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Noble gas transport into the mantle facilitated by high solubility in amphibole

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Noble gases trace the chemical evolution of both the Earth's atmosphere and mantle ¹⁻⁵.

A key aspect is the balance between the flux of noble gases leaving Earth's interior through magmatism and the flux of noble gases back into the mantle via recycling at subduction zones. It is traditionally assumed that recycling of noble gases is negligible ^{e.g.1}. However, analyses of natural samples suggest that the inward flux of noble gases is more significant than previously recognized ^{e.g.6-8}. The mechanisms (e.g. fluid encapsulation or mineral dissolution) responsible for returning noble gases to the mantle, however, remain unclear. Here we report high-pressure experimental measurements of noble gas solubility in amphibole, which is an important hydrous mineral in altered-oceanic crust (AOC) ⁹⁻¹¹. Noble gases are very soluble in amphibole (up to $1 \times 10^{-8} \text{ mol g}^{-1} \text{ bar}^{-1}$, helium), and solubility correlates with the concentration of unoccupied A-sites present. These correlations provide strong evidence that A-sites are energetically favorable locations for noble gas dissolution in amphibole. Thus, subduction of AOC provides a potential mechanism for recycling noble gases. Many hydrous minerals present in subducting slabs have lattice structures similar to the A-site in amphibole (serpentine & chlorite) and may provide even larger recycling pathways ^{7,11}.

The analysis of noble gases in basaltic materials derived from the mantle is complicated by ubiquitous atmospheric contamination ^{e.g.12}. The prevalence of these modern atmospheric

contaminants make it difficult to confidently determine if different mantle reservoirs contain an intrinsic recycled component that is ultimately derived from Earth's paleo-atmosphere. However, it is well established that radiogenic, and to a lesser degree non-radiogenic¹³, noble gas heterogeneity exists between different mantle reservoirs and between the atmosphere and mantle^{e.g.5,6,13-18}. The fact that this heterogeneity exists requires long time scales for mixing noble gases within the solid Earth and for mixing atmospheric noble gases into the mantle. At the same time, high-precision noble gas measurements of materials derived from the mantle now raise the possibility that substantial quantities of atmospheric noble gases have been recycled back into the mantle^{6-8,13-18}. The proposed recycling of chemically inert noble gases met resistance, in part because noble gas solubility in geologically relevant minerals was thought to be low. However, data relevant to the transport of noble gases in subduction zones are scarce^{e.g.7,8,19-21}, leaving potential transport mechanisms for noble gases into subduction zones and the convecting mantle unclear^{e.g.6,7}.

This study seeks to clarify the possible role of hydrothermally altered-oceanic crust (AOC) in noble gas recycling by measuring the solubility of noble gases (He and Ne) in amphibole (Figure 1), a common mineral in AOC. Amphibole comprises 1.5-12 % of bulk basaltic crust and can locally occupy 50% of AOC^{9,10}. As amphibole is a major volatile-bearing component of subducted crust, it has the potential to recycle noble gases and other volatile elements (e.g. H₂O, F, Cl). High solubility would imply that noble gases could be recycled via AOC (at least to the depth of amphibole breakdown, ~100 km) along with other volatiles, while low solubility would imply that amphibole is not a major carrier of noble gases.

Helium and neon solubilities were measured in six amphiboles that span a range of compositions (Supplementary Information, Table 1). The experiments consisted of gem-quality

crystals that were equilibrated with He-Ne-Ar gas mixtures at pressures up to 1.7 kbar and temperatures up to 875°C in an externally-heated, gas-pressure device. The crystals were then measured for noble gas concentration with a laser-ablation noble gas mass spectrometer (see Supplementary Information for detailed methods).

