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

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

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8
9 Abstract: Light noble gas (He-Ne-Ar) solubility has been experimentally determined in a
10 range of materials with six-member, tetrahedral ring structures: beryl, cordierite,
11 tourmaline, antigorite, muscovite, F-phlogopite, actinolite, and pargasite. Helium
12 solubility in these materials is relatively high, 4×10^{-10} - 3×10^{-7} mol g⁻¹ bar⁻¹, which is ~100
13 to 100,000× greater than He solubility in olivine, pyroxene, or spinel. Helium solubility
14 broadly correlates with the topology of ring structures within different minerals.
15 Distinctive He-Ne-Ar solubility patterns are associated with the different ring structure
16 topologies. Combined, these observations suggest ring structures have a strong influence
17 on noble gas solubility in materials and could facilitate the recycling of noble gases into
18 the mantle. Measurements of Ne and Ar solubility in antigorite, however, are highly
19 variable and correlated with each other, suggesting multiple factors contribute the
20 solubility of noble gases in serpentine-rich materials.

21
22 1.0 Introduction

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

36 The model of an efficient barrier to noble gas recycling has since been challenged
37 by a diverse set of observations. Measurements of hydrated mantle sections of exhumed
38 slabs (serpentinites) demonstrate deeper, and harder to devolatilize, horizons of the slab
39 are capable of hosting large quantities of seawater-derived noble gases (Kendrick et al.,
40 2011, Kendrick et al., 2013). Peridotitic rocks exhumed from the mantle wedge contain
41 noble gases with elemental ratios most consistent with a seawater origin (Sumino et al.,
42 2010). Samples of metasomatized subcontinental lithospheric mantle also show evidence
43 for atmospheric Ar-rich fluids (Nagao and Takahashi, 1993; Matsumoto et al., 2001;
44 Matsumoto et al., 2002; Yamamoto et al., 2004; Gautheron et al., 2005; Kim et al., 2005;
45 Matsumoto et al. 2005; Hopp and Ionov, 2011). Measurements of Xe isotopes derived
46 from both ridge and plume environments indicate the coexistence of atmospheric and

47 primordial Xe components in their mantle source, and the atmospheric component is
48 associated with noble gas recycling (Mukhopadhyay, 2012; Parai et al., 2012; Tucker et
49 al., 2012, Petö et al., 2013). Measurements of Kr and Xe from well gases that contain
50 mantle-derived volatiles also provide evidence for the coexistence of atmospheric and
51 primordial noble gases in the mantle (Caffee et al., 1999, Holland and Ballentine, 2006,
52 Holland et al., 2009). Thus, many lines of evidence suggest that large volumes of the
53 mantle have interacted with the noble gases from Earth's atmosphere, yet the recycling
54 process is sufficiently inefficient that very early-forming mantle-atmosphere
55 heterogeneities persist to the present day.

56   Despite the mounting evidence for the large scale recycling, the responsible
57 carrier phases remain poorly understood. Here, we seek to understand the materials and
58 mechanisms that are capable of transporting noble gases, and by extension, volatiles in
59 general, into and through subduction zones. We specifically focus on exploring the role
60 noble gas solubility in ring structure-bearing minerals, a common class of minerals in
61 hydrothermally altered slab lithologies that includes amphibole, serpentine, talc, clays,
62 mica, and chlorite. Ring structures are constituted by six $(\text{Si,Al})\text{O}_4^{-4,-5}$ tetrahedral units
63 bound in a hexagonal pattern (Figure 1). They are large radius structures in mineral
64 lattices and are commonly unoccupied. Noble gases are large radius, neutrally charged
65 elements. Following lattice strain theory (e.g. Wood and Blundy, 1997), unoccupied ring
66 structures are predicted to be energetically favorable locations for noble gas dissolution in
67 minerals (Damon and Kulp, 1958). Experiments corroborate this prediction (Smith and
68 Schreyer, 1962; Wartho et al., 2005; Jackson et al., 2013a), suggesting minerals with ring

69 structures are capable of the transporting significant quantities of noble gases in
70 subduction zones.

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

77

78 2.0 Methods

79

80 2.1 Starting Materials

81

82 Large specimens of beryl, cordierite, tourmaline, antigorite, muscovite, F-
83 phlogopite, actinolite, and pargasite materials were used as the starting materials in the
84 experiments. Major element compositions are given in Table 1. All specimens are
85 natural materials except the F-phlogopite. Bulk materials of beryl, cordierite, tourmaline,
86 antigorite, and pargasite were sectioned into sizes appropriate for the experiments,
87 approximately $2 \times 2 \times 1$ mm, using a low speed saw and diamond encrusted wafering
88 blade. The large volume of the run products allows for repeated, high-precision
89 measurements of noble gas contents in a particular material. No attempt was made to
90 crystallographically orient samples during sectioning. A single face of each sectioned
91 material was mechanically polished, finishing with 0.05 μm alumina grit. Each

92 mechanically polished face was then chemically polished using colloidal silica for >3
93 hours. Starting materials were not annealed prior to the experiment. This preparation is
94 designed to minimize any lattice damage induced by the cutting and mechanical polishing
95 procedure. Muscovite starting materials were purchased (SPI Supplies, V-1 grade) as cut
96 and cleaved ~3 mm diameter discs (~50 μm height) and used as purchased. The F-
97 phlogopite bulk material is synthetic and exists as inter-grown books. Starting materials
98 were prepared by cleaving books from the bulk F-phlogopite sample and cutting the
99 cleaved books into appropriate sizes using a razor blade. Actinolite starting materials
100 were prepared by cleaving laths from a larger specimen. Once prepared, but prior to the
101 experiment, starting materials were mapped for secondary phases using a 120 $\times$
102 stereoscope. All materials, except antigorite, are essentially devoid of observable
103 secondary phases. The antigorite material contains both macro- and micro-scale
104 magnetite as well as a separate fine-scale secondary phase (Figure 2). Macro-scale
105 magnetite was avoided during analysis, but micro-scale and the fine-scale secondary
106 phase were variably incorporated into the analyses of antigorite.

