto et al., 2002; Yamamoto et al., 2004; Gautheron et al., 2005; Kim et al., 2005; Matsumoto et al. 2005; Hopp and Ionov, 2011). Measurements of Xe isotopes derived from both ridge and plume environments indicate the coexistence of atmospheric and
Primordial Xe components in their mantle source, and the atmospheric component is associated with noble gas recycling (Mukhopadhyay, 2012; Parai et al., 2012; Tucker et al., 2012, Pető et al., 2013). Measurements of Kr and Xe from well gases that contain mantle-derived volatiles also provide evidence for the coexistence of atmospheric and primordial noble gases in the mantle (Caffee et al., 1999, Holland and Ballentine, 2006, Holland et al., 2009). Thus, many lines of evidence suggest that large volumes of the mantle have interacted with the noble gases from Earth’s atmosphere, yet the recycling process is sufficiently inefficient that very early-forming mantle-atmosphere heterogeneities persist to the present day.

Despite the mounting evidence for the large scale recycling, the responsible carrier phases remain poorly understood. Here, we seek to understand the materials and mechanisms that are capable of transporting noble gases, and by extension, volatiles in general, into and through subduction zones. We specifically focus on exploring the role noble gas solubility in ring structure-bearing minerals, a common class of minerals in hydrothermally altered slab lithologies that includes amphibole, serpentine, talc, clays, mica, and chlorite. Ring structures are constituted by six (Si,Al)O$_4$ tetrahedral units bound in a hexagonal pattern (Figure 1). They are large radius structures in mineral lattices and are commonly unoccupied. Noble gases are large radius, neutrally charged elements. Following lattice strain theory (e.g. Wood and Blundy, 1997), unoccupied ring structures are predicted to be energetically favorable locations for noble gas dissolution in minerals (Damon and Kulp, 1958). Experiments corroborate this prediction (Smith and Schreyer, 1962; Wartho et al., 2005; Jackson et al., 2013a), suggesting minerals with ring
structures are capable of the transporting significant quantities of noble gases in subduction zones.

The geometry of the ring structure hexagon (Figure 1) and the distribution of cation polyhedra local to the ring structure (combined, ring structure topology) vary between minerals. The topology of a ring structure will have a characteristic polarization and size, which, in turn, should affect the solubility of noble gases in the mineral that hosts the ring structure. To test this hypothesis, we experimentally quantify the solubility of light noble gases in materials that possess a range of ring structure topologies.

2.0 Methods

2.1 Starting Materials

Large specimens of beryl, cordierite, tourmaline, antigorite, muscovite, F-phlogopite, actinolite, and pargasite materials were used as the starting materials in the experiments. Major element compositions are given in Table 1. All specimens are natural materials except the F-phlogopite. Bulk materials of beryl, cordierite, tourmaline, antigorite, and pargasite were sectioned into sizes appropriate for the experiments, approximately $2 \times 2 \times 1$ mm, using a low speed saw and diamond encrusted wafering blade. The large volume of the run products allows for repeated, high-precision measurements of noble gas contents in a particular material. No attempt was made to crystallographically orient samples during sectioning. A single face of each sectioned material was mechanically polished, finishing with 0.05 $\mu$m alumina grit. Each
mechanically polished face was then chemically polished using colloidal silica for >3 hours. Starting materials were not annealed prior to the experiment. This preparation is designed to minimize any lattice damage induced by the cutting and mechanical polishing procedure. Muscovite starting materials were purchased (SPI Supplies, V-1 grade) as cut and cleaved ~3 mm diameter discs (~50 µm height) and used as purchased. The F-phlogopite bulk material is synthetic and exists as inter-grown books. Starting materials were prepared by cleaving books from the bulk F-phlogopite sample and cutting the cleaved books into appropriate sizes using a razor blade. Actinolite starting materials were prepared by cleaving laths from a larger specimen. Once prepared, but prior to the experiment, starting materials were mapped for secondary phases using a 120× stereoscope. All materials, except antigorite, are essentially devoid of observable secondary phases. The antigorite material contains both macro- and micro-scale magnetite as well as a separate fine-scale secondary phase (Figure 2). Macro-scale magnetite was avoided during analysis, but micro-scale and the fine-scale secondary phase were variably incorporated into the analyses of antigorite.

2.2 Noble Gas Solubility Experiments

Each experiment consists of three samples loaded into separate graphite capsules. The capsules were machined so that all three samples were contained within the hotspot, as determined by the temperature calibration of the pressure vessel assembly. A ~0.1 bar vacuum was drawn on the entire assembly before it was pressurized. The pressure medium was noble gases (He-Ne-Ar) ± methane for all experiments, allowing for precise
and sustained control of noble gas fugacity over the duration of the experiment. Methane was included in some initial experiments to provide a small fugacity of H$_2$O ($f_{H_2O}$) in order to prevent mineral decomposition but was found to be unnecessary and was not used for later experiments. Leakage of the gas pressure medium was <5% over the run duration. Temperatures were controlled by placing the molybdenum-hafnium-carbide alloy pressure vessel into a vertical furnace for EHPV (externally heated pressure vessel) series experiments or a horizontal furnace for CS (cold seal) series experiments. Temperatures ranged from 350 to 900°C and pressures ranged from 0.06 to 1.77 kbar. Convection within the pressure vessel was suppressed using graphite filler rods that extend the length of the pressure vessel above the sample capsules. Experiments were quenched by removing the pressure vessel from the furnace and allowing it to cool against air. The vessel cooled to ~50°C in 20 minutes. At this point, the pressure vessel was rapidly depressurized and unloaded.

2.3 Analytical Methods

2.3.1 Major Element Analysis

Major element compositions were determined using an electron microprobe ( Cameca SX-100, Brown University). Analyses were completed using wavelength dispersive spectrometry, and the standard PAP correction for Cameca electron microprobes was applied. Analytical parameters were 15 kV accelerating potential, 10 nA beam current, and a 10 µm beam diameter.
2.3.2 Noble Gas Analysis

Noble gas concentrations of the experimental run products were determined using a UV laser ablation-noble gas mass spectrometer system at the Open University (UK). A 193 nm ArF excimer laser was used to ablate all materials. Three SAES AP-10 getters in the extraction system removed active gases released during ablation before introduction into a MAP215-50 mass spectrometer. $^{4}$He, $^{22}$Ne and $^{40}$Ar were measured by an electron multiplier in peak hopping mode. The sensitivity of the mass spectrometer was determined by gas pipetting a known volume of noble gases with elemental ratios designed to allow for measurement without separation and atmospheric isotopic ratios into the mass spectrometer. Kelley et al. (1994) provides a more detailed description of the noble gas analytical method.