The solubility of He and Ne in amphibole is high relative to other silicates, and varies with amphibole composition. Pargasite and richterite have Henry's constants for He of $0.3\text{--}1 \times 10^{-9}$ ($\text{mol g}^{-1} \text{ bar}^{-1}$), while actinolite ($1\text{--}8 \times 10^{-9}$) and tremolite (1×10^{-8}) have significantly higher solubilities (Figure 2). The Henry's constants for He in amphibole are up to four orders of magnitude greater than in other Fe-Mg bearing silicates, such as olivine and pyroxene^{22,23} (assuming Henry's Law applies). Measured He solubilities are independent of temperature, run duration, and ablation pit depth, with the exception of two low temperature, short duration experiments (Supplementary Information, Figure 1). These findings demonstrate a close approach to equilibrium was achieved for He, and so diffusional disequilibrium effects do not appear to have influenced the measured concentrations. The lack of temperature dependence of He solubility indicates He dissolution in amphibole has a relatively small associated enthalpy. This allows for simple extrapolation of solubilities to higher (magmatic) or lower temperatures (hydrothermal). Likewise, Henry's constants for He are independent of P_{He} over the range explored here. This allows Henry's constants to be extrapolated to natural conditions.

Neon diffuses more slowly than He and so diffusional equilibrium was not obtained during the experiments (Supplementary Information, Figure 2). The solubility of Ne, however, can be quantified by extrapolating diffusion profiles of Ne to the surface of the crystal (assumed to be at equilibrium with the pressure medium). Due to analytical interferences and the extrapolation to the surface, uncertainties in Ne solubility are substantially greater than those for

He. However, the extrapolated results show, like He, Ne solubility is high, with actinolite having higher solubilities than pargasite and richterite. (Figure 3) The best-fit Henry's constants for Ne are 1×10^{-10} (mol g⁻¹ bar⁻¹) for richterite, 1×10^{-9} for amber pargasite, and $3\text{--}4 \times 10^{-9}$ for the actinolites (Figure 3a).

The higher precision of the new experimental data allows a range of outstanding questions to be addressed. Chief amongst these is where noble gases are located in silicate mineral structures. The variation in both He and Ne solubility between the amphiboles can be understood by considering the A-site, or ring site, in amphibole. This site is constituted by a pair of opposing six member (Si,Al)O₄^{-4,-5} tetrahedra rings (Figure 1). These ring sites host large ion lithophile elements (large radius), but are unoccupied (uncharged) when other cations within the amphibole structure satisfy charge balance. Following lattice strain theory, ring sites are energetically favorable locations for noble gases (large radius, uncharged elements) in mineral structures. Figure 2a shows that He solubility does not correlate with the concentration of ring sites present, which is similar for all of amphiboles. But He solubility does show an excellent correlation with the concentration of *unoccupied* ring sites in the amphiboles (Figure 2b). This correlation strongly implies that He partitions readily into the unoccupied (and uncharged) ring sites in amphibole. The affinity of He for these sites has substantial implications for recycling of noble gases, as similar ring sites (with variable occupancy) are present in a wide range of hydrous minerals.

Though analytical uncertainties are greater, Ne solubility also correlates with unoccupied ring concentration (Figure 3a). For actinolite and richterite, He is approximately twice as soluble as Ne, while He is marginally more soluble in pargasite (Figure 3b). Since noble gases do not have net charges, one way they can form bonds is for their electrons to localize in a polarized

environment, enabling the formation of dipole-induced dipole bonds. Noble gas polarizability correlates with atomic radius, and consequently, Ne is more polarizable than He. The fact that Ne is not more soluble than He implies that, while polarizability may play a role in noble gas solubility, it likely competes with other factors in determining solubility associated with the ring site.

The affinity of noble gases for ring sites is consistent with previous analyses of natural and experimental ring site-bearing materials. High concentrations of noble gases have been observed in a wide range of ring site-bearing minerals, such as beryl, cordierite, tourmaline, and amphibole^{24,25}. High concentrations of mantle-derived helium have been correlated with the presence of tremolitic (unoccupied ring site-rich) amphibole in AOC²⁶, consistent with the present experimental results. High concentrations of noble gases have also been observed in serpentinite⁷. Further, the ring site in leucite transforms from highly distorted to symmetrical with temperature, and this transformation is associated with a substantial increase in the Ar Henry's constant²⁷. Determinations of Ar solubility in melts suggest unoccupied (Si,Al)-O ring structures host noble gases in silicate liquids, and that ring structure collapse at high pressure is associated with a discontinuous drop in noble gas solubility²⁸. Combined, these observations suggest all noble gases may have a high affinity for unoccupied ring sites, regardless of the structure of the material surrounding the ring.