107

108 2.2 Noble Gas Solubility Experiments

109

110 Each experiment consists of three samples loaded into separate graphite capsules.
111 The capsules were machined so that all three samples were contained within the hotspot,
112 as determined by the temperature calibration of the pressure vessel assembly. A ~0.1 bar
113 vacuum was drawn on the entire assembly before it was pressurized. The pressure
114 medium was noble gases (He-Ne-Ar) $\pm$ methane for all experiments, allowing for precise

115 and sustained control of noble gas fugacity over the duration of the experiment. Methane
116 was included in some initial experiments to provide a small fugacity of H₂O ($f_{\text{H}_2\text{O}}$) in
117 order to prevent mineral decomposition but was found to be unnecessary and was not
118 used for later experiments. Leakage of the gas pressure medium was <5% over the run
119 duration. Temperatures were controlled by placing the molybdenum-hafnium-carbide
120 alloy pressure vessel into a vertical furnace for EHPV (externally heated pressure vessel)
121 series experiments or a horizontal furnace for CS (cold seal) series experiments.
122 Temperatures ranged from 350 to 900°C and pressures ranged from 0.06 to 1.77 kbar.
123 Convection within the pressure vessel was suppressed using graphite filler rods that
124 extend the length of the pressure vessel above the sample capsules. Experiments were
125 quenched by removing the pressure vessel from the furnace and allowing it to cool
126 against air. The vessel cooled to ~50°C in 20 minutes. At this point, the pressure vessel
127 was rapidly depressurized and unloaded.

128

129 2.3 Analytical Methods

130

131 2.3.1 Major Element Analysis

132

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

138

139 2.3.2 Noble Gas Analysis

140

141 Noble gas concentrations of the experimental run products were determined using
142 a UV laser ablation-noble gas mass spectrometer system at the Open University (UK). A
143 193 nm ArF excimer laser was used to ablate all materials. Three SAES AP-10 getters in
144 the extraction system removed active gases released during ablation before introduction
145 into a MAP215-50 mass spectrometer. ^4He , ^{22}Ne and ^{40}Ar were measured by an electron
146 multiplier in peak hopping mode. The sensitivity of the mass spectrometer was
147 determined by gas pipetting a known volume of noble gases with elemental ratios
148 designed to allow for measurement without separation and atmospheric isotopic ratios
149 into the mass spectrometer. Kelley et al. (1994) provides a more detailed description of
150 the noble gas analytical method.

151 Materials from each experiment were analyzed repeatedly for noble gas contents
152 using a combination of large diameter (40-400 μm) spots and single-line rasters. Pit
153 depths ranged up to $\sim 33 \mu\text{m}$ (average depth of a single pit). Blanks were typically run as
154 every fourth analysis. The blank for each analytical session was calculated as the mean
155 of individual blanks over the duration of that particular session, and the blank standard
156 deviation is calculated as the standard deviation on the blank mean. A session is defined
157 as a single day of analysis on a single port. Systematic changes in blanks were not
158 observed over a session. Blank levels were overwhelmingly dependent upon sample
159 degassing rather than background levels in the extraction system or mass spectrometer as

160 has previously been observed for analysis of He in experimental samples (Heber et al.,
161 2007).

162 No internal standard was available for noble gas analyses. To determine noble
163 gas concentration, we ratio the number of noble gas moles released to the volume of the
164 ablation pit. Pits volumes were measured using a white light interferometer (Zygo
165 Instruments, New View 6000 Series, Brown University). This device provides an image
166 of the ablated surface that requires minimal interpolation of pixels with unknown depth
167 values. A surface continuum is calculated by masking out the ablated area of the
168 interferometer image and interpolating across the masked region. The inpainted
169 interferometer image is subtracted from the surface continuum, isolating the relief
170 associated with the ablation pit. To calculate the pit volume, the individual volumes of
171 pixels are summed assuming rectangular prism geometry for each pixel. Shallow pits,
172 pits ablated into highly curved surfaces, and pits that require longer distances of
173 interpolation have greater uncertainties associated with their volume. We estimate an
174 uncertainty of 15% on volume calculations. Although, as discussed below, this is likely
175 an underestimate for some extremely shallow pits and an overestimate for deeper pits. A
176 small ring of vapor deposition forms along the circumference of the pits, creating a halo
177 of pixels with negative depth. We avoid including these pixels in the volume
178 determination by only summing pixels with positive depths. In general, >100,000 pixels
179 are summed for an ablation pit. Each topographic image contains 307,200 pixels ($480 \times$
180 640).

181 All materials were carbon coated prior to imaging for volume determinations.
182 This significantly improved the return signal, reducing the amount of interpolation

183 required for pit volume determinations. Carbon coat thickness was not measured
184 directly, but based on distance from source and coating time, thickness is estimated at 20
185 nm.

186

187 2.3.2.1 Noble Gas Data Processing

188

189 To convert pit volumes into mass, we apply densities from Deer et al. (1996),
190 accounting for Mg-Fe exchange. The pit depth associated with each analysis is the
191 average depth of pixels summed in the volume calculation. The ablation pits are not
192 perfectly flat bottomed, and thus, pit depth is a spatially averaged value. It should be
193 stressed that noble gas-laser ablation mass spectrometry is a micro-sampling technique
194 that analyzes the bulk contents of noble gases in an ablated volume. Noble gases are not
195 analyzed from a strict depth horizon within the sample. Rather, the concentration of a
196 noble gas in an analysis is a depth-averaged value. Individual measurements of noble gas
197 concentrations in experimental run products are reported in Supplementary Table 1.
198 Uncertainties on the number of moles of He, Ne, and Ar release during an analysis
199 include the standard deviation of the blank for the session in which the analysis occurred
200 and the regression uncertainties associated with extrapolation of the analytical signal to
201 the inlet time. Uncertainties on the reported noble gas concentrations include the
202 propagated uncertainties from the moles determination and the volume uncertainty
203 estimate (15%). All uncertainties are one standard deviation and independently
204 propagated. When no concentration gradient is observed, noble gas solubility is
205 calculated as the average noble gas concentration from an experiment, normalized to the

206 calculated fugacity of that gas. This calculation yields a Henry's constant, abbreviated
207 He_{HC} for He, with units of $\text{mol g}^{-1} \text{bar}^{-1}$.

