1 Title: Noble gases recycled into the mantle through cooler subduction
2 zones

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26 **Abstract**

27 Subduction of hydrous oceanic lithosphere replenishes the mantle volatile inventory.
28 Substantial uncertainties exist on the magnitudes of the recycled volatile fluxes and it
29 is unclear whether Earth surface reservoirs are undergoing net-loss or net-gain of H₂O
30 and CO₂. Here, we develop noble gases as tracers for deep volatile cycling.
31 Specifically, we construct and apply a kinetic model to estimate the effect of
32 subduction zone metamorphism on the elemental composition of noble gases in
33 amphibole – a common constituent of altered oceanic crust. We show that progressive
34 dehydration of the slab leads to the extraction of noble gases, linking noble gas deep
35 cycling to H₂O. Noble gases are strongly fractionated within hot subduction zones,
36 whereas minimal fractionation occurs along colder subduction geotherms. This
37 implies that the observed Ar-Kr-Xe elemental pattern of the mantle is dominated by
38 the injection of noble gases through colder subduction zones. We estimate a present-
39 day bulk recycling efficiency of 5-35% and 60-80% for ³⁶Ar and H₂O bound within
40 oceanic crust, respectively. Given that hotter subduction dominates over geologic
41 history, this result highlights the importance of cooler subduction zones in regassing
42 the mantle and in affecting modern volatile budget of Earth's interior.

43

44 **Keywords**

- 45 1. Noble gases
- 46 2. Subduction zone processes
- 47 3. Mantle geochemistry
- 48 4. Deep water cycle

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51 **1. Introduction**

52 Subduction governs the transfer of volatile element species from the Earth's exterior
53 into its deep interior. Volatiles, including H₂O, CO₂ and the noble gases, are enriched
54 in the oceanic crust before being delivered to subduction zones where they are
55 partially liberated from the down going slab through metamorphic reactions (Kerrick
56 and Connolly, 2001; Peacock, 1990). The distinct isotopic composition of noble gases
57 in the atmosphere and mantle has long been interpreted to indicate ineffective transfer
58 of volatiles to the mantle during subduction (Staudacher and Allègre, 1988).

59 However, the subduction barrier concept is being challenged by several important
60 observations that suggest noble gases are subducted beyond depths of arc magma
61 genesis and into the mantle. Measurements of exhumed portions of oceanic
62 lithosphere show that hydrated sections of the slab have a capacity to host significant
63 quantities of seawater-derived noble gases (Chavrit et al., 2016; Kendrick et al., 2013;
64 Kendrick et al., 2011). Metasomatised mantle wedge peridotites preserve elemental
65 noble gas compositions similar to sedimentary pore fluids (Kobayashi et al., 2016;
66 Sumino et al., 2010). This implies transport of seawater-derived noble gases to depths
67 approaching arc magma genesis. Mantle-derived well gases contain noble gas
68 abundance ratios similar to those of seawater (Holland and Ballentine, 2006), which is
69 distinctive from primordial components. This finding is corroborated by isotopic
70 observations that both MORB and OIB sources contain an atmospheric signature of
71 heavy noble gas abundances attributed to subduction (Caracausi et al., 2016; Holland
72 and Ballentine, 2006; Holland et al., 2009; Mukhopadhyay, 2012; Parai et al., 2012;
73 Pető et al., 2013). Furthermore, recent seismic tomographic imaging implies that slabs
74 have the potential to transport noble gases and associated volatiles through the mantle

transition zone, possibly to the core-mantle boundary (French and Romanowicz, 2015; Van der Hilst et al., 1997).

Despite observational evidence in support of noble gas recycling, the physical mechanism responsible for injecting noble gases into Earth's deep interior mantle remains unclear. An important constraint is that the elemental pattern of noble gases input into subduction zones is remarkably similar to the elemental pattern of noble gases that ultimately reach the post-arc mantle (Chavrit et al., 2016; Holland and Ballentine, 2006; Kendrick et al., 2011; Fig. 1). This implies that the physical process responsible for recycling noble gases must not impart elemental fractionations within the gases ultimately input into the mantle. This study seeks to identify the conditions that minimize noble gas fractionation during the subduction of oceanic crust – the lithology responsible for the majority of water recycling (van Keken et al., 2011).

Minimal elemental fractionation of recycled heavy noble gases is consistent with subduction of unbound pore waters (Holland and Ballentine, 2006), but this is physically implausible given the efficacy of porosity-reduction during subduction and open-system nature of the dehydrating slab (Connolly, 2010). Instead, we focus on recent experimental evidence highlighting the potential importance of mineral-bound noble gases in the deep noble gas cycle (Jackson et al., 2013, 2015). Specifically, it has been demonstrated that minerals with ring structures (e.g. amphibole, serpentine, and mica) have relatively high noble gas solubility. Given that these minerals are volumetrically significant constituents of altered oceanic crust (AOC), they have the potential to act as carrier phases for noble gases and H₂O.