Despite the high capacity for noble gases, it is not necessary that noble gases are recycled via amphibole in AOC. Recycling can be broken into two factors: abundance input into a subduction zone and percentage lost before slab material is transported to the convecting mantle. Thus, the flux of noble gases recycled via hydrothermal minerals primarily depends on two parameters: 1) the product of noble gas fugacity present during mineral equilibration (supplied

by brines derived from seawater or fluids generated by mineral decomposition) and noble gas Henry's constants for the applicable minerals, and 2) the depth at which noble gases are released from the slab during subduction (i.e. fore-arc, arc, or back-arc). The high solubility of noble gases in amphibole indicates that AOC has the *potential* to input large quantities noble gases, H₂O, Cl, and F into subduction zones. Amphibole alone is capable of transporting volatiles to ~100 km depth. Deeper transport may be facilitated by other ring-bearing minerals, like mica or antigorite, or a free fluid phase trapped within subducting materials. It is important to note that noble gas diffusion through minerals, including amphibole, is an inefficient transport mechanism. For example, using the fastest diffusion coefficient for Ne from this study, (Supplementary Information) the characteristic diffusion length scale is ~0.35 m in 100 Ma. Significant loss of noble gases from AOC likely requires advection via a fluid phase.

Elemental patterns of noble gases derived from the mantle suggest heavier noble gases are recycled in ratios in excess of seawater ⁶. This important observation can be used to investigate the materials responsible for noble gas recycling.

Helium appears to be more soluble than Ne in amphibole (Figure 3b); suggesting amphibole could facilitate preferential the subduction of light, rather than heavy, noble gases. Alone, this observation argues against AOC being a major contributor to noble gas recycling. Alternatively, AOC may contribute to noble gas recycling if other factors counter the apparent preference of amphibole for lighter noble gases. Factors may include preferential diffusive loss of lighter noble gases during the early stages of subduction or noble gas fractionations associated with amphibole breakdown and stabilization of deeper hydrous minerals. It is also possible that AOC can preferentially recycle light noble gases if the integrated recycling flux is dominated by other materials (minerals, defect structures, fluids) that preferentially recycle heavy noble gases.

Indeed, there is experimental and observational evidence that serpentine has a greater affinity for heavier noble gases^{7,20}. In either case, the high solubility of noble gases associated with unoccupied ring sites in amphibole demonstrates that minerals can transport significant amounts of noble gases in subduction zones and that minerals can induce strong inter-noble gas fractionations.

In addition to transporting seawater-derived noble gases into subduction zones, amphibole offers a mechanism to trap mantle-derived noble gases in the lithosphere. Low degree melts that infiltrate lithospheric mantle stabilize hydrous minerals, like amphibole²⁹. These amphibole-bearing lithologies, once subducted or delaminated, may be noble gas-rich and contribute to the heterogeneity of radiogenic and non-radiogenic noble gases observed within the mantle^{e.g.13,17,18}. Combining experimentally determined silicate melt solubility data³⁰ with the present dataset, we predict a He and Ne partition coefficient (amphibole-basaltic melt) for amphibole near 0.25 for an amphibole in equilibrium with peridotite (50% unoccupied rings)²⁹. This relatively high partition coefficient indicates amphibole can be a significant host of noble gases in lithospheric mantle environments.

An increasing number of observations suggest atmospheric noble gas isotopes of Ar, Kr, and Xe are recycled in significant quantities. Our new experimental measurements demonstrate that He and Ne are highly soluble in amphibole and that this solubility is associated with unoccupied ring sites. Similar sites exist in other hydrous minerals present in subducting lithosphere, potentially providing a range of transport mechanisms for noble gases both into subduction zones and the convecting mantle. Further work is now required to establish the extent to which noble gas recycling is coupled to recycling of water and other volatiles during

subduction, and therefore, to determine if noble gases can be used as tracers of volatile cycling in general.

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Additional information: Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to C.R.M.J.

Figure Legends:

Figure 1: Amphibole lattice structure. The A-site, or ring site, in amphibole is constituted by an opposing pair of tetrahedral rings bound in a hexagonal pattern. It is a large site and unoccupied when charge balance is satisfied by the other cations in amphibole. The ring site location is marked by larger black dots. The M4 site is marked by smaller grey dots. Noble gases are large radius, zero charged elements, and following lattice-strain theory, should partition into ring-sites.

