

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

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The chemical evolution of both the Earth's atmosphere and mantle can be traced using noble gases^{1–5}. Their abundance in mantle and atmosphere reflects a balance between the flux of noble gases from the Earth's interior through magmatism, and the recycling of noble gases from the atmosphere back into the mantle at subduction zones. The flux of noble gases back into the mantle has long been thought to be negligible¹. However, analyses of samples from the mantle now suggest that this recycling flux is more significant^{6–8}, but the responsible mechanisms are unclear. Here we present high-pressure experimental measurements that demonstrate high solubility of noble gases in amphibole, an important hydrous mineral in altered oceanic crust^{9–11}. Noble gas solubility correlates with the concentration of unoccupied A-sites, which consist of a pair of opposing tetrahedra rings. We conclude that A-sites are energetically favourable locations for noble gas dissolution in amphibole that could allow recycling of noble gases into the mantle by subduction of altered oceanic crust. As many hydrous minerals in subducting slabs, such as serpentine and chlorite, have lattice structures similar to the A-site in amphibole, we suggest that these minerals may provide even more significant recycling pathways^{7,11}.

The analysis of noble gases in basaltic materials derived from the mantle is complicated by ubiquitous atmospheric contamination¹². The prevalence of these modern atmospheric contaminants makes it difficult to confidently determine whether different mantle reservoirs contain an intrinsic recycled component that is ultimately derived from Earth's palaeo-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^{5,6,13–18}. The fact that this heterogeneity exists requires long timescales 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^{7,8,19–21}, leaving potential transport mechanisms for noble gases into subduction zones and the convecting mantle unclear^{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 (Fig. 1), a common mineral in AOC. Amphibole comprises 1.5–12% of bulk

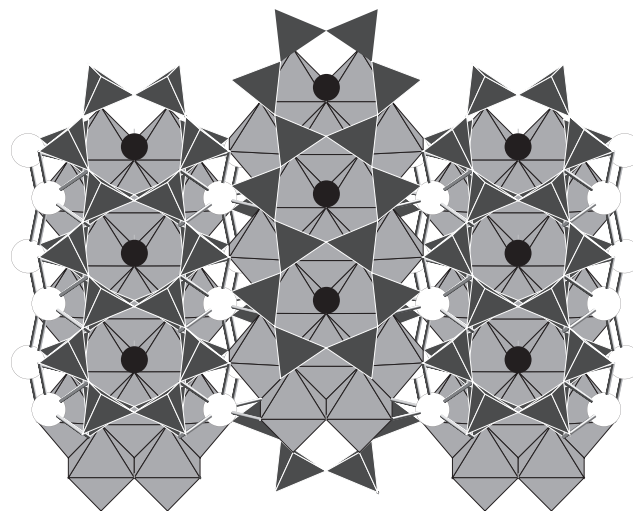


Figure 1 | Amphibole lattice structure. The A-site, or ring site, in amphibole consists of an opposing pair of tetrahedral rings bound in a hexagonal pattern. It is a large site and unoccupied when charge balance is satisfied by the other cations in amphibole. The ring site location is marked by larger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

basaltic crust and can locally occupy 50% of AOC (refs 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 (for example, H₂O, F, Cl). High solubility would imply that noble gases could be recycled through AOC (at least to the depth of amphibole breakdown, ~100 km) along with other volatiles, whereas 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 and Table S1). 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 (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 $0.2\text{--}1 \times 10^{-9}$ (mol g⁻¹ bar⁻¹), whereas actinolite ($0.7\text{--}1 \times 10^{-8}$) and tremolite

