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Noble gases recycled into the mantle through cold subduction zones

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ABSTRACT

Subduction of hydrous and carbonated oceanic lithosphere replenishes the mantle volatile inventory. Substantial uncertainties exist on the magnitudes of the recycled volatile fluxes and it is unclear whether Earth surface reservoirs are undergoing net-loss or net-gain of H_2O and CO_2. Here, we use noble gases as tracers for deep volatile cycling. Specifically, we construct and apply a kinetic model to estimate the effect of subduction zone metamorphism on the elemental composition of noble gases in amphibole – a common constituent of altered oceanic crust. We show that progressive dehydration of the slab leads to the extraction of noble gases, linking noble gas recycling to H_2O. Noble gases are strongly fractionated within hot subduction zones, whereas minimal fractionation occurs along colder subduction geotherms. In the context of our modelling, this implies that the mantle heavy noble gas inventory is dominated by the injection of noble gases through cold subduction zones. For cold subduction zones, we estimate a present-day bulk recycling efficiency, past the depth of amphibole breakdown, of 5–35% and 60–80% for ^{36}Ar and H_2O bound within oceanic crust, respectively. Given that hotter subduction dominates over geologic history, this result highlights the importance of cooler subduction zones in regassing the mantle and in affecting the modern volatile budget of Earth's interior.

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1. Introduction

Subduction governs the transfer of volatile elements from the Earth's exterior into its deep interior. Volatiles, including H_2O, CO_2 and the noble gases, are enriched in minerals within altered oceanic crust (AOC) before being delivered to subduction zones where they are partially liberated from the down going slab through metamorphic reactions (Kerrick and Connolly, 2001; Peacock, 1990). The distinct isotopic composition of noble gases in the atmosphere and mantle has long been interpreted to indicate their ineffective transfer to the mantle during subduction. Staudacher and Allègre (1988) estimated that ∼96% Ar and ∼98% Xe in AOC is removed during subduction in order to maintain mantle isotopic differences relative to air. It is important to note that this subduction barrier concept does not require total extraction of noble gases from the slab, but allows for a small, yet finite, flux of noble gases to be delivered to the mantle during subduction.

Several important observations also suggest that noble gases are subducted beyond depths of arc magma genesis and into the mantle. Early box modeling of mantle Xe isotope evolution was used to identify a finite flux of subducted atmospheric Xe (Porcelli and Wasserburg, 1995a). Measurements of exhumed portions of oceanic and continental lithosphere show that hydrated sections of the oceanic slab, as well as terrigenous lithologies, have a capacity to host significant quantities of seawater-derived noble gases (Baldwin and Das, 2015; Chavrit et al., 2016; Dai et al., 2016; Guo et al., 2017; Honda et al., 2012; Hopp et al., 2016; Kendrick et al., 2013, 2015, 2011; Moreira et al., 2003; Staudacher and Allègre, 1988). Metasomatized mantle wedge peridotites preserve elemental noble gas compositions similar to marine pore fluids (Kobayashi et al., 2016; Sumino et al., 2010). This implies transport of seawater-derived noble gases to depths approaching arc magma genesis. Orogenic peridotites preserve a correla-

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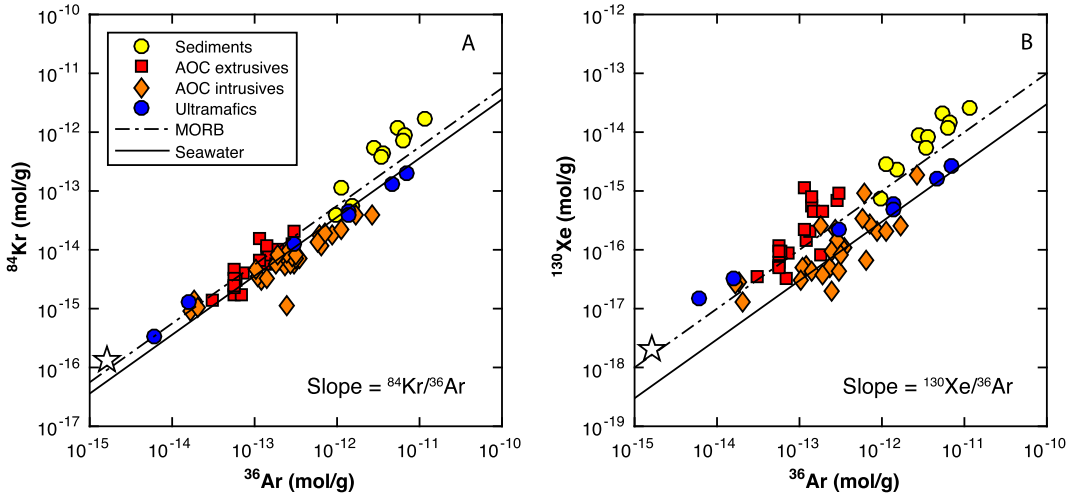