Here, we explore the combined roles of kinetic fractionation and mineral-fluid partitioning of noble gases during subduction to address the questions: 1) what controls the elemental fractionations of noble gases during subduction and 2) do the noble gases trace subducted water? Using reported solubility and diffusivity data for noble gases in amphibole, we formulate a kinetic model to simulate the diffusion- and solubility-controlled redistribution of noble gases between amphibole and fluid during subduction. We show that hot subduction zones promote elemental fractionations within the gases retained in the slab, which is inconsistent with observations surrounding noble gas recycling, while cooler subduction zones tend to recycle unfractionated noble gases. Thus, the noble gas elemental pattern of the MORB may be explained by cooler slabs controlling the distribution of volatiles in the mantle.

2. Noble gas behavior during subduction of oceanic crust

2.1 The role of amphibole

Our study focuses on amphibole because it is a ubiquitous and voluminous constituent of AOC and has been demonstrated to be a favorable mineral for noble gas incorporation (Chavrit et al., 2016; Jackson et al., 2013, 2015; Kendrick et al., 2015; Tolstikhin et al., 2016). Given these observations, we assume that amphibole controls the retention of noble gases in AOC. Amphibole forms during hydrothermal alteration of oceanic crust at temperatures above ~300 °C (Alt et al., 1985) and remains stable during subduction to ~3 GPa (Poli and Schmidt, 2002). During subduction amphibole breakdown is governed by continuous metamorphic reactions that release up to 2 wt.% H₂O (Kerrick and Connolly, 2001; Poli and Schmidt, 2002). Because serpentinite-group minerals, and not amphibole, are likely key carrier phases for noble gases in the hydrous oceanic mantle, we restrict our analysis to the oceanic crust,

comprising a sediment layer underlain by layers of volcanic dykes and gabbros, respectively. Figure 2 shows the calculated distribution of amphibole throughout oceanic crust undergoing subduction along P - T trajectories representative of cold (Honshu), intermediate (Nicaragua) and hot (Cascadia) subduction. In each of the subduction zones, amphibole is predicted to be stable from depths < 20 km to ~ 100 km, below which amphibole breaks down, marking the blueschist to eclogite transition.

2.2 Solubility and diffusivity of noble gases in amphibole

Elemental fractionations of noble gases derived from amphibole are controlled by their relative solubilities and diffusivities in the crystal lattice and grain boundary network. Recent experimental work constrains both the solubility and diffusivity of noble gases in amphibole (Jackson et al., 2013, 2015; Jackson et al., 2016). The similarity between ionic radii of Na and K and the noble gases permits noble gases to partition onto the amphibole ring-, or, A-site (Jackson et al., 2015). Jackson et al. (2013) showed that the solubility of He, Ne and Ar in gem-quality sodic amphibole are controlled by the density of unoccupied ring sites in the amphibole structure. Solubilities decrease with increasing ionic radius. Using these experimental data, Figure 3 shows a best-fit lattice strain parabola, extrapolated to predict the solubilities of Kr and Xe. Empirical and experimental evidence suggests that solubility of noble gases in silicate minerals and melts increases linearly with fugacity (Carroll and Stolper, 1993; Jackson et al., 2013, 2015). We estimate the magnitude of this effect for noble gas partitioning between amphibole and pure H_2O under the range of P and T associated with AOC dehydration using a modified Redlich-Kwong equation of state (EOS; Flowers, 1979; see SI for details). Results are shown in Fig. 3 in which

amphibole – fluid partition coefficients (K_D) are plotted as a function of P and T along the Nicaraguan slab-top geotherm. As P increases, the noble gases become less ideal and become increasingly soluble in the amphibole lattice; furthermore, this pressure-effect is greatest for the heavy noble gases such that Xe is predicted to become soluble ($D>1$) in the amphibole lattice at pressures in excess of ~ 10 kbar. Enhanced partitioning of noble gases into minerals with increasing P provides an alternative explanation to fluid-limited conditions for the ubiquitous presence of extraneous ^{40}Ar in high-pressure metamorphic minerals (Menold et al., 2016).

Diffusivities of noble gases in amphibole are low relative to other minerals under temperatures relevant to subduction (Harrison, 1982; Jackson et al., 2016). Unoccupied ring sites in amphibole act as traps for migrating noble gases. Independent of this effect, a compilation of these Arrhenius relationships, together with an existing Ar-in-hornblende diffusion relationship (Harrison, 1982), shows that diffusivity decreases with increasing ionic radius (Supplementary Figs. 1 and 2). Although there are no experimentally-determined diffusivities of Kr and Xe in amphibole, correlation between observed values of E_a and D_0 and noble gas ionic radii allows for extrapolation of He-Ar data to estimate Kr and Xe diffusivities (Van Orman et al., 2001), and estimates of both E_a and D_0 . Diffusion parameters are presented in Supplementary Table 1.