Materials from each experiment were analyzed repeatedly for noble gas contents using a combination of large diameter (40-400 µm) spots and single-line rasters. Pit depths ranged up to ~33 µm (average depth of a single pit). Blanks were typically run as every fourth analysis. The blank for each analytical session was calculated as the mean of individual blanks over the duration of that particular session, and the blank standard deviation is calculated as the standard deviation on the blank mean. A session is defined as a single day of analysis on a single port. Systematic changes in blanks were not observed over a session. Blank levels were overwhelmingly dependent upon sample degassing rather than background levels in the extraction system or mass spectrometer as
has previously been observed for analysis of He in experimental samples (Heber et al., 2007).

No internal standard was available for noble gas analyses. To determine noble gas concentration, we ratio the number of noble gas moles released to the volume of the ablation pit. Pits volumes were measured using a white light interferometer (Zygo Instruments, New View 6000 Series, Brown University). This device provides an image of the ablated surface that requires minimal interpolation of pixels with unknown depth values. A surface continuum is calculated by masking out the ablated area of the interferometer image and interpolating across the masked region. The inpainted interferometer image is subtracted from the surface continuum, isolating the relief associated with the ablation pit. To calculate the pit volume, the individual volumes of pixels are summed assuming rectangular prism geometry for each pixel. Shallow pits, pits ablated into highly curved surfaces, and pits that require longer distances of interpolation have greater uncertainties associated with their volume. We estimate an uncertainty of 15% on volume calculations. Although, as discussed below, this is likely an underestimate for some extremely shallow pits and an overestimate for deeper pits. A small ring of vapor deposition forms along the circumference of the pits, creating a halo of pixels with negative depth. We avoid including these pixels in the volume determination by only summing pixels with positive depths. In general, >100,000 pixels are summed for an ablation pit. Each topographic image contains 307,200 pixels (480 × 640).

All materials were carbon coated prior to imaging for volume determinations. This significantly improved the return signal, reducing the amount of interpolation
required for pit volume determinations. Carbon coat thickness was not measured
directly, but based on distance from source and coating time, thickness is estimated at 20
nm.

2.3.2.1 Noble Gas Data Processing

To convert pit volumes into mass, we apply densities from Deer et al. (1996),
accounting for Mg-Fe exchange. The pit depth associated with each analysis is the
average depth of pixels summed in the volume calculation. The ablation pits are not
perfectly flat bottomed, and thus, pit depth is a spatially averaged value. It should be
stressed that noble gas-laser ablation mass spectrometry is a micro-sampling technique
that analyzes the bulk contents of noble gases in an ablated volume. Noble gases are not
analyzed from a strict depth horizon within the sample. Rather, the concentration of a
noble gas in an analysis is a depth-averaged value. Individual measurements of noble gas
concentrations in experimental run products are reported in Supplementary Table 1.
Uncertainties on the number of moles of He, Ne, and Ar release during an analysis
include the standard deviation of the blank for the session in which the analysis occurred
and the regression uncertainties associated with extrapolation of the analytical signal to
the inlet time. Uncertainties on the reported noble gas concentrations include the
propagated uncertainties from the moles determination and the volume uncertainty
estimate (15%). All uncertainties are one standard deviation and independently
propagated. When no concentration gradient is observed, noble gas solubility is
calculated as the average noble gas concentration from an experiment, normalized to the
calculated fugacity of that gas. This calculation yields a Henry’s constant, abbreviated \( \text{He}_{\text{HC}} \) for He, with units of mol g\(^{-1}\) bar\(^{-1}\).

Noble gases are not ideal gases. This is particularly true for heavier noble gases in higher pressure, lower temperature systems. To account for the non-ideality of Ne and Ar, we calculate their fugacity in a given pressure medium using a modified Redlich-Kwong equation of state for gas mixtures (Flowers, 1979). Helium is assumed to behave as an ideal gas across the range of conditions explored here.

The solubilites of Ne and Ar in beryl, cordierite, actinolite #2, and pargasite #2 are calculated using He as an internal standard, applying the He solubility relationships determined here. We take this approach because the majority of ablation pits completed to measure Ne and Ar solubility in these phases are very shallow and prone to systematic underestimations of pit volume (detailed below). Using He as an internal standard allows for Ne and Ar concentration to be calculated for shallow pits without explicitly accounting for pit volume. A more detailed explanation of Ne and Ar solubility calculations in beryl, cordierite, actinolite #2, and pargasite #2 is provided in the Supplementary Information.

3.0 Results and Discussion

3.1 Major Element Results

Major element compositions for all materials investigated are reported in Table 1. Cations are reported as oxide wt. %, which causes low totals on an oxide basis for
minerals with significant F, Cl, and OH. Quality of analyses are evaluated by stoichiometry. Stoichiometry is calculated assuming that no oxy-component is present for hydrous minerals, i.e. OH sites host only F, Cl, and OH. Beryl contains stoichiometric Be, and tourmaline contains stoichiometric Li and B. Be, Li, and B were not analyzed, and so the abundances of these elements are assumed to be stoichiometric, i.e. three Be atoms per beryl formula unit, three B atoms per tourmaline formula unit, and 1.5 Li atoms per tourmaline formula unit. There is some uncertainty regarding the stoichiometric component of Li in tourmaline. We choose 1.5 atoms per formula unit because the chemistry of the tourmaline is close to the elbaite endmember. Changes in the assumed amount of Li in tourmaline do not have a significant effect on stoichiometry calculated for tourmaline. The stoichiometry of both micas suggests a small deficiency of K and Na (i.e. 0.85 < K + Na < 1 per functional unit). Deficiencies of K + Na in mica are manifested as unoccupied ring structures, suggesting these minerals have a small, but finite, concentration of ring structures capable of hosting noble gases. Electron microprobe analyses confirm that inclusions of magnetite are present the in antigorite material.

3.2. Noble Gas Results

3.2.1. Equilibrium Considerations: Depth Correlations

Several lines of evidence suggest the measured concentrations of He closely approach equilibrium values. Figure 3 plots all He analyses against the associated
ablation pit depth. Helium concentrations of individual analyses are normalized to $f_{\text{He}}$ of the experiment, yielding an effective Henry’s constant for each analysis. This approach is implemented to account for the variability in concentration directly related to changes noble gas fugacity and to allow the effects of other variables (e.g. depth) to be observed in inter-experiment comparisons. This approach is justified here because each investigated phase has been verified to follow Henrian solution behavior for He (Figure 4b; Jackson et al., 2013a for amphibole).

No correlation is observed between $He_{HC}$ and pit depth, neglecting some very shallow pits (see discussion below) and some experiments on muscovite and F-phlogopite. The general lack of correlation between $He_{HC}$ and depth supports the argument that the measured He concentrations are equilibrium values and are not affected by lattice damage induced during sample preparation or the inclusion of secondary phases during analysis. Henry’s constants for He are calculated for an experiment as equal-weight averages of the individual analyses on that experiment when no depth dependence for concentration is observed.