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

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

222

223 3.0 Results and Discussion

224

225 3.1 Major Element Results

226

227 Major element compositions for all materials investigated are reported in Table 1.
228 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 in antigorite material.

245

3.2. Noble Gas Results

247

3.2.1. Equilibrium Considerations: Depth Correlations

249

Several lines of evidence suggest the measured concentrations of He closely approach equilibrium values. Figure 3 plots all He analyses against the associated

251

252 ablation pit depth. Helium concentrations of individual analyses are normalized to f_{He} of
253 the experiment, yielding an effective Henry's constant for each analysis. This approach
254 is implemented to account for the variability in concentration directly related to changes
255 noble gas fugacity and to allow the effects of other variables (e.g. depth) to be observed
256 in inter-experiment comparisons. This approach is justified here because each
257 investigated phase has been verified to follow Henrian solution behavior for He (Figure
258 4b; Jackson et al., 2013a for amphibole).

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

267 The high He concentrations associated with shallow pits ($<0.33 \mu\text{m}$) are likely
268 artifacts. We argue these high concentrations result from systematic underestimations of
269 the ablation pit volume. Ablation pits with large radius/depth ratios are difficult to
270 measure accurately because small biases in the interpolation of the unablated surface can
271 lead to relatively large errors in volume calculations. The interpolation algorithms used
272 here tend to under-account for surface curvature, which results in systematic
273 underestimates of volume when curvature is concave in the direction of ablation (down).
274 All ablation pits on beryl, cordierite, tourmaline, antigorite, and pargasite #2 were drilled

275 into polished surfaces, and given the polishing techniques utilized here, these surfaces are
276 typically concave down. Shallower pits are more prone to this systematic bias, and
277 consequently, we only consider concentration data for ablation pits that are $>0.33\ \mu\text{m}$
278 deep as reliable. All analyses that are $<0.33\ \mu\text{m}$ deep are plotted as unfilled symbols.
279 The volume bias is most obvious for the shallow analyses of beryl but is also observed
280 for shallow analyses of tourmaline and pargasite #2. Shallow pits of cordierite were also
281 analyzed (Figure 3a), but no obvious volume bias is present, supporting the interpretation
282 that the high concentration analyses are apparent and not the result of He enrichment.
283 Several spurious, high concentration analyses were observed (also plotted as unfilled
284 symbols). We interpret these analyses to reflect the inadvertent incorporation of a gas-
285 rich secondary phase in the ablated volume. These data are not used in further analysis or
286 calculations of Henry's constants as the remainder of data are comparatively repeatable.

287   Several lower temperature, shorter duration experiments on micas display clear
288 He concentration gradients parallel to the C axis that extend several microns into the
289 mineral interior (symbols labeled "diffusion fit," Figure 3b). The fact that concentration
290 is depth dependent precludes calculating He Henry's constants as simple averages of
291 measurements. For these experiments, we fit diffusion profiles (tracer diffusion into a
292 semi-infinite medium from a reservoir of constant chemical potential) to quantify He
293 diffusion kinetics and solubility (Supplementary Table 2). Solubility in this circumstance
294 is taken as the modeled concentration of He at the surface (Thomas et al., 2008). Note,
295 however, that some micas run at similar temperatures and for similar durations do not
296 show a clear concentration profile but yield similar He_{HC} (see the muscovite and F-
297 phlogopite from CS_NG_EXP2 and the F-phlogopite from CS_NG_EXP15). The reason

298 for this discrepancy is unclear but may reflect that the diffusional length scale for these
299 samples was not the grain size (e.g., related to unobserved fracturing or cleaving).

300 Helium diffusivities fit for muscovite and F-phlogopite vary between 3×10^{-15} and
301 $2 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ at 500°C. The average of He diffusivities fit for muscovite is $9 \pm 5 \times 10^{-17} \text{ m}^2$
302 s^{-1} , and this value is $\sim 100\times$ slower than previous step-degassing based determinations of
303 He diffusion in muscovite at 500°C (Lippolt and Weigel, 1988). Micas in this study were
304 prepared as cleaved discs and were consequently ablated parallel to the C axis during
305 analysis, far from grain edges. This analytical approach effectively isolates diffusion
306 that occur across, rather than parallel to, the interlayer structures. Thus, the slow He
307 diffusivities measured here are consistent with noble gas diffusion being strongly
308 anisotropic in mica, where diffusion preferentially occurs through interlayers. Similar
309 observations have been made for Ar diffusion in mica (Giletti, 1974).

310

311 3.2.2. Equilibrium Considerations: Duration, f_{He} , and Temperature Correlations

312

313 Figure 4 plots the He_{HC} determined for each experiment against the respective
314 experimental duration, f_{He} , and temperature. Where no concentration profile was
315 observed in a run product, He_{HC} is calculated as an equal-weight average of the
316 population of individual analyses. Where a concentration profile was observed (i.e.
317 micas), He_{HC} is calculated by fitting a diffusion profile and using the surface
318 concentration as solubility. He_{HC} values for each experiment are provided in Table 2
319 along with associated experimental parameters.