3. Model formulation

To investigate the elemental fractionation of noble gases during subduction and AOC devolatilization, we develop a numerical modeling approach that consists of the following steps: (1) output from existing thermomechanical models of subduction

(Syracuse et al., 2010) are discretized to yield a *P-T-time* evolution of a vertical 1-D column passing through the subduction zone; (2) the discretized *P-T-time* relations are then input into a Gibbs energy minimization routine that predicts stable phase equilibria for the subducting column. Water liberated by dehydration reactions is transported vertically upwards, equilibrating with each depth-increment of the column and simulating open-system fluid transport on the scale of the subducting oceanic crust; (3) calculated volumes of amphibole and aqueous fluid for each cell in the column are used as input for a kinetic calculation of intracrystalline diffusion, amphibole – fluid partitioning and mineral growth/dissolution. Computed phase abundances are shown in Supplementary Fig. 3. Noble gases incorporated into the fluid phase are transported upwards in the column with the fluid and kinetically equilibrate with the amphibole fraction in the overlying cell. Noble gases retained in the amphibole fraction are transported within the column. This modeling approach simulates fluid release, fluid and noble gas transport and noble gas elemental fractionation, and predicts the composition of amphibole-derived noble gases from burial and heating along specific subduction zones *P-T* paths (Syracuse et al., 2010).

Phase relations within the subducting slab were calculated as a function of subduction progress using the approach adopted by ref (Konrad - Schmolke et al., 2016). Output from the D80 finite element thermal models from Syracuse et al. (2010) was used as input to Perple_X v.6 (Connolly, 2005), combined with the 2011 version of the Holland and Powell thermodynamic database (Holland and Powell, 2011). The thermal structure of each subduction zone was discretized into a series of slab parallel paths that were divided into a constant number of nodes. Phase relations were calculated at each node along each path starting at the bottom of the slab. Free water

200 was transferred upward into the vertically overlying node where it was added to the
201 bulk rock composition. The solid bulk rock composition, modified to account for
202 re/dehydration, is transferred slab parallel into the adjacent node. This approach
203 simulates progressive movement of a slab perpendicular rock column (the subducted
204 slab) accompanied by a vertical fluid migration. The subducting lithosphere was
205 divided into the following layers, each with a thickness scaling factor: sediments (2),
206 dykes (4), gabbros (5), wet upper slab mantle (6) and dry upper slab mantle layer (6).
207 We do not consider the lowermost mantle wedge. At the initiation of subduction pore
208 fluids are assumed to have been expelled and all water is structurally bound in
209 hydrous phases. Bulk compositions for each layer are presented in Supplementary
210 Table 2. Following the arguments presented in van Keken et al. (2011), we specify
211 that the upper slab mantle contains 2 wt.% H₂O. We do not consider the hydrous
212 oceanic mantle in our kinetic modeling of noble gas transport because amphibole is
213 subordinate to serpentinite group minerals. Fluid was treated as pure H₂O (i.e. XCO₂
214 = 0) using a compensated Redlich-Kwong EOS (Holland and Powell, 1991). Details
215 of the solid-solution models used are provided in Supplementary Table 3. Water
216 released during breakdown of hydrous phases is transported vertically upwards and
217 allowed to equilibrate at each increment within the column. This means that areas of
218 the subducting package that were initially water undersaturated may undergo
219 hydration reactions through invasion of water released by dehydration reactions
220 occurring at depth. Calculated phase relations are used in a mass-balance based
221 diffusion – growth/dissolution calculation to compute the distribution of noble gases
222 between amphibole and fluid at each time step. Details of the numerical model are
223 presented in the SI. Significant portions of *P-T* space in subducting slabs are
224 characterized by fluid-absent conditions. In our model, such conditions are accounted

for by allowing noble gases to accumulate within the rock volume from which release occurred.

4. Model results

Our modeling shows that the transport and distribution of noble gases in the oceanic crust is controlled primarily by the production and availability of a grain-boundary fluid phase. This suggests that noble gases recycled into the mantle preserve a time-integrated record of fluid flux in subduction zones.

Fractional release curves for Ne and Ar in the gabbroic, dyke and sedimentary sections of AOC are shown in Fig. 4. Amphibole in the gabbros loses Ne at shallower depths than the dykes and sediments despite being insulated from heating associated with mantle wedge heating. This is because small volume fractions (~ 0.001) of fluid are computed to be thermodynamically stable in the gabbros from ~ 35 km depth to the depths of amphibole breakdown, allowing Ne to diffuse through the amphibole lattice. Conversely, Ar is relatively less diffusive in amphibole at temperatures < 600 °C (Harrison, 1982), thus, Ar release from the gabbros is due to amphibole dissolution and not diffusion. This is important because noble gas loss by dissolution or breakdown minimizes elemental fractionations.

In contrast to the gabbros, the dykes begin to dehydrate at ~ 50 km and the sediments at ~ 60 km. In both cases, temperatures at those depths are insufficient for significant diffusive loss of the heavy noble gases (Ar-Kr-Xe), implying that amphibole in upper oceanic crust has potential to transport unfractionated heavy noble gases to depths of amphibole breakdown. The stability of amphibole is highest within the gabbros

250 compared to the dykes or sediments within cooler slabs, and therefore, the deepest
251 transport of noble gases is also controlled by the gabbros.