Figure 2: Helium Henry's constants in amphiboles plotted against ring site concentration (mol g^{-1}) (A) and unoccupied ring site concentration (B). Helium solubility is high compared to mantle minerals and correlates with the concentration of unoccupied ring-sites rather the concentration of total ring-sites. This correlation provides experimental support for the hypothesis that noble gases partition strongly onto ring sites. Ring site-bearing lithologies have

the potential to deliver significant quantities of noble gases, water, and halogens to subduction zones. Thus, atmospheric noble gas isotopes may be useful tracers of volatile element recycling. Error bars are one standard deviation of replicate analyses.

Figure 3: Neon Henry's constants in amphiboles plotted against unoccupied ring site concentration (A) and He/Ne (solubility ratio) (B). Data in (A) are fit from Ne concentration profiles using a diffusion model (Supplementary Information). Similar to He, Ne solubility is high compared to mantle minerals and correlates with the concentration of unoccupied ring sites rather than the concentration of total ring sites (A). The ring site in amphibole appears to favor He over Ne (B), suggesting lighter noble gases have a greater affinity for this site compared to heavier noble gases. Error bars are one standard deviation. Dashed error bars indicate uncertainty is undefined.

Noble gas transport into the mantle facilitated by high solubility in amphibole

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Supplementary Figure 1: Henry's constants for He plotted as function of P_{He} (A), duration (B), depth (C), and temperature (D) for amphibole. Each point is an individual analysis. In general, trends are horizontal, indicating close approaches to equilibrium and applicability to natural systems. Exceptions are plotted as open symbols (see text). Henry's constants do not correlate with P_{He} (A), indicating Henry's Law applies over the range of P_{He} explored (1.7 kbar) and that data are applicable to natural systems with significantly lower noble gas fugacities. Henry's constants do not vary with duration or depth (B and C). This strongly argues for a close approach to equilibrium that is unaffected by surficial phenomena. Henry's constants are not measurably sensitive to changes in temperature between 680 and 875° C (D), allowing for simple extrapolation of results to hydrothermal or magmatic systems. Open symbols labeled "kinetic" are data from relatively low temperature, short duration experiments that have near-surface concentration profiles. Helium solubilities are determined for these experiments by fitting diffusion models (Supplementary Figure 4). Error bars are one standard deviation.

Supplementary Figure 2: Ne/He (molar) plotted as function of depth (μm) for longest duration, highest temperature experiments with Ne present (experiments 34 and 36). Each data point is an individual analysis. Data show decreasing Ne/He with increasing pit depth, consistent with decreasing degrees of equilibration for Ne with respect to He. Data for pentagons were acquired by slowly ablating along a line, generating a very shallow ($\sim 0.25 \mu\text{m}$ but highly variable) trench. We report only Ne/He for these pits because the precision on volume calculations for this geometry type is poor. At shallowest depths, data trend towards a Ne/He ~ 0.5 , indicating Ne is approximately half as soluble in amphibole as He.

Supplementary Figure 3: Expanded views of data from experiment 34 and 36 (Supplementary Figure3) showing resolvable Ne concentration gradients with fitted diffusion curves. Boxes (left plots) are individual data points acquired by ablating different locations on a crystal face to variable depths. Black curves (left plots) are the best-fit solution for a depth-averaged diffusion model based on the box data points. See the supplementary text below for a more detailed description of the diffusion model. Dashed grey curves (left plots) are the standard complimentary error function for the given set of fitted parameters. Uncertainty envelopes (black shapes, right plots) fail to define useful limits in some cases (B, D, & E), although there is good agreement between the various best-fit Ne diffusivities. Black circles (right plots) are the best-fit solution. For comparison, neon diffusivity in amphibole is similar at 850-875° C to values reported for olivine by [31](black diamond) but 1000x slower than reported by [32] (black square). Neon solubility in olivine is taken from [23]. Error bars are one standard deviation and no error is associated with the depth measurement.