320   He_{HC} values are independent of duration, f_{He} , and temperature (Figure 4). Many
321 of the minerals investigated here are hydrous and, thus, prone to decomposition under the
322 imposed experimental conditions (i.e. high temperature, low $f_{\text{H}_2\text{O}}$ systems). The lack of
323 correlation between He_{HC} and duration argues against H loss or decomposition affecting
324 the concentrations of He measurements. Similarly, higher temperatures promote more
325 rapid loss of H and decomposition. No correlation is observed between He_{HC} and
326 temperature, also arguing against H loss and decomposition affecting He concentrations.
327 Moreover, the lack of correlation between He_{He} and temperature indicates that there is a
328 small enthalpy associated with the dissolution of He into the ring structure-bearing
329 minerals explored here. This is consistent with the weak bonding between noble gases
330 and their mineral hosts and allows for simple extrapolations to higher and lower
331 temperatures.

332   Experiments were conducted at unnaturally high noble gas fugacity in order to
333 achieve precise analyses. As such, the applicability of Henry's Law must be evaluated
334 before solubility relationships can be applied to modeling the behavior of noble gases in
335 natural systems. Henrian solution behavior requires that the concentration of an element
336 dissolved into a phase is linearly proportional to the fugacity of that element in the
337 system, or equivalently, the Henry's constant is invariant with changes in fugacity.
338 Figure 4b demonstrates the invariance of He_{HC} over a range of f_{He} , indicting Henry's
339 Law is obeyed. The repeatability of He_{HC} across the range of f_{He} suggests the solubility
340 relationships determined for He are robust and meaningful for natural systems. It is
341 possible that other solution mechanisms become significant at lower noble gas fugacity.

342 If true, then the noble gas solubilities documented here represent lower limits for natural
343 systems.

344 At higher f_{He} , it is expected that the available ring structures approach complete
345 occupancy, resulting in a non-linear relationship between f_{He} and He solubility, i.e. a
346 Langmuir Isotherm. However, the occupancy of ring structures by noble gases, up to the
347 highest f_{He} explored here, remains relatively small. Cordierite shows the strongest
348 affinity for He, but only ~15% of available ring structures are occupied by He at $f_{\text{He}} =$
349 1.77 kbar (two ring sites per formula unit).

350

351 3.2.3. Correlations Between He_{HC} and Ring Structure Topology

352

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

359 Figure 5 plots He_{HC} normalized to the concentration of unoccupied ring structures
360 ($\text{He}_{\text{HC-ring norm.}}, \text{He mol ring mol}^{-1} f_{\text{He bar}}^{-1}$) for the various unoccupied ring structure-
361 bearing minerals studied here, ordered in ascending $\text{He}_{\text{HC-ring norm.}}$. Solubility data are
362 normalized to the concentration of unoccupied ring structures to provide the most direct
363 comparisons between differing ring topologies. Helium is highly soluble in all ring
364 structure-bearing minerals, (He_{HC} varies between ~100 to 100,000× olivine He_{HC}), but

365 there is considerable variability in determinations of $\text{He}_{\text{HC-ring norm.}}$ between the different
366 minerals explored here. We seek here to understand the cause of this variability by
367 considering variations in ring structure topology.

368

369 3.2.3.1. Antigorite and Tourmaline $\text{He}_{\text{HC-ring norm.}}$

370

371 Antigorite and tourmaline have similar $\text{He}_{\text{HC-ring norm.}}$ and share similar topologies
372 about their ring structures (Figure 5). Specifically, both minerals have groups of
373 octahedra above and below a single ring, and the tetrahedral units in the ring are oriented
374 with an apex pointed towards the upper octahedra. In tourmaline, the ring structure exists
375 as an isolated unit and is commonly occupied by Na, and to a lesser extent, Ca. Each of
376 the octahedra associated with the ring structure in tourmaline shares an oxygen ion with a
377 trigonally coordinated B ion. The ring structure in antigorite is defined by an upper and
378 lower octahedral sheet with a tetrahedral sheet of rings bound to the upper octahedra.
379 Nominally, all the ring structures in antigorite are unoccupied. Compared to the other
380 minerals with unoccupied ring structures, tourmaline and antigorite have the lowest
381 associated $\text{He}_{\text{HC-ring norm.}}, \sim 1 \times 10^{-6} \text{ mol mol}^{-1} \text{ bar}^{-1}$, suggesting He has the weakest affinity
382 for this general topology.

383

384 3.2.3.2. Amphibole (actinolite) $\text{He}_{\text{HC-ring norm.}}$

385

386 The ring structure in amphibole is constituted by an opposing pair of rings that are
387 offset by distorted polyhedra of Ca and Na ions. Octahedral polyhedra border the pair of

388 rings, both above and below. The ring structure in amphibole is commonly occupied by
389 Na, and to a lesser degree, K. $\text{He}_{\text{HC-ring norm.}}$ for both amphiboles is $\sim 1 \times 10^{-5} \text{ mol mol}^{-1} \text{ bar}^{-1}$
390 ¹, suggesting He favors the amphibole ring structure topology compared to the topology
391 present in antigorite and tourmaline.