252
253 The extent and depth of dehydration in the oceanic crust is diverse amongst global
254 subduction zones and depends strongly on thermal structure (Fig. 2; van Keken et al.,
255 2011). Whereas cold slabs, such as Honshu, only begin to lose H₂O when they contact
256 the hot overlying mantle wedge at depths >80 km, hot slabs, such as Cascadia, lose a
257 significant fraction of the trench input H₂O flux beneath the fore arc. Figure 5 shows
258 depth-dependent release curves calculated for Ne, Ar, Kr and Xe in cold, intermediate
259 and hot slabs, respectively. Each curve represents the cumulative amount of noble gas
260 residing in amphibole within the oceanic crust as a function of depth to the slab top.

261
262 Our results show that noble gas composition near the depth of amphibole-out in cold
263 and intermediate subduction zones (Fig. 5a and 5b) is essentially unfractionated and
264 that loss is dominated by dissolution or breakdown reactions. Diffusive release of Ne
265 is predicted to occur throughout the entire depth interval of amphibole stability in hot
266 slabs and in the shallower interval in intermediate slabs. All noble gases are
267 diffusively mobile in hot slabs before amphibole breakdown, maximizing elemental
268 fractionations. The effects of sluggish diffusion and pressure-enhanced solubility in
269 amphibole are apparent for Kr and Xe in hot slabs (Fig. 5c). Critically, these results
270 show that the magnitude of noble gas elemental fractionation in amphibole of the
271 oceanic crust is strongly correlated with the thermal grade of subduction and,
272 therefore, with the depth-dependent flux of H₂O from the slab.

We also note that within cooler subduction zones, the noble gases transported deepest by amphibole contain Ne that is unfractionated from Ar-Kr-Xe. This result highlights that Ne could be recycled following the same pathways as heavier noble gases and raises the possibility that a solar nebula component is required to explain the relatively high $^{20}\text{Ne}/^{22}\text{Ne}$ ratios associated with the modern mantle (Holland and Ballentine, 2006; Moreira et al., 1998).

5. Discussion

5.1 Observational support

Several empirical observations support the primary conclusion of our modeling: that light noble gases are preferentially mobilized in hot subduction zones relative to heavy noble gases. Firstly, mantle wedge and forearc peridotites are enriched in Ne and Ar relative to Kr and Xe (Hopp and Ionov, 2011; Kobayashi et al., 2016). This can be interpreted to result from the production of slab fluid at temperatures where Ne and Ar are mobile but Kr and Xe are immobile. Secondly, Hopp et al. (2016) recently showed that clinopyroxene from mafic eclogites of the Dabie-Shan-Sulu continental collision belt preserve a noble gas elemental composition that is consistent with preferential loss of Ar relative to Kr and Xe during subduction to peak metamorphic conditions of 3.1 – 4.4 GPa and 680 – 620 °C. This observation supports the notion that the elemental fractionation predicted to occur under amphibole stability conditions can be transferred to eclogite-facies minerals that can potentially convey the signal into the deep mantle. Finally, Baldwin and Das (2015) used Ar and Ne isotopic data for omphacite and phengite from Late Miocene coesite eclogite in Papua New Guinea to argue that atmospheric Ar and Ne were incorporated during sub-solidus crystallization beneath the forearc. Our described mechanism of preferential

removal of light noble gases during prograde subduction would account for the source of these atmosphere-derived gases.

5.2 Transport of noble gases past amphibole-out

Additional processes are required to preserve the elemental noble gas pattern imparted to subducting oceanic crust by amphibole past depths of arc-magma genesis. Such processes could plausibly involve solubility trapping in eclogite-facies minerals: garnet, omphacite, and phengite, stable as an assemblage to depths in excess of 200 km. Micas, in particular, have a relatively high affinity for noble gases (Baldwin and Das, 2015; Jackson et al., 2015; Li et al., 1994), implying an important role for phengite as a carrier phase during deep subduction. Alternatively, deeper recycling of noble gases may be linked to sections of the slab that remain closed to fluid loss after amphibole-out. Given that a typical mafic eclogite is predicted to contain <2 wt.% H₂O, compared to >4 wt.% in a mafic blueschist (Hacker, 2008; van Keken et al., 2011), a significant fraction of the fluid released during amphibole breakdown should be lost from the oceanic crust (Fig. 2). Combined, this suggests that the flux of surface-derived noble gases will be reduced across the blueschist to eclogite transition. In light of these caveats, we now consider the implications of our modeling for the subduction of noble gases and H₂O.

5.3 Implications for recycling noble gases and water

Isotope analyses of heavy noble gases indicate that 80-90 % Xe and a large fraction of non-radiogenic Ar and Kr in the convecting mantle are ultimately sourced from the atmosphere (Ballentine and Holland, 2008; Holland and Ballentine, 2006; Holland et al., 2009; Moreira et al., 1998; Parai and Mukhopadhyay, 2015; Tucker et al., 2012).