The high He concentrations associated with shallow pits (<0.33 µm) are likely artifacts. We argue these high concentrations result from systematic underestimations of the ablation pit volume. Ablation pits with large radius/depth ratios are difficult to measure accurately because small biases in the interpolation of the unablated surface can lead to relatively large errors in volume calculations. The interpolation algorithms used here tend to under-account for surface curvature, which results in systematic underestimates of volume when curvature is concave in the direction of ablation (down). All ablation pits on beryl, cordierite, tourmaline, antigorite, and pargasite #2 were drilled
into polished surfaces, and given the polishing techniques utilized here, these surfaces are typically concave down. Shallower pits are more prone to this systematic bias, and consequently, we only consider concentration data for ablation pits that are >0.33 µm deep as reliable. All analyses that are <0.33 µm deep are plotted as unfilled symbols. The volume bias is most obvious for the shallow analyses of beryl but is also observed for shallow analyses of tourmaline and pargasite #2. Shallow pits of cordierite were also analyzed (Figure 3a), but no obvious volume bias is present, supporting the interpretation that the high concentration analyses are apparent and not the result of He enrichment. Several spurious, high concentration analyses were observed (also plotted as unfilled symbols). We interpret these analyses to reflect the inadvertent incorporation of a gas-rich secondary phase in the ablated volume. These data are not used in further analysis or calculations of Henry’s constants as the remainder of data are comparatively repeatable.

Several lower temperature, shorter duration experiments on micas display clear He concentration gradients parallel to the C axis that extend several microns into the mineral interior (symbols labeled “diffusion fit,” Figure 3b). The fact that concentration is depth dependent precludes calculating He Henry’s constants as simple averages of measurements. For these experiments, we fit diffusion profiles (tracer diffusion into a semi-infinite medium from a reservoir of constant chemical potential) to quantify He diffusion kinetics and solubility (Supplementary Table 2). Solubility in this circumstance is taken as the modeled concentration of He at the surface (Thomas et al., 2008). Note, however, that some micas run at similar temperatures and for similar durations do not show a clear concentration profile but yield similar He_{HC} (see the muscovite and F-phlogopite from CS_NG_EXP2 and the F-phlogopite from CS_NG_EXP15). The reason
for this discrepancy is unclear but may reflect that the diffusional length scale for these samples was not the grain size (e.g., related to unobserved fracturing or cleaving).

Helium diffusivities fit for muscovite and F-phlogopite vary between $3 \times 10^{-15}$ and $2 \times 10^{-17}$ m$^2$ s$^{-1}$ at 500°C. The average of He diffusivities fit for muscovite is $9 \pm 5 \times 10^{-17}$ m$^2$ s$^{-1}$, and this value is $\sim 100\times$ slower than previous step-degassing based determinations of He diffusion in muscovite at 500°C (Lippolt and Weigel, 1988). Micas in this study were prepared as cleaved discs and were consequently ablated parallel to the C axis during analysis, far from grain edges. This analytical approach effectively isolates diffusion that occur across, rather than parallel to, the interlayer structures. Thus, the slow He diffusivities measured here are consistent with noble gas diffusion being strongly anisotropic in mica, where diffusion preferentially occurs through interlayers. Similar observations have been made for Ar diffusion in mica (Giletti, 1974).

3.2.2. Equilibrium Considerations: Duration, $f_{He}$, and Temperature Correlations

Figure 4 plots the $He_{HC}$ determined for each experiment against the respective experimental duration, $f_{He}$, and temperature. Where no concentration profile was observed in a run product, $He_{HC}$ is calculated as an equal-weight average of the population of individual analyses. Where a concentration profile was observed (i.e. micas), $He_{HC}$ is calculated by fitting a diffusion profile and using the surface concentration as solubility. $He_{HC}$ values for each experiment are provided in Table 2 along with associated experimental parameters.
He\textsubscript{HC} values are independent of duration, \( f_{\text{He}} \), and temperature (Figure 4). Many of the minerals investigated here are hydrous and, thus, prone to decomposition under the imposed experimental conditions (i.e. high temperature, low \( f_{\text{H}_2\text{O}} \) systems). The lack of correlation between He\textsubscript{HC} and duration argues against H loss or decomposition affecting the concentrations of He measurements. Similarly, higher temperatures promote more rapid loss of H and decomposition. No correlation is observed between He\textsubscript{HC} and temperature, also arguing against H loss and decomposition affecting He concentrations. Moreover, the lack of correlation between He\textsubscript{HC} and temperature indicates that there is a small enthalpy associated with the dissolution of He into the ring structure-bearing minerals explored here. This is consistent with the weak bonding between noble gases and their mineral hosts and allows for simple extrapolations to higher and lower temperatures.

Experiments were conducted at unnaturally high noble gas fugacity in order to achieve precise analyses. As such, the applicability of Henry’s Law must be evaluated before solubility relationships can be applied to modeling the behavior of noble gases in natural systems. Henrian solution behavior requires that the concentration of an element dissolved into a phase is linearly proportional to the fugacity of that element in the system, or equivalently, the Henry’s constant is invariant with changes in fugacity. Figure 4b demonstrates the invariance of He\textsubscript{HC} over a range of \( f_{\text{He}} \), indicting Henry’s Law is obeyed. The repeatability of He\textsubscript{HC} across the range of \( f_{\text{He}} \) suggests the solubility relationships determined for He are robust and meaningful for natural systems. It is possible that other solution mechanisms become significant at lower noble gas fugacity.
If true, then the noble gas solubilities documented here represent lower limits for natural systems.

At higher $f_{\text{He}}$, it is expected that the available ring structures approach complete occupancy, resulting in a non-linear relationship between $f_{\text{He}}$ and He solubility, i.e. a Langmuir Isotherm. However, the occupancy of ring structures by noble gases, up to the highest $f_{\text{He}}$ explored here, remains relatively small. Cordierite shows the strongest affinity for He, but only $\sim15\%$ of available ring structures are occupied by He at $f_{\text{He}} = 1.77$ kbar (two ring sites per formula unit).

3.2.3. Correlations Between $\text{He}_{\text{HC}}$ and Ring Structure Topology

Ring structures tend to generate large radius interstices that are potential hosts for noble gases. However, the geometry of the ring structure hexagon (Figure 1) and the distribution of cation polyhedra local to the ring structure (combined, ring structure topology) are not constant between minerals (Figure 5). Thus, the solubility of noble gases in ring structure-bearing minerals may be sensitive to changes in ring structure topology.

Figure 5 plots $\text{He}_{\text{HC}}$ normalized to the concentration of unoccupied ring structures ($\text{He}_{\text{HC-ring norm.}}, \text{He mol ring mol}^{-1} f_{\text{He}} \text{ bar}^{-1}$) for the various unoccupied ring structure-bearing minerals studied here, ordered in ascending $\text{He}_{\text{HC-ring norm.}}$. Solubility data are normalized to the concentration of unoccupied ring structures to provide the most direct comparisons between differing ring topologies. Helium is highly soluble in all ring structure-bearing minerals, ($\text{He}_{\text{HC}}$ varies between $\sim100$ to $100,000 \times$ olivine $\text{He}_{\text{HC}}$), but
there is considerable variability in determinations of He$_{\text{HC-ring norm.}}$ between the different minerals explored here. We seek here to understand the cause of this variability by considering variations in ring structure topology.