Fig. 1. Noble gas isotope concentrations in altered oceanic crust. Data are from Chavrit et al. (2016), Kendrick et al. (2013, 2011), Matsuda and Nagao (1986), Moreira et al. (2003) and Staudacher and Allègre (1988). The compositions of MORB and seawater are shown as reference slopes and the white stars correspond to the composition of the MORB mantle (Holland and Ballentine, 2006). Note the slight enrichment towards heavier noble gases with respect to seawater.

tion between concentrations of ^{3}He and ^{36}Ar (Matsumoto et al., 2001). This is interpreted to result from mixing between an atmospheric noble gas component in the convecting mantle with noble gases from the degassed upper-mantle. Mantle-derived well gases contain noble gas abundance ratios similar to those of seawater, with minor degrees of Kr and Xe enrichment (Holland and Ballentine, 2006), which is distinctive from primordial components. This finding is corroborated by isotopic observations that both MORB and OIB sources contain an atmospheric signature of heavy noble gases attributed to subduction (Caracausi et al., 2016; Holland and Ballentine, 2006; Holland et al., 2009; Mukhopadhyay, 2012; Parai et al., 2012; Pető et al., 2013; Sarda et al., 1999; Tucker et al., 2012; Yamamoto et al., 2004). Furthermore, recent seismic tomographic imaging shows that slabs have the potential to penetrate the mantle transition zone (French and Romanowicz, 2015; Van der Hilst et al., 1997). If noble gases and associated volatile phases are retained within the slab during subduction, this provides a pathway to transport noble gases and associated volatiles into the deep mantle, possibly to the core–mantle boundary.

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. Subduction of H_2O to sub-arc depths is thought to occur by a series of depth-dependent dehydration and hydration reactions in which aqueous fluids, and, potentially, fluid-mobile volatiles, are passed between different minerals (Hacker, 2008; van Keken et al., 2011). The extent to which this mechanism explains the subduction of noble gases is uncertain.

An important constraint is that the elemental abundance pattern of heavy noble gases (Ar, Kr, Xe) in the MORB mantle is strikingly similar to the elemental pattern of heavy noble gases input into subduction zones (Fig. 1). Whilst the MORB mantle heavy noble gas composition is constrained by only two datasets (Bravo Dome, Holland and Ballentine, 2006 and Popping Rock, Moreira et al., 1998), it is important to note that the elemental patterns of Ar, Kr and Xe from both Bravo Dome and Popping Rock localities are similar if extrapolated to a common ^{20}Ne/^{22}Ne value of 12.5 (Ballentine et al., 2005). At face value, this implies that the physical process responsible for recycling heavy noble gases must not impart significant elemental fractionations within the gases ultimately input into the mantle. Whilst kinetic and transport processes that operate during subduction of AOC are expected to generate some degree of elemental fractionation (Kendrick et al., 2011), preservation of the MORB mantle heavy noble gas signature means that either these processes work against one another to minimize fractionations, or the magnitude of fractionation they impart to slab-bound noble gases is minor. This study seeks to identify the conditions that minimize noble gas fractionation during the subduction of oceanic crust – a critical pathway for the transport of volatiles past sub-arc depths (e.g. van Keken et al., 2011).

Minimal elemental fractionation of recycled heavy noble gases is consistent with subduction of unbound marine 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 and melting 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 solubilities. 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 H_2O.

We focus specifically on amphibole because of the available experimental data, its high affinity for noble gases, and ubiquitous presence in hydrothermally-altered and subducted oceanic crust. This focus is not meant to suggest that amphibole is the only carrier of noble gases and H_2O in subducting slabs. Rather, it is likely an important carrier phase whose behavior in fluid–mineral systems can guide understanding of noble gas transport during subduction in general.

We explore the combined roles of kinetic fractionation and mineral–fluid partitioning of noble gases during subduction to address the following 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 mantle may be explained by cooler slabs controlling the distribution of volatiles in the mantle.