This implies pervasive exosphere – mantle mixing over Earth history. The elemental pattern of noble gases input into subduction zones, as constrained by analyses of altered sections of slab (Chavrit et al., 2016; Kendrick et al., 2015; Kendrick et al., 2011), is similar to the elemental pattern of noble gases in the mantle (Fig.1). This implies that the time-integrated noble gas flux into the mantle produced minimal fractionations. Our modeling shows that an unfractionated influx of noble gases is only achieved along cold and intermediate subduction zones; hotter slabs preferentially lose lighter noble gases at shallow depths, transporting an elementally fractionated signature to the deeper mantle (Fig. 5).

Furthermore, our results allow for a quantitative link between the subducted fluxes of noble gases and mineralogically-bound water in AOC. Assuming that the ^{36}Ar concentration of the MORB mantle is in a steady state, where the ridge flux equals the subducted flux (Porcelli and Wasserburg, 1995), demands a subduction flux of ^{36}Ar $\sim 7 \times 10^{26}$ atoms/yr (calculated using a ^3He flux of 3.2×10^{26} atoms/yr, Bianchi et al. (2010) and the $^3\text{He}/^{36}\text{Ar}$ ratio of popping rock Moreira et al. (1998)). The flux of subducted oceanic crust is 6.2×10^{16} g/yr (Peacock, 1990), and this yields an average ^{36}Ar concentration of $\sim 10^{10}$ atoms/g, taking oceanic crust to be the only lithology involved in recycling noble gases. The initial concentration of ^{36}Ar in AOC is log-normally distributed with an average of $\sim 10^{11}$ ^{36}Ar atoms/g (Supplementary Fig. 4), an order of magnitude larger than the steady-state subduction flux. This implies that on a globally averaged basis $\sim 90\%$ of ^{36}Ar is extracted from subducting AOC prior to Ar-loss closure. Taking into account the standard deviation on the average ^{36}Ar concentration within AOC translates to 65-95% extraction.

Cold and intermediate slabs dominate the modern subduction flux (van Keken et al., 2011), and within these environments, 65-95% extraction of Ar is predicted to occur near the maximum depth of amphibole stability (Chavrit et al., 2016; ~100 km, Figs. 5 and 6). At 100 km depth, 40-20% of the initial H₂O within AOC has also been extracted (Fig. 6). Assuming Ar and H₂O closure are synchronous implies the subduction efficiency of H₂O within cooler subduction zones is 60-80%, and this estimate does not depend strongly on initial assumptions regarding hydration state of the slab. Our estimates are consistent with closure of the AOC to efficient volatile loss beneath the arc volcanic front, ~100 km shallower than previously assumed (van Keken et al., 2011). A full accounting of all potential noble gas carrier phases, such as chlorite, phengite and the serpentinite-group minerals, or a MORB mantle that is experiencing net outgassing of ³⁶Ar will serve to increase the depth of Ar closure, and correspondingly, decrease estimates of H₂O subduction efficiency within AOC. Loss of noble gases prior to amphibole stability will decrease the depth of Ar closure.

Since it is reasonable to assume that hot slabs, more similar to Cascadia, have dominated throughout Earth history, our modeling shows that the modern mantle volatile budget preserves a record of recent recycling associated with cooler subduction environments. We link noble gases to volatiles in general because the extraction of noble gases in down-going slabs is controlled by the production and extraction of fluids, which is, in turn controlled by thermal grade (van Keken et al., 2011). The link between mantle regassing and modern subduction is supported by Xe isotopes of the mantle strongly resembling those of the modern atmosphere, which is distinctive from the ancient atmosphere (Pujol et al., 2011). Cooler subduction zones appear disproportionately important for the volatile budget of the mantle.

374

375 **6. Conclusions**

376 We have modeled the kinetic fractionation of noble gases hosted in amphibole during
377 subduction of hydrous oceanic crust. Model results show that the fractionation of light
378 (Ne) from heavy (Ar-Kr-Xe) noble gases is primarily controlled by the availability of
379 a free grain-boundary fluid phase, which, in turn, is controlled by the thermal grade of
380 subduction. Hot slabs undergo extensive dehydration at depths corresponding to
381 amphibole stability, resulting in the loss of light noble gases from the slab; minimal
382 fractionations are predicted in cold slabs. Interpreted in the context of this finding, the
383 non-fractionated Ar-Kr-Xe pattern of the convecting mantle is consistent with input of
384 noble gases and, by inference, other major volatile phases, through cold and
385 intermediate subduction zones. Due to secular cooling of the Earth's mantle, this
386 process is expected to have increased in efficiency with time. Finally, we have only
387 considered the role of amphibole as a noble gas carrier phase, but the findings of our
388 study are applicable to other minerals. Specifically, if noble gases are diffusively
389 mobile through a mineral lattice at temperatures cooler than the thermal limit of the
390 mineral's stability field, then fractionations are expected to occur. This provides an
391 impetus to understand noble gas kinetics in other carrier phases, including chlorite,
392 lawsonite and antigorite.