3.2.3.1. Antigorite and Tourmaline He$_{\text{HC-ring norm.}}$

Antigorite and tourmaline have similar He$_{\text{HC-ring norm.}}$ and share similar topologies about their ring structures (Figure 5). Specifically, both minerals have groups of octahedra above and below a single ring, and the tetrahedral units in the ring are oriented with an apex pointed towards the upper octahedra. In tourmaline, the ring structure exists as an isolated unit and is commonly occupied by Na, and to a lesser extent, Ca. Each of the octahedra associated with the ring structure in tourmaline shares an oxygen ion with a trigonally coordinated B ion. The ring structure in antigorite is defined by an upper and lower octahedral sheet with a tetrahedral sheet of rings bound to the upper octahedra. Nominally, all the ring structures in antigorite are unoccupied. Compared to the other minerals with unoccupied ring structures, tourmaline and antigorite have the lowest associated He$_{\text{HC-ring norm.}}$, $\sim1\times10^{-6}$ mol mol$^{-1}$ bar$^{-1}$, suggesting He has the weakest affinity for this general topology.

3.2.3.2. Amphibole (actinolite) He$_{\text{HC-ring norm.}}$

The ring structure in amphibole is constituted by an opposing pair of rings that are offset by distorted polyhedra of Ca and Na ions. Octahedral polyhedra border the pair of
rings, both above and below. The ring structure in amphibole is commonly occupied by Na, and to a lesser degree, K. He$_{\text{HC-ring norm}}$ for both amphiboles is $\sim 1 \times 10^{-5}$ mol mol$^{-1}$ bar$^{-1}$, suggesting He favors the amphibole ring structure topology compared to the topology present in antigorite and tourmaline.

3.2.3.3. Beryl and Cordierite He$_{\text{HC-ring norm}}$

Beryl and high-cordierite are isomorphous, hexagonal minerals, but under most geologic conditions cordierite reverts to its low, orthorhombic form. The orthorhombic transition causes a small distortion to the ring in cordierite compared to beryl (see Figure 1c and 1d). Nonetheless, beryl and low-cordierite share a similar ring structure topology. The tetrahedra that comprise the rings in beryl and cordierite are oriented such that no apex is pointed normal the ring plane, and the rings are stacked continuously along the c-axis, forming “ring channels.” A larger ring of tetrahedral and octahedral cations is positioned between the purely tetrahedral rings. The alternating channel structure creates two distinct environments: a larger radius interstice in the plane of the tetrahedral-octahedral ring and smaller radius interstice in the plane of the tetrahedral ring. Both locations have been shown to host large radius species such as alkali cations, Ar, and H$_2$O (Smith and Schreyer, 1962; Goldman et al., 1977). The present experiments on beryl and cordierite confirm that channel structures are also capable of hosting smaller radii noble gases. Indeed, He$_{\text{HC-ring norm}}$ determined for beryl and cordierite is exceptionally high compared to other ring structure topologies: $\sim 5 \times 10^{-5}$ mol mol$^{-1}$ bar$^{-1}$ (Figure 5). This suggests He has the strongest affinity for the topology of ring structures.
in beryl and cordierite compared to the other topologies considered here. Additional work is needed, however, to determine if the distribution of noble gases between the different ring environments in cordierite and beryl.

3.2.4. He-Ne-Ar Solubility Patterns

Figure 6 plots determinations of $\text{He}_{\text{HC}}$, $\text{Ne}_{\text{HC}}$, and $\text{Ar}_{\text{HC}}$ for experiments where He-Ne-Ar solubility data were collected. Extrapolated Henry’s constants were calculated by dividing the measured Henry’s constant by the fraction of unoccupied ring structures. Ne and Ar data are normalized to $f_{\text{Ne}}$ and $f_{\text{Ar}}$, respectively, for comparison purposes, but explicit demonstrations of Henry’s Law applicability have not been made for these data.

To a first order, $\text{Ne}_{\text{HC}}$ and $\text{Ar}_{\text{HC}}$ measurements are similar to $\text{He}_{\text{HC}}$ measurements made on the same material: $\text{He}_{\text{HC}}$, $\text{Ne}_{\text{HC}}$, and $\text{Ar}_{\text{HC}}$ are high for beryl and cordierite, intermediate for amphibole, and low for antigorite. However, distinctive $\text{He}_{\text{HC}}$-$\text{Ne}_{\text{HC}}$-$\text{Ar}_{\text{HC}}$ patterns are present in minerals that correlate with the different classes of ring structures. Beryl and cordierite display a chevron $\text{He}_{\text{HC}}$-$\text{Ne}_{\text{HC}}$-$\text{Ar}_{\text{HC}}$ pattern, where $\text{He}_{\text{HC}}$ and $\text{Ar}_{\text{HC}}$ are lower than $\text{Ne}_{\text{HC}}$. The $\sim3\times$ difference between $\text{He}_{\text{HC}}$ for beryl and cordierite (Figure 5) remains similar for $\text{Ne}_{\text{HC}}$ and expands for $\text{Ar}_{\text{HC}}$. Both amphiboles have negatively sloped $\text{He}_{\text{HC}}$-$\text{Ne}_{\text{HC}}$-$\text{Ar}_{\text{HC}}$ patterns, although $\text{He}_{\text{HC}}$-$\text{Ne}_{\text{HC}}$-$\text{Ar}_{\text{HC}}$ measurements on pargasite #2 show a more moderate slope compared to actinolite #2. These noble gas solubility measurements in amphibole are consistent with those reported by Jackson et al. (2013a). Antigorite displays an inverted chevron $\text{He}_{\text{HC}}$-$\text{Ne}_{\text{HC}}$-$\text{Ar}_{\text{HC}}$ pattern, opposite to the pattern observed for beryl and cordierite. The slope between $\text{He}_{\text{HC}}$ and $\text{Ne}_{\text{HC}}$ for
antigorite is negative and steep compared to that observed for amphibole. There appears
435 to be a reversal in slope between Ne\textsubscript{HC} and Ar\textsubscript{HC}, but considerable variability is present in
436 both the Ne and Ar data for antigorite (Figure 6). Because of this variability, we do not
437 interpret the Ne\textsubscript{HC} and Ar\textsubscript{HC} data as simply being reflective of solubility in pure
438 antigorite. The source for this variability is not immediately clear, as He\textsubscript{HC} data are
439 highly reproducible. Possible root causes for this variability are explored below.
440
441 3.2.5. Ne\textsubscript{HC} and Ar\textsubscript{HC} Variability in Antigorite
442
443 The antigorite studied here is not a mono-mineralic sample. This contrasts with
444 the other materials used here for He, Ne and Ar solubility determinations. Transmitted
445 light images of a representative antigorite sample are provided in Figure 2. Multiple
446 secondary phases are present. The most visually obvious secondary phase is magnetite,
447 identified as opaque, black masses. Magnetite is mostly present as macro-scale
448 inclusions. Micro-scale magnetite inclusions are also distributed throughout the sample.
449 A separate secondary phase is also present throughout the antigorite. The nature of this
450 separate secondary phase is more difficult to determine given its very fine scale, but on
451 the sample-scale this phase causes a cloudy appearance and is heterogeneously
452 distributed (Figure 2a and 2b). The experimental antigorite samples were taken from the
453 more translucent sections of the starting material, similar to material on the left side of
454 Figure 2a, limiting the net effect of the clouding phase. However, the clouding phase is
455 present throughout the antigorite and has the potential to affect the abundances of noble
456 gases concentrated in the antigorite material.
Figure 7 correlates individual measurements of He$_{HC}$ and Ne$_{HC}$ against Ar$_{HC}$ in antigorite where a He-Ne-Ar pressure medium was used (experiments CS_NG_21, 22, and 25). He$_{HC}$ measurements are repeatable, clustering near 1.5x10^{-9} mol g^{-1} bar^{-1}. Simultaneous measurements of Ar$_{HC}$ are scattered in excess of analytical precision, ranging between 4x10^{-10} and 4x10^{-9} mol g^{-1} bar^{-1} (Figure 7a). Similarly, simultaneous measurements of Ne$_{HC}$ and Ar$_{HC}$ are correlated, with a slope of 0.12±0.03 1σ (Figure 7b), neglecting two data points with strongly negative Ne$_{HC}$. The fact that Ar$_{HC}$ variability is not correlated with He$_{HC}$ variability, yet correlated with Ne$_{HC}$, suggests that a secondary, noble gas-rich phase was variably included in the analyses of antigorite samples. Given the relationships present in Figure 7, it appears this secondary phase prefers Ar, and to a lesser extent Ne, compared to He.