392

393 3.2.3.3. Beryl and Cordierite $\text{He}_{\text{HC-ring norm.}}$

394

395 Beryl and high-cordierite are isostructural, hexagonal minerals, but under most
396 geologic conditions cordierite reverts to its low, orthorhombic form. The orthorhombic
397 transition causes a small distortion to the ring in cordierite compared to beryl (see Figure
398 1c and 1d). Nonetheless, beryl and low-cordierite share a similar ring structure topology.
399 The tetrahedra that comprise the rings in beryl and cordierite are oriented such that no
400 apex is pointed normal the ring plane, and the rings are stacked continuously along the c-
401 axis, forming “ring channels.” A larger ring of tetrahedral and octahedral cations is
402 positioned between the purely tetrahedral rings. The alternating channel structure creates
403 two distinct environments: a larger radius interstice in the plane of the tetrahedral-
404 octahedral ring and smaller radius interstice in the plane of the tetrahedral ring. Both
405 locations have been shown to host large radius species such as alkali cations, Ar, and
406 H₂O (Smith and Schreyer, 1962; Goldman et al., 1977). The present experiments on
407 beryl and cordierite confirm that channel structures are also capable of hosting smaller
408 radii noble gases. Indeed, $\text{He}_{\text{HC-ring norm.}}$ determined for beryl and cordierite is
409 exceptionally high compared to other ring structure topologies: $\sim 5 \times 10^{-5} \text{ mol mol}^{-1} \text{ bar}^{-1}$
410 (Figure 5). This suggests He has the strongest affinity for the topology of ring structures

411 in beryl and cordierite compared to the other topologies considered here. Additional
412 work is needed, however, to determine if the distribution of noble gases between the
413 different ring environments in cordierite and beryl.

414

415 3.2.4. He-Ne-Ar Solubility Patterns

416

417 Figure 6 plots determinations of He_{HC} , Ne_{HC} , and Ar_{HC} for experiments where He-
418 Ne-Ar solubility data were collected. Extrapolated Henry's constants were calculated by
419 dividing the measured Henry's constant by the fraction of unoccupied ring structures. Ne
420 and Ar data are normalized to f_{Ne} and f_{Ar} , respectively, for comparison purposes, but
421 explicit demonstrations of Henry's Law applicability have not been made for these data.

422 To a first order, Ne_{HC} and Ar_{HC} measurements are similar to He_{HC} measurements
423 made on the same material: He_{HC} , Ne_{HC} , and Ar_{HC} are high for beryl and cordierite,
424 intermediate for amphibole, and low for antigorite. However, distinctive $\text{He}_{\text{HC}}\text{-Ne}_{\text{HC}}\text{-}$
425 Ar_{HC} patterns are present in minerals that correlate with the different classes of ring
426 structures. Beryl and cordierite display a chevron $\text{He}_{\text{HC}}\text{-Ne}_{\text{HC}}\text{-Ar}_{\text{HC}}$ pattern, where He_{HC}
427 and Ar_{HC} are lower than Ne_{HC} . The $\sim 3\times$ difference between He_{HC} for beryl and cordierite
428 (Figure 5) remains similar for Ne_{HC} and expands for Ar_{HC} . Both amphiboles have
429 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
430 pargasite #2 show a more moderate slope compared to actinolite #2. These noble gas
431 solubility measurements in amphibole are consistent with those reported by Jackson et al.
432 (2013a). Antigorite displays an inverted chevron $\text{He}_{\text{HC}}\text{-Ne}_{\text{HC}}\text{-Ar}_{\text{HC}}$ pattern, opposite to
433 the pattern observed for beryl and cordierite. The slope between He_{HC} and Ne_{HC} for

antigorite is negative and steep compared to that observed for amphibole. There appears to be a reversal in slope between Ne_{HC} and Ar_{HC} , but considerable variability is present in both the Ne and Ar data for antigorite (Figure 6). Because of this variability, we do not interpret the Ne_{HC} and Ar_{HC} data as simply being reflective of solubility in pure antigorite. The source for this variability is not immediately clear, as He_{HC} data are highly reproducible. Possible root causes for this variability are explored below.

440

441 3.2.5. Ne_{HC} and Ar_{HC} Variability in Antigorite

442

The antigorite studied here is not a mono-mineralic sample. This contrasts with the other materials used here for He, Ne and Ar solubility determinations. Transmitted light images of a representative antigorite sample are provided in Figure 2. Multiple secondary phases are present. The most visually obvious secondary phase is magnetite, identified as opaque, black masses. Magnetite is mostly present as macro-scale inclusions. Micro-scale magnetite inclusions are also distributed throughout the sample. A separate secondary phase is also present throughout the antigorite. The nature of this separate secondary phase is more difficult to determine given its very fine scale, but on the sample-scale this phase causes a cloudy appearance and is heterogeneously distributed (Figure 2a and 2b). The experimental antigorite samples were taken from the more translucent sections of the starting material, similar to material on the left side of Figure 2a, limiting the net effect of the clouding phase. However, the clouding phase is present throughout the antigorite and has the potential to affect the abundances of noble gases concentrated in the antigorite material.

457   Figure 7 correlates individual measurements of He_{HC} and Ne_{HC} against Ar_{HC} in
458 antigorite where a He-Ne-Ar pressure medium was used (experiments CS_NG_21, 22,
459 and 25). He_{HC} measurements are repeatable, clustering near 1.5×10^{-9} mol g⁻¹ bar⁻¹.
460 Simultaneous measurements of Ar_{HC} are scattered in excess of analytical precision,
461 ranging between 4×10^{-10} and 4×10^{-9} mol g⁻¹ bar⁻¹ (Figure 7a). Similarly, simultaneous
462 measurements of Ne_{HC} and Ar_{HC} are correlated, with a slope of 0.12 ± 0.03 1 σ (Figure 7b),
463 neglecting two data points with strongly negative Ne_{HC}. The fact that Ar_{HC} variability is
464 not correlated with He_{HC} variability, yet correlated with Ne_{HC}, suggests that a secondary,
465 noble gas-rich phase was variably included in the analyses of antigorite samples. Given
466 the relationships present in Figure 7, it appears this secondary phase prefers Ar, and to a
467 lesser extent Ne, compared to He.