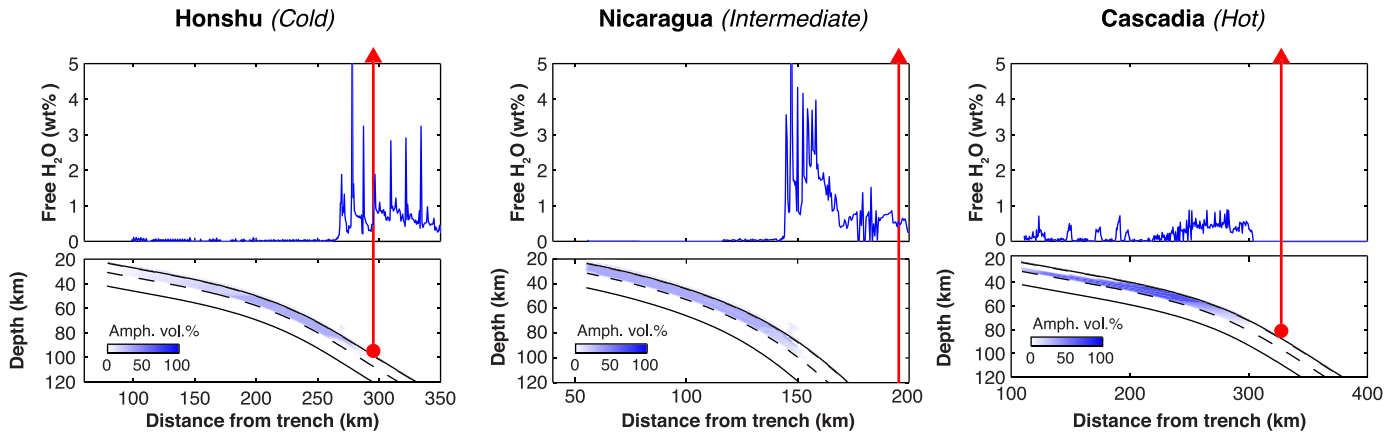

Fig. 2. Amphibole stability and dehydration during subduction. Upper panels show the dehydration flux across the slab–mantle interface for Honshu, Nicaragua and Cascadia subduction zones. Lower panels show the distribution of amphibole in AOC. Red lines illustrate the position of the arc front relative to the slab. Dashed black lines represent the base of the AOC. Subduction zone thermal models and depth to slab-tops are from Syracuse et al. (2010). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 constituent of AOC, comprising 1.2–15% by volume of AOC (Carlson, 2003; Ito et al., 1983), 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). Hydrothermal amphibole is characterized by elevated Cl concentrations (100's to 1000's ppm), consistent with growth during hydrothermal metamorphism of oceanic crustal rocks involving fluids with salinities ranging from seawater to hyper-saline brine (Alt et al., 1985; Jacobson, 1975; Kendrick et al., 2015; Nehlig and Juteau, 1988; Vanko, 1986). Whilst preservation of primary magmatic amphibole is possible, such amphibole is characterized by significantly lower Cl contents and is typically subordinate to high-Cl amphibole in the AOC (e.g. Coogan et al., 2001). The requirement of a fluid phase for the formation of hydrothermal amphibole means that the initial hydration state and the pre-subduction concentration of noble gases in the AOC are correlated.

During subduction, amphibole remains stable to ~3 GPa (Poli and Schmidt, 2002). The breakdown of amphibole is governed by continuous metamorphic reactions that release up to 2 wt.% H_2O (Kerrick and Connolly, 2001; Poli and Schmidt, 2002). Because serpentine 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. Fig. 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, 2016). The similarity between ionic radii of Na and K and the atomic radii of 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, Fig. 3 shows a best-fit lattice strain parabola, extrapolated to predict the solubilities of Kr and Xe. Empirical and experimental evidence suggests that the 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 gases 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. The solubility of noble gases in amphibole increases with P. At low P, solubility follows Henry's Law, whilst at high P conditions the noble gases become increasingly non-ideal and solubility departs from a linear P-dependence. Pressure-enhanced solubility 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 ~1 GPa. 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; Smye et al., 2013).

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. S1 and S2). 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 S1.