Micro-scale inclusions of magnetite and a fine-scale “clouding” phase are present throughout the sample, and these materials have likely been variably incorporated into the analyzed antigorite. The edge of a macro-scale magnetite inclusion was intentionally incorporated into the final analysis of the antigorite sample from experiment CS_NG_EXP30 (noted in Supplementary Table 1). A He-only pressure medium was used in CS_NG_EXP30, so the combined He-Ne-Ar effect of magnetite inclusions remains uncertain. However, the concentration of He in the final analysis was 2.1 ± 0.3x10^{-6} mol g^{-1}, which is high compared to the average of the other antigorite analyses in CS_NG_EXP30 (1.49 ± 0.03x10^{-6} mol g^{-1}). From this single comparison it appears that magnetite inclusions or magnetite-antigorite grain boundaries are potentially noble gas-rich materials. More work is needed to confirm this result and extend the analysis to Ne.
and Ar. The effect of the clouding secondary phases has not been isolated, and thus, it also remains a potential source for the observed variability in Ne and Ar.

The general preference of the gas-rich secondary phase for heavy noble gases is consistent the properties of aqueous fluids, i.e. fluid inclusions. However, between 75°C and the critical point (374°C), Ar is approximately twice as soluble as Ne in water (Potter and Clynne, 1978; Crovetto et al., 1982), and dissolved salts are expected to make Ar and Ne solubility converge (Smith and Kennedy, 1983). Given the relatively moderate slope of the Ne_{HC}-Ar_{HC} correlation (0.12 ± 0.03 1σ, Figure 7b), aqueous fluid inclusions alone do not appear to be the source of Ne and Ar variability.

Regardless of the source of Ne and Ar variability, several inferences can be drawn for the solubility of noble gases in pure antigorite (antigorite in the absence of gas-rich secondary phases). Ne_{HC} is ~10× lower than He_{HC}, despite the skew of Ne to higher concentrations. Several analyses of Ne_{HC} are within error of or below zero, suggesting He_{HC} in pure antigorite is > 10× greater than Ne_{HC}. Many simultaneous analyses of Ar_{HC} and He_{HC} have Ar_{HC}/He_{HC} ratios less than unity, suggesting He_{HC}>Ar_{HC} in pure antigorite. Moreover, Ar_{HC} analyses of antigorite from EHPV_NG_EXP53 and CS_NG_EXP18 are either within error of zero or low compared to the remainder of Ar_{HC} analyses (Table 2). Applying the axiom that the highest Ar_{HC} determinations reflect the strongest contribution from gas-rich secondary phases, the low Ar_{HC} analyses also imply a low value of Ar_{HC} and a low Ar_{HC}/He_{HC} ratio for pure antigorite. However, we do not adopt the low determinations of Ar_{HC} from EHPV_NG_EXP53 and CS_NG_EXP18 as being necessarily representative of pure antigorite. Both EHPV_NG_EXP53 and CS_NG_EXP18 were run simultaneously and shared a pressure medium. Moreover,
EHPV_NG_EXP53 and CS_NG_EXP18 were the only two experiments that had a methane + Ar pressure medium. Correlated experimental factors may have contributed to the low Ar\textsubscript{HCl} measurements on EHPV_NG_EXP53 and CS_NG_EXP18. With the current data, it is impossible to completely deconvolve the competing effects of gas-rich secondary phases, pure antigorite, and systematic experimental factors in interpreting the concentrations of noble gases analyzed in antigorite. Nonetheless, it appears that in bulk antigorite, ring structures compete with secondary phases to determine bulk noble gas solubility. The relatively low noble gas solubility associated with ring structures in antigorite makes the bulk noble gas solubility in serpentinites more easily influenced by other factors.

4.0. Implications for Noble Gas Recycling

4.1 Effect of Noble Gas Solubility in Unoccupied Ring Structure-Bearing Minerals

Atmospheric noble gases are introduced into slab materials during hydrothermal alteration (Staudacher and Allègre, 1988, Kumagai et al., 2003; Moreira et al., 2003; Kendrick et al., 2011; Kendrick et al., 2013). Seawater is the ultimate source of hydrothermal fluids and, thus, it is expected that noble gases are initially introduced into the slab in elemental proportions equal to those found in seawater (Holland and Ballentine, 2006). The noble gas isotopic signature of seawater is identical to the atmosphere but is elementally enriched in heavier noble gases compared to the
atmosphere following noble gas solubility in saline water at surface temperatures (Potter and Clynne, 1978; Crovetto et al., 1982). If no fractionations occur during noble gas uptake and devolatilization of the slab, then noble gases should be recycled in seawater-like elemental proportions with atmospheric isotopic signatures. Note, helium is not retained in Earth’s atmosphere, and so, in comparison to other noble gases, helium in the mantle is much less susceptible to overprinting by atmospheric signatures.