393

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399

400 **Figure and Table Captions**

401 **Figure 1. Noble gas concentrations in altered oceanic crust.** Data from Chavrit et
402 al. (2016), Kendrick et al. (2013), Kendrick et al. (2011), Matsuda and Nagao (1986),
403 Moreira et al. (2003) and Staudacher and Allègre (1988). The compositions of MORB
404 and seawater are shown as reference slopes. The composition for the least
405 contaminated mantle is from Kendrick et al. (2011). Note the slight enrichment
406 towards heavier noble gases with respect to seawater.

407

408 **Figure 2. Amphibole stability and dehydration during subduction.** Upper panels
409 show the dehydration flux across the slab-mantle interface for Honshu, Nicaragua and
410 Cascadia subduction zones. Lower panels show the distribution of amphibole in AOC.
411 Red lines illustrate the position of the arc front relative to the slab. Dashed black lines
412 represent the base of the AOC. Subduction zone thermal models and depth to slab-
413 tops are from Syracuse et al. (2010).

414

415 **Figure 3. Solubility of noble gases in amphibole.** Panel **a.** Lattice strain parabola
416 (Blundy and Wood, 1994) fitted to experimentally determined Henry's Law solubility
417 coefficients (Jackson et al., 2013, 2015) for He, Ne and Ar in unoccupied ring site-
418 rich amphibole (actinolite). Solubility coefficients for Kr and Xe are calculated by
419 extrapolation (open symbols). Best fit parabola ($H_0^{n+} = 7.08 \times 10^9$ mol/g.bar and $E_M^{n+} =$
420 4.6×10^{21}) calculated using a non-linear least squares fitting routine. Ionic radii are van
421 der Waals radii values taken from Dean (1985). Data point uncertainties are 2σ . Panel
422 **b.** Variation of noble gas mineral – fluid partition coefficient (K_D) as a function of T
423 and P along the Nicaraguan slab-top geotherm (Syracuse et al., 2010). Curves

calculated using the Redlich-Kwong EOS (Flowers, 1979) and the solubility coefficients presented in panel **a**. Increasing non-ideality of noble gases at higher pressure causes values of K_d to increase up- P .

Figure 4. Fractional release curves for Ar and Ne in the AOC. Calculations are for the Nicaraguan subduction zone. Note that uptake of Ar in panel **a** occurs in response to the increased solubility of Ar in amphibole up-pressure as amphibole crystal rims equilibrate with Ar-bearing fluids released from underlying rock volumes.

Figure 5. Depth-dependent release of noble gases. Panels show the cumulative mass fraction of amphibole-borne Ne, Ar, Kr and Xe in the descending oceanic crust for representative cold (**a**), intermediate (**b**) and hot (**c**) subduction zones. Yellow shaded regions represent depth-intervals over which amphibole is not stable.

Figure 6. Concentrations of ^{36}Ar and mineral-bound H_2O in AOC. Vertical arrow in left panel represents the steady-state (SS) AOC ^{36}Ar concentration. Horizontal arrows connect maximum and minimum AOC ^{36}Ar concentrations with respective mineral-bound H_2O concentrations.

Supplementary Figure 1. Correlation of E_a and D_0 with ionic radius for noble gases in amphibole. Lines in panels **a** and **b** are second-order polynomial curves fit to the measured Arrhenius parameters for He, Ne and Ar described in the text. Values for Kr and Xe are obtained by extrapolation. Ionic radii are van der Waals values taken from Dean (1985).

Supplementary Figure 2. Arrhenius relationships for noble gas diffusion in amphibole.

Supplementary Figure 3. Calculated mineral abundances' for AOC undergoing subduction.

Supplementary Figure 4: Log-normal distribution of AOC ^{36}Ar concentrations.
Data sources as Fig.1.

Supplementary Table 1. Noble gas in amphibole diffusion parameters.

Supplementary Table 2. AOC compositions used for phase equilibria modeling.

Supplementary Table 3. Solution models used for phase equilibria modeling.

Supplementary Information

1. Noble gas solubility in amphibole and aqueous fluids

Amphibole typical of the AOC (e.g. glaucophane) is predicted to have a high density of unoccupied ring sites that can accommodate noble gases. We use average values for He, Ne and Ar amphibole Henry's Law constants that are calculated from experimentally determined values for gem quality actinolite and pargasite (Jackson et al., 2013, 2015) ($H_{\text{He}} = 1 \times 10^{-9}$, $H_{\text{Ne}} = 9 \times 10^{-10}$, $H_{\text{Ar}} = 7 \times 10^{-10}$ mol/g.bar). Solubility constants for Kr and Xe are calculated through extrapolation of a lattice strain parabola using a non-linear least squares fitting procedure (Fig. 3; $H_{\text{Kr}} = 0.15 \times 10^{-8}$, $H_{\text{Xe}} = 0.04 \times 10^{-8}$ mol/g.bar). Whilst in reality, amphibole stabilized during

hydrothermal alteration of oceanic crust will continuously recrystallize during subduction, the effect of changing amphibole composition on solubility is small compared to the effects of burial, heating and fluid abundance (Jackson et al., 2016). Therefore, we chose not to incorporate the effect of amphibole composition on amphibole noble gas solubility.