468   Micro-scale inclusions of magnetite and a fine-scale “clouding” phase are present
469 throughout the sample, and these materials have likely been variably incorporated into
470 the analyzed antigorite. The edge of a macro-scale magnetite inclusion was intentionally
471 incorporated into the final analysis of the antigorite sample from experiment
472 CS_NG_EXP30 (noted in Supplementary Table 1). A He-only pressure medium was
473 used in CS_NG_EXP30, so the combined He-Ne-Ar effect of magnetite inclusions
474 remains uncertain. However, the concentration of He in the final analysis was $2.1 \pm$
475 0.3×10^{-6} mol g⁻¹, which is high compared to the average of the other antigorite analyses in
476 CS_NG_EXP30 ($1.49 \pm 0.03 \times 10^{-6}$ mol g⁻¹). From this single comparison it appears that
477 magnetite inclusions or magnetite-antigorite grain boundaries are potentially noble gas-
478 rich materials. More work is needed to confirm this result and extend the analysis to Ne

479 and Ar. The effect of the clouding secondary phases has not been isolated, and thus, it
480 also remains a potential source for the observed variability in Ne and Ar.

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

488 Regardless of the source of Ne and Ar variability, several inferences can be drawn
489 for the solubility of noble gases in pure antigorite (antigorite in the absence of gas-rich
490 secondary phases). Ne_{HC} is $\sim 10\times$ lower than He_{HC} , despite the skew of Ne to higher
491 concentrations. Several analyses of Ne_{HC} are within error of or below zero, suggesting
492 He_{HC} in pure antigorite is $> 10\times$ greater than Ne_{HC} . Many simultaneous analyses of Ar_{HC}
493 and He_{HC} have $\text{Ar}_{\text{HC}}/\text{He}_{\text{HC}}$ ratios less than unity, suggesting $\text{He}_{\text{HC}} > \text{Ar}_{\text{HC}}$ in pure antigorite.
494 Moreover, Ar_{HC} analyses of antigorite from EHPV_NG_EXP53 and CS_NG_EXP18 are
495 either within error of zero or low compared to the remainder of Ar_{HC} analyses (Table 2).
496 Applying the axiom that the highest Ar_{HC} determinations reflect the strongest contribution
497 from gas-rich secondary phases, the low Ar_{HC} analyses also imply a low value of Ar_{HC}
498 and a low $\text{Ar}_{\text{HC}}/\text{He}_{\text{HC}}$ ratio for pure antigorite. However, we do not adopt the low
499 determinations of Ar_{HC} from EHPV_NG_EXP53 and CS_NG_EXP18 as being
500 necessarily representative of pure antigorite. Both EHPV_NG_EXP53 and
501 CS_NG_EXP18 were run simultaneously and shared a pressure medium. Moreover,

502 EHPV_NG_EXP53 and CS_NG_EXP18 were the only two experiments that had a
503 methane + Ar pressure medium. Correlated experimental factors may have contributed to
504 the low Ar_{HC} measurements on EHPV_NG_EXP53 and CS_NG_EXP18. With the
505 current data, it is impossible to completely deconvolve the competing effects of gas-rich
506 secondary phases, pure antigorite, and systematic experimental factors in interpreting the
507 concentrations of noble gases analyzed in antigorite. Nonetheless, it appears that in bulk
508 antigorite, ring structures compete with secondary phases to determine bulk noble gas
509 solubility. The relatively low noble gas solubility associated with ring structures in
510 antigorite makes the bulk noble gas solubility in serpentinites more easily influenced by
511 other factors.

512

513 4.0. Implications for Noble Gas Recycling

514

515 4.1 Effect of Noble Gas Solubility in Unoccupied Ring Structure-Bearing 516 Minerals

517

518 Atmospheric noble gases are introduced into slab materials during hydrothermal
519 alteration (Staudacher and Allègre, 1988, Kumagai et al., 2003; Moreira et al., 2003;
520 Kendrick et al., 2011; Kendrick et al., 2013). Seawater is the ultimate source of
521 hydrothermal fluids and, thus, it is expected that noble gases are initially introduced into
522 the slab in elemental proportions equal to those found in seawater (Holland and
523 Ballentine, 2006). The noble gas isotopic signature of seawater is identical to the
524 atmosphere but is elementally enriched in heavier noble gases compared to the

525 atmosphere following noble gas solubility in saline water at surface temperatures (Potter
526 and Clyne, 1978; Crovetto et al., 1982). If no fractionations occur during noble gas
527 uptake and devolatilization of the slab, then noble gases should be recycled in seawater-
528 like elemental proportions with atmospheric isotopic signatures. Note, helium is not
529 retained in Earth's atmosphere, and so, in comparison to other noble gases, helium in the
530 mantle is much less susceptible to overprinting by atmospheric signatures.

531   Measurements of mantle-derived Ne indicate that less than 30% of non-
532 nucleogenic Ne in the mantle is recycled (Moreira et al., 1998; Yokochi and Marty, 2004;
533 Ballentine et al., 2005; Mukhopadhyay, 2012). In contrast, measurements of mantle-
534 derived Xe indicate that ~85% of Xe in the mantle is recycled (Holland and Ballentine,
535 2006; Mukhopadhyay, 2012; Tucker et al., 2012; Petö et al., 2013). Using modern noble
536 gas elemental concentrations for the mantle and seawater (Holland and Ballentine, 2006),
537 these measurements suggest that the Ne/Xe ratio associated with the flux of recycled
538 noble gases is either close to that of seawater or favors preferential recycling of heavier
539 noble gases. Elemental abundance measurements of noble gases derived from the mantle
540 have also been argued to reflect preferential recycling of heavier noble gases compared to
541 their proportions in seawater (Holland and Ballentine, 2006). Thus, current observations
542 suggest the recycling flux is not enriched in the light noble gases.