Measurements of mantle-derived Ne indicate that less than 30% of non-nucleogenic Ne in the mantle is recycled (Moreira et al., 1998; Yokochi and Marty, 2004; Ballentine et al., 2005; Mukhopadhyay, 2012). In contrast, measurements of mantle-derived Xe indicate that ~85% of Xe in the mantle is recycled (Holland and Ballentine, 2006; Mukhopadhyay, 2012; Tucker et al., 2012; Petö et al., 2013). Using modern noble gas elemental concentrations for the mantle and seawater (Holland and Ballentine, 2006), these measurements suggest that the Ne/Xe ratio associated with the flux of recycled noble gases is either close to that of seawater or favors preferential recycling of heavier noble gases. Elemental abundance measurements of noble gases derived from the mantle have also been argued to reflect preferential recycling of heavier noble gases compared to their proportions in seawater (Holland and Ballentine, 2006). Thus, current observations suggest the recycling flux is not enriched in the light noble gases.

We have demonstrated that noble gases have a relatively strong affinity for unoccupied ring structures and that ring structure topology has a secondary influence on the He-Ne-Ar solubility pattern in minerals. However, none of the ring structure topologies studied here have a clear preference for larger radii, heavier noble gases (Figure 6 and 7). The minerals that are most relevant to noble gas recycling, antigorite in
its pure form and amphibole, appear to favor He compared heavier noble gases. Simple extrapolation of amphibole and pure antigorite He-Ne-Ar solubility patterns to heavier noble gases suggests that these minerals would preferentially facilitate the recycling of lighter noble gases, opposite to the inferred pattern for noble gas recycling. Other minerals with unoccupied ring structures are formed during hydrothermal alteration of slab materials, including talc, chlorite, clays, and the lower temperature polymorphs of antigorite, chrysotile and lizardite. All of these minerals may contribute significantly to the flux of recycled noble gases. However, these minerals are all phyllosilicates, and thus, share a ring structure topology similar to antigorite. Correspondingly, these minerals do not offer an obvious balance to the preference of amphibole and antigorite for light noble gases.

If the solubility of He-Ne-Ar in unoccupied ring structures influences the pattern of recycled noble gases, then other factors appear to be required to maintain a recycling flux of that is not elementally enriched in lighter noble gases. Other factors may include elemental fractionations associated with diffusion kinetics associated with loss of noble gases from slab minerals, adsorption at low temperatures, interactions with fluids enriched in heavier noble gases, closed system incorporation of seawater noble gases, or a balancing flux of materials that have a preference for heavier noble gases.

It is also worth stressing that the majority of ring site-bearing minerals are not stable to pressures sufficient to transport noble gases past depths associated with the generations of arc magmas. The complete recycling of noble gases appears to require the retention of noble gases in down-going materials despite the production of fluids due to the breakdown of volatile-bearing minerals and the transport of fluids into the overlying
mantle wedge. The transport of noble gas-bearing fluids out of the slab will reduce the overall efficiency of noble gas recycling and has the potential to further elementally fractionate the noble gases that are ultimately destined for recycling. The elemental fractionations associated with the loss of fluids from down-going materials will be modulated by the solubility and diffusivity of noble gases in the materials that interact with the migrating fluid.

4.2 He-Ne-Ar Behavior in Bulk Antigorite

We have focused on determining He-Ne-Ar solubility in pure minerals in order to understand the mineral lattice controls on noble gas recycling. However, recycled lithologies are an aggregate of minerals, grain boundaries, and fluid inclusions. It is the combined affinity of these materials for noble gases that act to determine the concentration of noble gases in a lithology following hydrothermal alteration, provided hydrothermal alteration occurs as an open system. The antigorite studied here is multiphase and contains many grain boundaries, making it a more complete analog of recycled serpentinite. When considered as a bulk system, and not a pure phase, antigorite has a strong affinity for Ar and for Ar compared to Ne. Measurements of $\text{Ar}_{\text{HC-ring norm.}}$ in antigorite are uniformly greater than $\text{Ne}_{\text{HC-ring norm.}}$ and commonly surpass $\text{He}_{\text{HC-ring norm.}}$ (Figure 7). These measurements suggest that serpentinites may act to preferentially incorporate Ar compared to Ne during their equilibration with hydrothermal fluids and that serpentinites may have a strong affinity for noble gases in general.
There is corroborating evidence for this behavior of Ne and Ar in natural serpentinites. Measurements of antigorite schists (serpentinites) that are inferred to be exhumed slab materials indicate that serpentinite can host high concentrations of seawater-derived noble gases, with \(^{36}\)Ar abundances in serpentinite reaching \(\sim 100 \times\) the abundance of \(^{36}\)Ar in the depleted mantle (Kendrick et al. 2011, Kendrick et al., 2013). Measured Ne/Ar ratios in slab serpentine are typically \(\sim 2 \times\) lower than seawater values, although considerable scatter is observed. This fractionation of Ne from Ar is consistent with our measurements of Ne\(_{HC}\) and Ar\(_{HC}\) in bulk antigorite. Previous experimental work defining noble gas solubility in bulk serpentine also supports Ne being less soluble compared to Ar (Zaikowski and Schaeffer, 1979). Combined, these results are consistent with the solubility of noble gases in materials affecting the elemental patterns of noble gases associated with hydrothermally altered lithologies.

Another important observation regarding the behavior of He-Ne-Ar in bulk antigorite is the rate of equilibration of between the pressure medium and the antigorite specimen. The kinetics of equilibration between bulk antigorite and the pressure medium have not been directly quantified here, but limits can be evaluated. Experiments on antigorite were conducted at temperatures \(\leq 450^\circ\)C, which are low compared to the remainder of experiments presented here. Despite the low temperatures, He\(_{HC}\), Ne\(_{HC}\), and Ar\(_{HC}\) do not correlate with ablation pit depth, indicating that these gases equilibrated with the antigorite to at least a depth of 33 \(\mu\)m over the experimental durations and that noble gas losses from bulk antigorite prior to analysis were small (Supplementary Table 2). This rate of equilibration is extremely rapid compared to the other materials investigated here, particularly for Ar. For example, Ar diffusion profiles in both
amphiboles analyzed extended <1 μm deep after 161 hours at 900 °C (Supplementary Information). The rapid nature of noble gas uptake is consistent with observed degassing behaviors of serpentinites during step-degassing noble gas analysis, i.e. heating of 20-40 mg chips of serpentinite at 300°C for 20 minutes typically extracts >20% of total $^{36}$Ar from the sample (Kendrick et al, 2013). It is likely that grain boundaries and the relatively open sheet structures facilitate rapid diffusion of noble gases through serpentinites. Consequently, an equilibrium distribution of noble gases between serpentinite and hydrothermal fluids should be closely approached in natural systems, even at the relatively low temperature associated with serpentine stability. It is also worth noting that He, Ne, and Ar concentrations do not decrease with decreasing pit depth in the experimental antigorite samples, indicating loss of noble gases prior to analysis in the present experiments is negligible. Further experiments are needed to confirm these rapid noble gas diffusion rates, but these preliminary observations suggest that noble gases subducted by serpentinites will be particularly vulnerable to extraction by migrating slab fluids.