The solubility of the noble gases in aqueous fluid as a function of P and T was calculated using a modified Redlich-Kwong EOS (Flowers, 1979). Noble gases were treated as non-polar molecules. Molar volumes and fugacity coefficients for the H_2O + noble gas mixture were calculated using equations 1 and 21 from Flowers (1979), combined with the relevant critical point P and T values. Resultant fugacity coefficients were used to calculate fugacities, assuming lithostatic fluid pressures. Partition coefficients between aqueous fluid and amphibole as a function of P and T were computed using the experimentally-determined Henry's constants derived by Jackson et al. (2013, 2015). The RKE EOS predicts that the noble gases become increasingly non-ideal with pressure, favoring stronger mineral partitioning (Fig. 3). This is consistent with the experimental evidence showing an increase in the solubility of Ar in silicate melts with increasing pressure (White et al., 1989) and provides an attractive explanation for the ubiquitous presence of extraneous ^{40}Ar in high-pressure metamorphic rocks (e.g. Smye et al., 2013).

2. Noble gas diffusivity in amphibole

Diffusivity parameters for He and Ne were taken from the experimental work of Jackson et al. (2016). We used average values of E_a and D_0 from those determined for richterite and tremolite (Jackson et al., 2016). Combined with an Ar-in-hornblende

diffusion relationship from Harrison (1982), the correlation of both E_a and D_0 with ionic radius (Supplementary Fig. 1) allows us to extrapolate to estimate values for E_a and D_0 for Kr and Xe, respectively. The resultant Arrhenius relationships are presented in Supplementary Fig. 2. Both E_a and D_0 increase with increasing ionic radius, causing a progressive decrease in diffusivity through amphibole from Ne to Xe at temperatures relevant to amphibole stability. Diffusivity parameters used for the calculations are presented in Supplementary Table 1.

3. Kinetic model description

During each time step and at each spatial node within the subducting column we consider closed system redistribution of noble gases between amphibole and grain boundary fluid. We define the reactive volume as 1 cc comprising volumes of amphibole (V_{amph}) and fluid (V_f) that are calculated by thermodynamic phase-equilibria modeling (see Methods section of the main text); the remainder of the reactive volume is considered as non-reactive with respect to the noble gases. Natural rocks contain amphibole with a range of grain sizes and crystal geometries. Here, we simplify the kinetic model by assuming isotropic diffusion in spherical crystals with a homogenous radius, R . Grain size is determined by the number of amphibole crystals assigned to the reactive volume; our preferred value of 2000 nucleation points per cc gives typical grain sizes between 200 and 1000 μm , depending on the volume of amphibole predicted. These simplifications mean that the net diffusive flux of noble gases through amphibole will be the same independent of direction and reduces the model to a single spatial variable, r . We do not consider diffusion in the fluid domain on the grounds that diffusion of noble gases in aqueous fluid is likely to be several orders of magnitude faster than through the amphibole. Amphibole growth or

dissolution is simulated using a power-law relationship and values of R for adjacent time steps. Time steps are calculated using the convergence rates presented in Syracuse et al. (2010). Finally, the equilibrated noble gas concentration of the fluid phase is passed to the vertically overlying cell where the calculations are repeated; in this scheme, the noble gases follow the same path as the fluid phase. In the case where there is no fluid predicted to be stable noble gases are retained in amphibole. With these assumptions our governing equations describing the re-equilibration of noble gases between amphibole and aqueous fluid are as follows:

(i) The conservative form of the diffusion equation for amphibole:

$$\frac{\partial}{\partial t} (r_j^\gamma C_s^i) + \frac{\partial}{\partial r} (r_j^\gamma F_c C_s^i) = 0 \text{ on } \Omega_s \in [r_{min}, R] \times [0, t_j], \quad \text{Eq. S1}$$

where, r_j is the radial index, C_s^i is the concentration of noble gas, i , in the amphibole crystal (solid), γ reflects the radial dependence of volume and area in cylindrical and spherical coordinates, where $\gamma=1$ is cylindrical and $\gamma=2$ is spherical. The terms $r_j^\gamma C_s^i$ and F_c represent the accumulation and diffusive flux of noble gases in the amphibole grain, respectively. Fick's first law gives the diffusive flux as:

$$F_c = -D^i \frac{\partial C_s^i}{\partial r}, \quad \text{Eq. S2}$$

(ii) Local equilibrium between the fluid and surface of the amphibole:

$$C_s^i|_{r=R} = K_D^i C_f^i, \quad \text{Eq. S3}$$

546 where, C_f^i represents the concentration of noble gas i in the fluid phase and K_D^i is the
 547 corresponding partition coefficient.