543   We have demonstrated that noble gases have a relatively strong affinity for
544 unoccupied ring structures and that ring structure topology has a secondary influence on
545 the He-Ne-Ar solubility pattern in minerals. However, none of the ring structure
546 topologies studied here have a clear preference for larger radii, heavier noble gases
547 (Figure 6 and 7). The minerals that are most relevant to noble gas recycling, antigorite in

548 its pure form and amphibole, appear to favor He compared heavier noble gases. Simple
549 extrapolation of amphibole and pure antigorite He-Ne-Ar solubility patterns to heavier
550 noble gases suggests that these minerals would preferentially facilitate the recycling of
551 lighter noble gases, opposite to the inferred pattern for noble gas recycling. Other
552 minerals with unoccupied ring structures are formed during hydrothermal alteration of
553 slab materials, including talc, chlorite, clays, and the lower temperature polymorphs of
554 antigorite, chrysotile and lizardite. All of these minerals may contribute significantly to
555 the flux of recycled noble gases. However, these minerals are all phyllosilicates, and
556 thus, share a ring structure topology similar to antigorite. Correspondingly, these
557 minerals do not offer an obvious balance to the preference of amphibole and antigorite
558 for light noble gases.

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

566   It is also worth stressing that the majority of ring site-bearing minerals are not
567 stable to pressures sufficient to transport noble gases past depths associated with the
568 generations of arc magmas. The complete recycling of noble gases appears to require the
569 retention of noble gases in down-going materials despite the production of fluids due to
570 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 $Ar_{HC-ring\ norm.}$ in antigorite are uniformly greater than $Ne_{HC-ring\ norm.}$ and commonly surpass $He_{HC-ring\ norm.}$ (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.

593   There is corroborating evidence for this behavior of Ne and Ar in natural
594 serpentinites. Measurements of antigorite schists (serpentinites) that are inferred to be
595 exhumed slab materials indicate that serpentinite can host high concentrations of
596 seawater-derived noble gases, with ^{36}Ar abundances in serpentinite reaching $\sim 100\times$ the
597 abundance of ^{36}Ar in the depleted mantle (Kendrick et al. 2011, Kendrick et al., 2013).
598 Measured Ne/Ar ratios in slab serpentine are typically $\sim 2\times$ lower than seawater values,
599 although considerable scatter is observed. This fractionation of Ne from Ar is consistent
600 with our measurements of Ne_{HC} and Ar_{HC} in bulk antigorite. Previous experimental work
601 defining noble gas solubility in bulk serpentine also supports Ne being less soluble
602 compared to Ar (Zaikowski and Schaeffer, 1979). Combined, these results are consistent
603 with the solubility of noble gases in materials affecting the elemental patterns of noble
604 gases associated with hydrothermally altered lithologies.

605   Another important observation regarding the behavior of He-Ne-Ar in bulk
606 antigorite is the rate of equilibration of between the pressure medium and the antigorite
607 specimen. The kinetics of equilibration between bulk antigorite and the pressure medium
608 have not been directly quantified here, but limits can be evaluated. Experiments on
609 antigorite were conducted at temperatures $\leq 450^\circ\text{C}$, which are low compared to the
610 remainder of experiments presented here. Despite the low temperatures, He_{HC} , Ne_{HC} ,
611 and Ar_{HC} do not correlate with ablation pit depth, indicating that these gases equilibrated
612 with the antigorite to at least a depth of $33\ \mu\text{m}$ over the experimental durations and that
613 noble gas losses from bulk antigorite prior to analysis were small (Supplementary Table
614 2). This rate of equilibration is extremely rapid compared to the other materials
615 investigated here, particularly for Ar. For example, Ar diffusion profiles in both

616 amphiboles analyzed extended $<1\ \mu\text{m}$ deep after 161 hours at $900\ ^\circ\text{C}$ (Supplementary
617 Information). The rapid nature of noble gas uptake is consistent with observed degassing
618 behaviors of serpentinites during step-degassing noble gas analysis, i.e. heating of 20-40
619 mg chips of serpentinite at 300°C for 20 minutes typically extracts $>20\%$ of total ^{36}Ar
620 from the sample (Kendrick et al, 2013). It is likely that grain boundaries and the
621 relatively open sheet structures facilitate rapid diffusion of noble gases through
622 serpentinites. Consequently, an equilibrium distribution of noble gases between
623 serpentinite and hydrothermal fluids should be closely approached in natural systems,
624 even at the relatively low temperature associated with serpentine stability. It is also
625 worth noting that He, Ne, and Ar concentrations do not decrease with decreasing pit
626 depth in the experimental antigorite samples, indicating loss of noble gases prior to
627 analysis in the present experiments is negligible. Further experiments are needed to
628 confirm these rapid noble gas diffusion rates, but these preliminary observations suggest
629 that noble gases subducted by serpentinites will be particularly vulnerable to extraction
630 by migrating slab fluids.

631

632 4.3 Deep Recycling of Noble Gases and Alternative Recycling Environments

633

634 Helium solubility in mica (muscovite and F-phlogopite) is lower than other
635 minerals with high concentrations of unoccupied ring structures (Figure 4). Interlayer
636 cation deficiencies are ubiquitous in micas, which manifest as unoccupied ring structures,
637 but are present in minor concentrations ($<15\%$ of K site, Table 1, Rieder et al., 1999).
638 The high occupancy of ring structures in micas suggests other locations may

639 accommodate a large component of dissolved noble gases. Dioctahedral micas, such as
640 muscovite, contain abundant unoccupied interstices in their octahedral sheets. These
641 interstices provide additional porosity that is not available in trioctahedral micas, such as
642 F-phlogopite. The similar values of He_{HC} measured for muscovite and F-phlogopite,
643 however, argue for the octahedral sheets being only minor hosts for He and, by extension,
644 other noble gases in mica. This result is also supported by the similarity of He solubility
645 measurements in pyroxene, olivine, and spinel with variable concentrations of Mg-site
646 vacancies (Heber et al., 2007; Jackson et al., 2013b). The small solubility associated with
647 octahedral vacancies suggests that noble gases are hosted in the mica interlayer, either
648 interstitially or in unoccupied ring structures. The strong diffusional anisotropy inferred
649 for micas (Section 3.2.1) also supports the argument that the octahedral sheets are
650 relatively high-energy locations for noble gases.