4.3 Deep Recycling of Noble Gases and Alternative Recycling Environments

Helium solubility in mica (muscovite and F-phlogopite) is lower than other minerals with high concentrations of unoccupied ring structures (Figure 4). Interlayer cation deficiencies are ubiquitous in micas, which manifest as unoccupied ring structures, but are present in minor concentrations (<15 % of K site, Table 1, Rieder et al., 1999). The high occupancy of ring structures in micas suggests other locations may
accommodate a large component of dissolved noble gases. Dioctahedral micas, such as muscovite, contain abundant unoccupied interstices in their octahedral sheets. These interstices provide additional porosity that is not available in trioctahedral micas, such as F-phlogopite. The similar values of He$_{\text{HC}}$ measured for muscovite and F-phlogopite, however, argue for the octahedral sheets being only minor hosts for He and, by extension, other noble gases in mica. This result is also supported by the similarity of He solubility measurements in pyroxene, olivine, and spinel with variable concentrations of Mg-site vacancies (Heber et al., 2007; Jackson et al., 2013b). The small solubility associated with octahedral vacancies suggests that noble gases are hosted in the mica interlayer, either interstitially or in unoccupied ring structures. The strong diffusional anisotropy inferred for micas (Section 3.2.1) also supports the argument that the octahedral sheets are relatively high-energy locations for noble gases.

Micas, such as phengite, are stable to high pressures and temperatures compared to the majority of hydrous minerals in slabs. Consequently, mica is capable of sequestering and transporting water deep in subduction zones (Schmidt and Poli, 1998; Hacker et al., 2008). Measurements of He$_{\text{HC}}$ in muscovite and F-phlogopite are similar to each other and ~100× higher compared to mantle minerals, such as olivine (Jackson et al., 2013b), which suggests that mica could be an important host for noble gases deeper in subduction zones, particularly for slabs where serpentine stability is restricted.

Mica and amphibole are also stable in the metasomatized, lithospheric mantle (e.g. Pilet et al., 2008; Green et al., 2010) and hydrated sections of lower continental crust (e.g. Rapp and Watson, 1995, Liu et al., 1996). Both the lower crust and lithospheric mantle can become sufficiently dense that they are delaminated and returned to the
convecting mantle (e.g. Bird, 1979, Ducea and Saleeby, 1996; Davidson et al., 2008, Jagoutz and Behn, 2013). Depending on physics of delamination, these recycled lithologies can retain significant amounts of their initial volatiles upon recycling (Elkins-Tanton, 2007). If enriched in mica and amphibole, these lithologies may also provide alternative environments for noble gas recycling. The noble gases hosted in these delaminated lithologies can be either dominated by mantle noble gases or atmospheric noble gases depending on the ultimate origin for the metasomatic fluid.

5.0 Conclusions

We have experimentally determined the solubility of noble gases in a series of materials that are broadly applicable to noble gas recycling in subduction zones. For pure minerals, the availability and topology of unoccupied ring structures has a strong control on the solubility of He. Distinctive He\textsubscript{HC}-Ne\textsubscript{HC}-Ar\textsubscript{HC} patterns for pure minerals have also been identified. These patterns correlate with ring structure topology and do not appear to favor dissolution of heavier noble gases. Secondary phases, such as those present in antigorite, have the potential to concentrate noble gases, and thus, affect the solubility of noble gases in bulk materials. This is especially true for antigorite because He, Ne, and Ar appear relatively insoluble the pure mineral. In contrast to ring structures, secondary phases may favor the uptake of heavier noble gases, and the variable presence secondary phases may contribute to local elemental fractionations and concentration variations in natural systems. In this context, secondary phases may be important in contributors to the transport and elemental fractionations of noble gases into and through subduction
zones, particularly in the ultramafic sections of slabs. Micas, and other ring structure-bearing minerals that are stable to high pressure, have the potential to transport noble gases past mantle wedge depths associated with arc magma genesis.

Figure Captions:

Figure 1: Different geometries of six-member, tetrahedral ring structures. A) Regular hexagon with apexes pointed normal to the plane of the ring. B) Distorted hexagon with apexes pointed normal to the plane of the ring. This geometry is similar to that found in tourmaline. C) Regular hexagon with apexes pointed oblique to the plane of the ring. This geometry is similar to that found in beryl and high-cordierite. D) Distorted hexagon with apxes pointed oblique to plane. This geometry is similar to that found in low-cordierite, which is the common form for geological samples.

Figure 2: Images of representative antigorite material. A) Large scale transmitted light micrograph. Note the presence of macro- and micro-scale inclusions of magnetite as well as a “clouding” phase that is concentrated on the right side of the image. The gap in material on the left is a partial cut of the antigorite using the wafering blades. B) Small scale transmitted light micrograph. Image is taken from boxed region in A).

Figure 3: He$_{HC}$ measurements versus ablation pit depth. Each data point is an individual measurement of He concentration normalized to $f_{He}$ for the experiment. Error bars are 1σ and include analytical and pit volume determination uncertainties. Data for beryl,
cordierite, antigorite, actinolite #2, pargasite #2, and tourmaline are plotted in A). Data for muscovite and F-phlogopite are plotted in B). Note the change in axis scales between A) and B). No correlations are observed between He$_{\text{HC}}$ and pit depth excepting shallow measurements on beryl, pargasite #2, and tourmaline (A) and some experiments on micas (B). Data points not used for solubility determinations for a given phase are plotted as open symbols with the corresponding shape and color outline.

Figure 4: He$_{\text{HC}}$ determinations for an experiment versus experimental A) duration, B) $f_{\text{He}}$, and C) temperature. He$_{\text{HC}}$ values are determined by either averaging individual measurements of He$_{\text{HC}}$ in an experiment or fitting diffusion profiles to individual measurements He$_{\text{HC}}$ in an experiment. Error bars are 1σ and are calculated as standard deviations of the mean or from diffusion profile fits. He$_{\text{HC}}$ is not correlated with experimental duration, $f_{\text{He}}$, or temperature for all materials investigated.

Figure 5: He$_{\text{HC}}$-ring norm. determinations for each material type plotted in ascending order, left to right. He$_{\text{HC}}$-ring norm. values are determined by either averaging individual measurements of He$_{\text{HC}}$ in an experiment or fitting diffusion profiles to individual measurements He$_{\text{HC}}$ in an experiment. The cation polyhedra local to the ring structures (ring structure topology) in each mineral are provided along the x-axis below the respective He$_{\text{HC}}$-ring norm. data. There is a broad correlation between the topology local to ring structures and He$_{\text{HC}}$-ring norm.
Figure 6: \( \text{He}_{\text{HC}}-\text{Ne}_{\text{HC}}-\text{Ar}_{\text{HC}} \) determinations for materials where \( \text{He}-\text{Ne}-\text{Ar} \) data were collected. \( \text{He}_{\text{HC}}-\text{Ne}_{\text{HC}}-\text{Ar}_{\text{HC}} \) values are determined by averaging individual measurement in an experiment. Distinctive patterns present for material types: beryl and cordierite display a chevron \( \text{He}_{\text{HC}}-\text{Ne}_{\text{HC}}-\text{Ar}_{\text{HC}} \) pattern, amphibole displays a negative slope between \( \text{He}_{\text{HC}} \) and \( \text{Ar}_{\text{HC}} \), and antigorite displays an inverted chevron \( \text{He}_{\text{HC}}-\text{Ne}_{\text{HC}}-\text{Ar}_{\text{HC}} \) pattern, although considerable variability is present in \( \text{Ne}_{\text{HC}} \) and \( \text{Ar}_{\text{HC}} \) determinations for antigorite.