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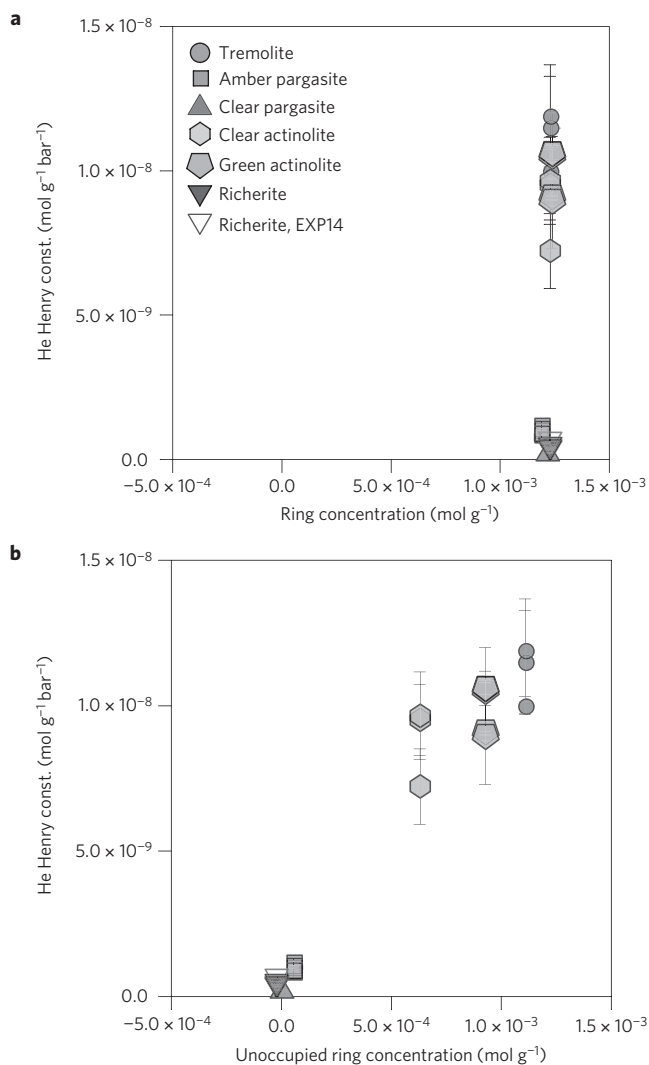


Figure 2 | Helium solubility in amphibole. a,b, Helium Henry's constants in amphiboles plotted against ring-site concentration (mol g^{-1}) (**a**) and unoccupied ring-site concentration (**b**). Helium solubility is high compared with mantle minerals and correlates with the concentration of unoccupied ring sites rather than 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.

(1×10^{-8}) have significantly higher solubilities (Fig. 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 Fig. S1). These findings demonstrate a close approach to equilibrium was achieved for He, and so diffusional disequilibrium effects do not seem to have influenced the measured concentrations. The lack of temperature dependence of He solubility indicates that 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 Fig. S2). 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). Owing 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 that, as for He, Ne solubility is high, with actinolite having higher solubilities than pargasite and richterite (Fig. 3). The best-fit Henry's constants for Ne are 1×10^{-10} ($\text{mol g}^{-1} \text{bar}^{-1}$) for richterite, $8\text{--}9 \times 10^{-10}$ for amber pargasite, and $3\text{--}4 \times 10^{-9}$ for the actinolites (Fig. 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 $(\text{Si, Al})\text{O}_4^{-4,-5}$ tetrahedra rings (Fig. 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 favourable 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 amphiboles. However, He solubility does show an excellent correlation with the concentration of unoccupied ring sites in the amphiboles (Fig. 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.

Although analytical uncertainties are greater, Ne solubility also correlates with unoccupied ring concentration (Fig. 3a). For actinolite and richterite, He is approximately twice as soluble as Ne, whereas He is marginally more soluble in pargasite (Fig. 3b). As 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, although polarizability may play a role in noble gas solubility, it probably 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 AOC (ref. 26), 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 that unoccupied $(\text{Si, Al})\text{--O}$ 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 that all noble gases may have a high affinity for unoccupied ring sites, regardless of the structure of the material surrounding the ring.

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Acknowledgements

We thank N. Chatterjee for his assistance with major element analysis and M. Chon for his assistance with the pit volume analysis. This work was supported by NSF EAR-1019229.

Author contributions

All authors contributed to writing the manuscript and interpretation of the data. C.R.M.J. and S.W.P. developed the hypothesis leading to the experiments. C.R.M.J. conducted the experiments. S.P.K. developed analytical techniques for the noble gas analysis and oversaw analysis of experiments.

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.

Competing financial interests

The authors declare no competing financial interests.