Supplementary Figure 4: Expanded views of data from experiment 29 and 30 showing resolvable He concentration gradients (“kinetic” in Supplementary Figure1) with fitted diffusion curves. Boxes (left plots) are individual data points acquired by ablating different locations on a crystal face to variable depths. Black curves (left plots) are the best-fit solution for a depth-averaged diffusion model based on the box data points. See the supplementary text below for a more detailed description of the diffusion model. Dashed grey curves (left plots) are the standard complimentary error function for the given set of fitted parameters. Uncertainty envelopes (black shapes, right plots) are relatively tight compared to Ne diffusion models. Both green actinolite fitted He diffusion coefficients and solubilities agree well and are marginally slower than the values fit for the clear actinolite, although their confidence envelopes overlap. Black circle on right plots is the best fit solution. Compared to He diffusion in olivine, He diffusion in these amphiboles is 10-1000x slower at 680°C e.g.^{33,34} (black diamond and square, following reference order). Helium solubility in olivine taken from [23]. It should be noted, however, that other amphiboles have more He equilibrated profiles for equivalent conditions or conditions less conducive to diffusion, suggesting composition may have a significant effect on noble gas diffusion in amphibole. Error bars are one standard deviation and no error is associated with the depth measurement.

Methods:

Starting Materials:

Starting materials were gem quality amphibole. Major element compositions were determined by electron microprobe at MIT (WDS, 10 nA and 15 kV accelerating voltage) and are given in Supplementary Table 1. A focused beam was used and the raw data were corrected using CITZAF³⁵. Bulk crystals were sectioned into appropriate sizes (2 x 2 x 0.5 mm) using either a low speed diamond blade wafering saw or by cleaving. Cut faces were polished using alumina (0.05 μm) and colloidal silica. Cleaved faces were not prepared further. Once prepared, but prior to analysis, the crystals were mapped for inclusions using a 120x stereoscope. Any areas affected by inclusions were avoided during analysis.

Amphibole A-site, or ring site, occupancy was calculated by assigning all Ca to the M4 site. Additional Na was added to the M4 site to achieve two cations per formula unit. The remainder of Na and K were partitioned on to the A site, defining the occupancy. Density was estimated by assuming a constant unit cell volume of 900 μm^3 and applying the mass of the formula unit as calculated from the stoichiometry. Compositional and associated data are given in Supplementary Table 1.

Experimental and Analytical Methods:

We dissolved noble gases into amphibole using a TZM-type externally-heated pressure vessel apparatus. Either pure He or an equal mixture of He-Ne-Ar gas was used as the pressure medium for all experiments, allowing for precise and sustained control of noble gas fugacity. Typical change of the gas pressure was $\sim 1\%$ over the run duration with a

maximum observed leakage of 10%. Reported pressures are those recorded directly before quench. Temperatures ranged from 680° to 875°C and pressures ranged from 0.7 to 1.7 kbar. Convection within the pressure vessel was suppressed using graphite filler rods that extend the length of the pressure vessel above the capsules. Run conditions are given in Supplementary Table 2.

All experiments consisted of three separate crystals loaded into graphite capsules, excepting experiments 7, 8, and 14, where fired pyrophyllite capsules were used. Capsule type does not have a significant effect on the He solubility results, and there was no apparent reaction between crystals and capsule. A capsule loaded with brucite, MgO, and H₂O was placed directly above the third capsule to generate a small water fugacity. All three crystals were contained within the hotspot, as determined by temperature calibration of the pressure vessel assembly.

Experiments were quenched by removing the TZM 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. Essentially, the experimental method was a constant source diffusion approach.

Noble gas concentrations of the experimental run products were determined using a UV laser ablation-mass spectrometer system at the Open University. A 193 nm NeF excimer laser was used to ablate all minerals. Laser power varied between 10 and 40 % (200 mJ pulse⁻¹ at 20 Hz and 100% power), and laser pulse frequency was varied between 1 and 20 Hz to achieve desired ablation pit volumes and depths (200 mJ pulse⁻¹ at 20 Hz and 100% power). Three SAES AP-10 getters removed active gases released during ablation before introduction into a MAP215-50 mass spectrometer. ⁴He, ²²Ne and ⁴⁰Ar

were measured by a multiplier collector in peak hopping mode. The sensitivity of the mass spectrometer was determined by gas pipetting a known volume of noble gases with atmospheric isotopic ratios into the mass spectrometer. A session blank was calculated as the mean of the all the blanks for a particular session (defined as a single day of analysis on a single port). No significant trends were present. Further details regarding the basic laser ablation technique can be found in [36].