Figure 7: Simultaneous measurements of A) \( \text{He}_{\text{HC}} \) and \( \text{Ar}_{\text{HC}} \) and B) \( \text{Ne}_{\text{HC}} \) and \( \text{Ar}_{\text{HC}} \) in antigorite. Each data point is an individual measurement of antigorite. Error bars are 1σ and include analytical and pit volume determination uncertainties. A) \( \text{He}_{\text{HC}} \) measurements are repeatable, but \( \text{Ar}_{\text{HC}} \) measurements are highly variable. B) \( \text{Ar}_{\text{HC}} \) variability is correlated with \( \text{Ne}_{\text{HC}} \), suggesting \( \text{Ar}_{\text{HC}} \) and \( \text{Ne}_{\text{HC}} \) variability are controlled by the same factor. Two data points from CS_NG_21, 22, and 25 are not included in the regression of Figure 7 because the \( \text{Ne}_{\text{HC}} \) measurements are anomalously negative.

Acknowledgements: We thank Joe Bosenburg for his assistance with the electron microprobe measurements and Michael Chon for his assistance with the pit volume measurements. Reviews by Hirochika Sumino, Rita Parai, and an anonymous reviewer all helped to improve this manuscript. Editorial handling by Pete Burnard was top-notch.

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Figure 1
Figure 2:

a) macro-scale magnetite

b) micro-scale magnetite
Figure 3:
Figure 4:
Figure 5:
Figure 6:

He-Ne-Ar, $h/c$ (mol g$^{-1}$ bar$^{-1}$)

- Beryl
- Cordierite
- Tourmaline
- Antigorite
- Actinolite #2
- Pargasite #2
Figure 7:

![Graph showing data points with error bars for HeHC, NeHC, and ArHC mol g^-1 bar^-1 against ArHC mol g^-1 bar^-1.

Ne/Ar slope: 0.12±0.015, r^2 = 0.46]
Supplementary Information for “Light noble gas dissolution into ring structure-bearing materials and lattice influences on noble gas recycling”

1.0 He solubility calculations for muscovite and F-phlogopite

Supplementary Figure 1 displays He concentrations profiles observed in mica fit with diffusion profiles. Profiles are calculated based on tracer diffusion from a reservoir of constant chemical potential into a semi-infinite medium. Solid curves are the depth-averaged model, where the He concentration at each depth is the average He concentration from that depth to the surface. Dashed curves are the corresponding modeled concentrations at each discrete depth. Error bars on data points are 1σ and include analytical and pit volume determination uncertainties. He solubility calculated as fit surface concentration.

2.0 Ne and Ar solubility calculations for beryl and cordierite

Supplementary Figure 2 displays Ne/He and Ar/He measurements in beryl and cordierite as a function of depth. Neon solubility in beryl and cordierite is calculated as the product of the measured Ne/He ratio and the measured solubility of He. We use this approach because many of the ablation pits on beryl and cordierite where Ne was present are extremely shallow. Consequently, the volume of these shallow pits is highly uncertain and likely biased to lower values, leading to systematically higher concentrations. This approach is valid for Ne because there is no correlation between Ne/He and pit depth for either beryl or cordierite (Supplementary Figure 2). Argon concentrations, however, must be determined using an approach similar to that taken for He in mica because Ar/He
measurements are not constant with depth (Supplementary Figure 2). We fit these data using a diffusion model, and Ar solubility is calculated as the product of the modeled surface Ar/He ratio and the measured He solubility. Error bars for Ne/He and Ar/He ratios in Supplementary Figure 2 are 1 σ and only include the propagated the analytical uncertainties. Volume uncertainties are not factored into elemental ratios. The uncertainties reported for Ne and Ar solubility are include the uncertainty on the elemental solubility ratio and the uncertainty on He solubility, propagated independently. It is assumed that He is evenly distributed with depth in beryl and cordierite, and following this, the diffusivity required to fit the Ar/He depth profiles is taken as the diffusivity of Ar.

3.0 Ne and Ar solubility calculations for amphibole

Supplementary Figure 3 displays Ne/He and Ar/He measurements in the two amphiboles investigated (actinolite #2 and pargasite #2) as a function of depth. Surface Ne/He and Ar/He ratios are calculated using the same diffusion model applied to experiments on muscovite, F-phlogopite, cordierite, and beryl. The diffusion model results are also plotted in Supplementary Figure 3. Error bars for Ne/He and Ar/He ratios in Supplementary Figure 2 are 1 σ and only include the propagated the analytical uncertainties. Volume uncertainties are not factored into elemental ratios. Neon and Ar solubility in amphibole are calculated using the same approach applied to calculate Ar solubility in cordierite: the surface ratio fit by the diffusion model, Ne/He or Ar/He, is multiplied by the solubility of He, as determined by deeper pits. The uncertainties reported for Ne and Ar solubility are include the uncertainty on the elemental solubility ratio and the uncertainty on He solubility, propagated independently. It is assumed that
He is evenly distributed with depth in both actinolite #2 and pargasite #2, and following this, the diffusivity required to fit the Ne/He and Ar/He depth profiles is taken as the diffusivity of Ne and Ar, respectively.

4.0 SEM images of antigorite

Supplementary Figure 4 displays two series of SEM BSE images from the antigorite material. The antigorite material was prepared following the same techniques used to prepare the experimental starting materials. The first series (left column) shows an area centered in the region of the sample that has a higher concentration of the “clouding” material (see lower-left image for location of series), and images are ordered from lowest magnification at the top to highest magnification at the bottom. Micron scale pitting is observed throughout the sample and appears concentrated in certain regions. The second series shows an area centered in the region on the sample that has a lower concentration of “clouding” material. Pitting is still observed, although pits appear more evenly distributed. Several grains of micron-scale magnetite were identified throughout the sample as well, and their composition was confirmed by EDS analysis to be nearly pure iron oxide (not shown). The mode of micron-scale magnetite <<1 %, but greater amounts of magnetite may form during the experiments due to hydrogen loss.
Supplementary Figure 1: He in mica
Supplementary Figure 2: Ne and Ar in beryl and cordierite
Supplementary Figure 3:
Ne and Ar in amphibole
Supplementary Figure 4: SEM-BSE images of antigorite

1. micro-scale magnetite
2. macro-scale magnetite