548

549 (iii) Symmetry condition at the center of the amphibole grain:

550

$$551 \quad \left. \frac{\partial C_s^i}{\partial r} \right|_{r=0} = 0, \quad \text{Eq. S4}$$

552 (iv) Initial conditions in the amphibole and fluid fractions are given by:

553

$$554 \quad C_s^i(r, 0) = C_s^{i,0}, \quad \text{Eq. S5a}$$

$$555 \quad C_f^i(0) = 0, \quad \text{Eq. S5b}$$

556 (v) Fluid-present boundary condition: mass balance of the diffusive flux between
 557 amphibole and the fluid:

558

$$559 \quad \frac{d(V_f C_f^i)}{dt} = - \frac{d}{dt} \left\{ \sum_j N \int_0^R 4\pi r_j^2 C_s^i dr_j \right\},$$

560 Eq. S6

561 (vi) Fluid-absent boundary condition: retention of noble gases in the amphibole
 562 crystal:

563

$$564 \quad \left. \frac{\partial C_s^i}{\partial r} \right|_{r=R} = 0, \quad \text{Eq. S7}$$

565 where V_f is the volume of fluid present and N is the number of amphibole grains in the
 566 rock volume. The volume integral on the right hand side of Eq. S6 includes the effects
 567 of both amphibole growth/dissolution and diffusion.

568

569 (vii) Power-law evolution of the amphibole-fluid interface:

570

571 $R = R_0 + (R_{fin} - R_0)/(t/t_{fin})^m,$ Eq. S8

572 (viii) Diffusivity is calculated using the temperature-dependent Arrhenius function:

573

574 $D^i = D_0^i \exp\left(-\frac{E_a^i}{QT}\right),$ Eq. S9

575 where D_0^i and E_a^i represent the exponential prefactor and the activation energy; Q is

576 the universal gas constant.

577

578 Equations 1-9 are solved numerically using a fully implicit finite volume

579 discretization, following the approach presented by Hesse (2012). Concentration at

580 the amphibole-fluid interface is discretized by combining equations S1, S3 and S6/S7.

581 At each time step the concentration of noble gas in the amphibole and fluid phases is

582 calculated simultaneously. For each amphibole grain spatial nodes are added or

583 removed to represent growth or dissolution, respectively. The algorithm is

584 unconditionally stable and fully recovers mass in the solid and fluid phases at each

585 time step.

586

587 Initial (t_0) amphibole noble gas concentrations were derived from a compilation of

588 AOC analyses (Fig. 1): Ne = 5.8×10^{-12} mol/g, Ar = 1.5×10^{-10} mol/g, Kr = 1.7×10^{-12}

589 mol/g and Xe = 2.2×10^{-13} mol/g.

590

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Figure 1

Honshu (*Cold*)

Nicaragua (*Intermediate*)

Cascadia (*Hot*)

Figure 2

Figure 3

Figure 4

Honshu (Cold)

Nicaragua (Intermediate)

Cascadia (Hot)

Figure 5

Figure 6

Figure S1

Figure S2

Figure S3

Figure S4

Table S1: Amphibole noble gas diffusion parameters.

	E_a (J/mol)	D₀ (um²/s)	Source
He	1.19E+05	4.77E+06	Jackson et al. 2016
Ne	1.56E+05	6.75E+05	Jackson et al. 2016
Ar	2.68E+05	2.40E+06	Harrison 1981
Kr	3.04E+05	4.56E+06	Extrapolation
Xe	4.26E+05	5.89E+07	Extrapolation

Table S2: AOC compositions (wt. %) used for phase equilibria modeling.

	H₂O	SiO₂	Al₂O₃	FeO	MgO	CaO	Na₂O	K₂O	Source
Upper slab mantle	2.00	44.71	3.98	8.18	38.73	3.17	0.13	0.00	DMM, Workman & Hart 2005
Gabbros	7.85	49.51	16.75	8.05	9.74	12.50	2.18	0.07	N-MORB, Workman & Hart 2005
Dykes	7.85	49.51	16.75	8.05	9.74	12.50	2.18	0.07	N-MORB, Workman & Hart 2005
Sediments	7.29	58.57	11.91	5.21	2.48	5.95	2.43	2.04	GLOSS, Plank and Langmuir 1998

Table S3: Activity models used for phase equilibria modeling.

Mineral	Model	Source
Na-Ca Amphibole	Amph(DPW)	Dale et al 2005
Clinopyroxene	Omph(HP)	Holland and Powell 2006
Garnet	Gt(HP)	Holland and Powell 1998
Feldspar	feldspar	Fuhrman and Lindsley 1988
Chlorite	Chl(HP)	Holland et al 1998
Epidote	Ep(HP)	Holland and Powell 1998
Olivine	O(HP)	Holland and Powell 1998
Orthopyroxene	Opx(HP)	Holland and Powell 2003
Mica	Pheng(HP)	Holland and Powell 1998
Chloritoid	Ctd(HP)	White et al 2000
Biotite	Bio(HP)	Powell and Holland 1991
Antigorite	Atg	Ideal
A-phase	A-phase	Ideal
Lawsonite	law	Ideal
Zoisite	zo	Ideal
Brucite	B	Ideal
Carpholite	car	Ideal
Clinohumite	chum	Ideal
Talc	T	Ideal
Pumpellyite	pump	Ideal
Prehnite	pre	Ideal
Stilpnomelane	stlb	Ideal