The volume of ablation pits were measured using a white light interferometer (Zygo Instruments, Brown University). This device provides an image of the ablated surface that requires minimal “inpainting” (interpolation of pixels with unknown 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, creating a positive relief topographic image that has been rotated into a horizontal plane. To calculate the pit volume, the individual volumes of all remaining pixels are summed assuming rectangular prism geometry for each pixel. A small ring of high topography was occasionally observed along the circumference of the pits, creating a halo of negative volume after continuum correction. We avoid including the negative volume halo in the volume calculation by only summing the pixels with positive depths. There is additional scatter in data from shallow pits and pits with more complex surrounding surface geometry. Both qualities make it more difficult to precisely determine a surface continuum and to accurately determine pit volumes. Using multiple interpolation methods we estimate a $\pm 15\%$ uncertainty in the pit volume calculation.

All minerals were carbon coated prior to imaging with the white light interferometer to improve reflectivity. More reflective minerals provide an image with

greater returned signal and require less “inpainting.” This is particularly beneficial in imaging clear minerals.

Uncertainties:

Uncertainty in noble gas concentration is a product of analytical and ablation pit volume uncertainties. Reported uncertainties include the following sources and are propagated assuming that they are independent from each other and random: 1) Statistical uncertainty associated with blank variability and noble gas analysis regressions (typically ~1% for ^4He and ~15% for ^{22}Ne from experiment 34 and 36, but can be >100% for very low-voltage analyses), 2) Pit volume determination. Volume uncertainty is greatest for very shallow pits (<1 μm) and pits with complexly curved surrounding surfaces. Using various interpolation and masking methods on very shallow pits with complex shaped surrounding surfaces we observe $\pm\sim 15\%$ variability in volume calculations, and we take this as a reasonable high-end uncertainty. We ignore any uncertainty associated with density calculations (~3%, estimated from variability in amphibole unit cell volume and molar mass calculation) and composition of calibration gas (~1%) [23]. The calibration gas contains atmospheric ratios of noble gas isotopes but the elemental abundances are non-atmospheric to facilitate analysis. Helium measurements are generally >10x the absolute value of the He blank but can approach 2x for small volume analyses on low solubility amphiboles (e.g. richterite). Neon measurements are generally >5x the absolute value of the Ne blank but approach for the blank small volume analyses on low solubility amphiboles. All uncertainties are one standard deviation.

Evidence for Measurement of Solubility:

Henry's constants for He dissolved into amphibole are plotted against P_{He} , duration, depth, and temperature in Supplementary Figure 1 A, B, C, and D respectively. No obvious systematics are present. Fact the Henry's constants do not vary with P_{He} indicates that Henry's Law applies for the experimental conditions explored ($P_{\text{He}} < 1.5$ kbar) and that reported Henry's constants are applicable to systems with natural (lower) noble gas fugacities. The lack of temperature or duration dependence for He solubility strongly argues for a close approach to equilibrium that is unaffected by decomposition of the amphibole. Importantly, the insignificant temperature dependence for He solubility supports extrapolation of results to both hydrothermal and magmatic systems.

Depth profiling was accomplished by ablating sequentially deeper pits at different locations on the mineral surface, effectively increasing the average depth of material sampled in a single analysis (Supplementary Figure 1C, 2, 3, and 4). In general, no systematic He gradients (plotted as apparent Henry's Law constants) were observed, providing supporting evidence for a close approach to equilibrium for a given experiment. The notable exceptions are actinolites from experiments 29 and 30. These experiments are relatively cool (680°C) and short duration experiments (17 and 40 hrs, respectively), suggesting the profiles are diffusion gradients. However, depth profiling of other amphibole run at similar conditions or conditions less conducive to obtaining near surface equilibrium do not reveal He concentration gradients. It has been argued that Ar diffusion in amphibole is more rapid when the ring sites are unoccupied³⁷. Current observations support the notion that He diffusion is affected by amphibole composition but the correlation does not appear to be a simple positive relationship to unoccupied ring site

concentration. No attempt was made to orient the samples, and it is possible anisotropy could cause some of the variability in the data.