651 Micas, such as phengite, are stable to high pressures and temperatures compared
652 to the majority of hydrous minerals in slabs. Consequently, mica is capable of
653 sequestering and transporting water deep in subduction zones (Schmidt and Poli, 1998;
654 Hacker et al., 2008). Measurements of He_{HC} in muscovite and F-phlogopite are similar to
655 each other and $\sim 100\times$ higher compared to mantle minerals, such as olivine (Jackson et al.,
656 2013b), which suggests that mica could be an important host for noble gases deeper in
657 subduction zones, particularly for slabs where serpentine stability is restricted.

658 Mica and amphibole are also stable in the metasomatized, lithospheric mantle
659 (e.g. Pilet et al., 2008; Green et al., 2010) and hydrated sections of lower continental crust
660 (e.g. Rapp and Watson, 1995, Liu et al., 1996). Both the lower crust and lithospheric
661 mantle can become sufficiently dense that they are delaminated and returned to the

662 convecting mantle (e.g. Bird, 1979, Ducea and Saleeby, 1996; Davidson et al., 2008,
663 Jagoutz and Behn, 2013). Depending on physics of delamination, these recycled
664 lithologies can retain significant amounts of their initial volatiles upon recycling (Elkins-
665 Tanton, 2007). If enriched in mica and amphibole, these lithologies may also provide
666 alternative environments for noble gas recycling. The noble gases hosted in these
667 delaminated lithologies can be either dominated by mantle noble gases or atmospheric
668 noble gases depending on the ultimate origin for the metasomatic fluid.

669

670 5.0 Conclusions

671

672 We have experimentally determined the solubility of noble gases in a series of
673 materials that are broadly applicable to noble gas recycling in subduction zones. For pure
674 minerals, the availability and topology of unoccupied ring structures has a strong control
675 on the solubility of He. Distinctive $\text{He}_{\text{HC}}\text{-Ne}_{\text{HC}}\text{-Ar}_{\text{HC}}$ patterns for pure minerals have also
676 been identified. These patterns correlate with ring structure topology and do not appear
677 to favor dissolution of heavier noble gases. Secondary phases, such as those present in
678 antigorite, have the potential to concentrate noble gases, and thus, affect the solubility of
679 noble gases in bulk materials. This is especially true for antigorite because He, Ne, and
680 Ar appear relatively insoluble the pure mineral. In contrast to ring structures, secondary
681 phases may favor the uptake of heavier noble gases, and the variable presence secondary
682 phases may contribute to local elemental fractionations and concentration variations in
683 natural systems. In this context, secondary phases may be important in contributors to
684 the transport and elemental fractionations of noble gases into and through subduction

685 zones, particularly in the ultramafic sections of slabs. Micas, and other ring structure-
686 bearing minerals that are stable to high pressure, have the potential to transport noble
687 gases past mantle wedge depths associated with arc magma genesis.

688

689 Figure Captions:

690

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

698

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

704

705 Figure 3: He_{HC} measurements versus ablation pit depth. Each data point is an individual
706 measurement of He concentration normalized to f_{He} for the experiment. Error bars are 1σ
707 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_{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.

714

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

721

Figure 5: $\text{He}_{\text{HC-ring norm.}}$ determinations for each material type plotted in ascending order, left to right. $\text{He}_{\text{HC-ring norm.}}$ values are determined by either averaging individual measurements of He_{HC} in an experiment or fitting diffusion profiles to individual measurements He_{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 $\text{He}_{\text{HC-ring norm.}}$ data. There is a broad correlation between the topology local to ring structures and $\text{He}_{\text{HC-ring norm.}}$.

729

730 Figure 6: $\text{He}_{\text{HC}}\text{-Ne}_{\text{HC}}\text{-Ar}_{\text{HC}}$ determinations for materials where He-Ne-Ar data were
731 collected. $\text{He}_{\text{HC}}\text{-Ne}_{\text{HC}}\text{-Ar}_{\text{HC}}$ values are determined by averaging individual measurement
732 in an experiment. Distinctive patterns present for material types: beryl and cordierite
733 display a chevron $\text{He}_{\text{HC}}\text{-Ne}_{\text{HC}}\text{-Ar}_{\text{HC}}$ pattern, amphibole displays a negative slope between
734 He_{HC} and Ar_{HC} , and antigorite displays an inverted chevron $\text{He}_{\text{HC}}\text{-Ne}_{\text{HC}}\text{-Ar}_{\text{HC}}$ pattern,
735 although considerable variability is present in Ne_{HC} and Ar_{HC} determinations for
736 antigorite.

737

738 Figure 7: Simultaneous measurements of A) He_{HC} and Ar_{HC} and B) Ne_{HC} and Ar_{HC} in
739 antigorite. Each data point is an individual measurement of antigorite. Error bars are 1σ
740 and include analytical and pit volume determination uncertainties. A) He_{HC}
741 measurements are repeatable, but Ar_{HC} measurements are highly variable. B) Ar_{HC}
742 variability is correlated with Ne_{HC} , suggesting Ar_{HC} and Ne_{HC} variability are controlled by
743 the same factor. Two data points from CS_NG_21, 22, and 25 are not included in the
744 regression of Figure 7 because the Ne_{HC} measurements are anomalously negative.

745

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Figure 1

Figure 2:

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Figure 4:

Figure 5:

Figure 6:

Figure 7:

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 1σ and only include the propagated analytical uncertainties. Volume uncertainties are not factored into elemental ratios. The uncertainties reported for Ne and Ar solubility 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 1σ and only include the propagated 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 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 $\ll 1$ %, 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