Helium solubility is calculated as the uncertainty-weighted mean of the individual measurements for a single phase, unless there were clear concentration gradients, as noted for actinolites in experiment 29 and 30. The solubility for experiments with concentration gradients is estimated by applying a diffusion model to the data and fitting for diffusivity and surface concentration. Surface concentrations are assumed to be solubility. This method is discussed further below.

Helium data from richterite in experiment 14 are significantly higher than the other three richterite experiments conducted (experiment 23, 33, and 34). Given the close agreement in the later experiments, we consider experiment 14 an outlier. No other amphibole was run in experiment 14, so it is unclear if the apparent high He solubility is the result of an experimental or starting material artifact. Nonetheless, the shift is relatively small and does not affect the conclusions of this work.

Calculation of Solubility and Diffusivity from Concentration Profiles:

Neon solubility in amphibole can be estimated using either near-surface depth profiling or by using He as an internal standard. These approaches allow for solubility estimations of slower diffusing noble gases that only equilibrate with the near-surface of the mineral. In Supplementary Figure 2, Ne/He (molar ratio) is plotted against pit depth for the longest duration, highest temperature experiments where Ne was present (34 and 36).

Higher Ne/He is observed for progressively shallower pits, as expected for a system where Ne is less equilibrated than He. To quantify solubility and diffusivity, a one-dimensional, semi-infinite medium, constant source diffusion model is fit to the concentration-depth data. Because the reported concentrations are depth averages rather than concentrations at discrete depths, the model calculates the predicted depth-averaged concentration for each pit depth and fits for a least squares solution for diffusivity and surface concentration (solubility, Supplementary Figure 3). Uncertainty envelopes (Supplementary Figure 3) are calculated using an F-Test and show a negative correlation between solubility and diffusivity. Often this correlation results in extreme uncertainty towards high solubility and low diffusivity, but some (3) experiments yield reasonable uncertainty limits for solubility and diffusivity. There is good agreement between calculated Ne solubility for the same phase run in different experiments despite large calculated uncertainties, and Ne solubility correlates with He solubility. Both of these observations suggest that Ne solubility estimations are accurate. In addition to the depth profiling, a series of very shallow trenches were ablated on the green actinolite from experiment 36. The geometry of these trenches is not amenable to precise volume determinations, but the Ne/He ratio can be quantified nonetheless. These data are plotted as larger symbols at 0 μm depth (Supplementary Figure 2) and represent lower bounds for the solubility ratio of Ne to He. Uncertainty on Ne/He for trenches is propagated as independent and random error associated with the noble gas analysis and does not include error in the pit volume. Actual average depths for trenches are $\sim 0.25 \mu\text{m}$ but poorly known and variable. The absolute noble gas concentrations of these trenches are not reported because the volume calculations are deemed unreliable.

Comparison of Ne and He data indicates Ne is approximately half as soluble on a molar basis (Figure 3, Supplementary Figure 2). Notably, Ne solubility also correlates with the density of unoccupied rings, indicating unoccupied ring sites host noble gases heavier than He. Uncertainty in fitted Ne solubility and diffusivity is considerable, but to a first order, the data scatter around a diffusion coefficient of $5 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ for a temperature of 850-875 °C. This value is faster (50x) than predicted Ar diffusion coefficients for the same conditions based on aggregate stepped heating experiments, where radiogenic Ar was degassed ³⁸. Based on the diffusion parameters for Ar determined by stepped heating experiments, the characteristic Ar diffusive length scale for experiment 36 (92 hr duration) is $\sim 1 \text{ } \mu\text{m}$, which is resolvable by the 193 nm laser used in this study. The lack of a concentration profile suggests that Ar uptake from the pressure medium is slower than outgassing of radiogenic Ar, but more work is needed to verify this initial observation.

Neon was present in experiment 33 but concentrations were too low to allow for any estimation for the surface concentration or diffusivity. Argon was present in experiments 33, 34, and 36. As with Ne in experiment 33, the concentrations were too low for solubility or diffusivity estimations, although the highest concentrations come from the shallowest pits measured for this experiment.

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