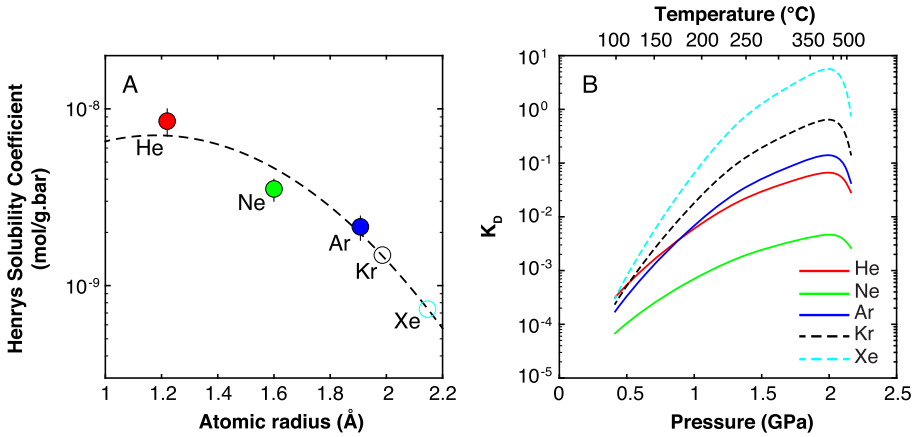

Fig. 3. Solubility of noble gases in amphibole. Panel **a**. Lattice strain parabola (Blundy and Wood, 1994) fitted to experimentally determined Henry's Law solubility coefficients for He, Ne and Ar in unoccupied ring site-rich amphibole (actinolite; Jackson et al., 2013, 2015). Solubility coefficients for Kr and Xe are calculated by extrapolation (open symbols). Best fit parabola calculated using a non-linear least squares fitting routine ($H_0^{n+} = 7.08 \times 10^9$ mol/g.bar) and $E_M^{n+} = 4.6 \times 10^{21}$ – lattice strain parameters from Blundy and Wood (1994). Ionic radii are van der Waals radii values taken from Dean (1985). Data point uncertainties are 2σ. Panel **b**. Variation of noble gas mineral–fluid partition coefficient (K_D) as a function of T and P along the Nicaraguan slab-top geotherm. Curves calculated using the Redlich–Kwong EOS and the solubility coefficients presented in panel **a**. Values of K_d increase up-P due to Henrian-type behavior, modified by the effects of non-ideality. Maximum values of K_d occur at ∼2 GPa and are followed by decreasing values due to the large temperature increase associated with the slab contacting the convecting mantle.

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. S3. 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 zone *P–T* paths.

Phase relations within the subducting slab were calculated as a function of subduction progress using the approach adopted by 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 was transferred upward into the vertically overlying node where it was added to the bulk rock composition. The solid bulk rock composition, modified to account for re/dehydration, is transferred slab parallel into the adjacent node. This approach simulates progressive movement of a slab perpendicular rock column (the subducted slab) accompanied by a vertical fluid migration. The subducting lithosphere was divided into the following layers, each with a thickness scaling factor given in brackets: sediments (2), dykes (4), gabbros (5), wet upper slab mantle (6) and dry upper slab mantle layer (6). We do not consider the lowermost mantle wedge. At the initiation of subduction pore fluids are assumed to have been expelled and all water is structurally bound in hydrous phases. Bulk chemical compositions for each layer are presented in Supplementary Table S2. Following the arguments presented by van Keken et al. (2011), we specify that the upper slab mantle contains 2 wt.% H_2O. We do not consider the hydrous oceanic mantle in our kinetic modeling of noble gas transport because amphibole is subordinate to serpentine group minerals. Fluid was treated as pure H_2O (i.e. $XCO_2 = 0$) using a compensated Redlich–Kwong EOS (Holland and Powell, 1991). Details of the solid-solution models used are provided in Supplementary Table S3. Water released during breakdown of hydrous phases is transported vertically upwards and allowed to equilibrate at each increment within the column. This means that areas of the subducting package that were initially water undersaturated may undergo hydration reactions through invasion of water released by dehydration reactions occurring at depth. Calculated phase relations are used in a mass-balance based diffusion–growth/dissolution calculation to compute the distribution of noble gases between amphibole and fluid at each time step. Details of the numerical model are presented in the SI. Significant portions of *P–T* space in subducting slabs are 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 calculated to be thermodynamically stable in the gabbros from ∼35 km to the depth of amphibole breakdown, ∼95 km, allowing Ne to diffuse through the amphibole lattice. Conversely, Ar

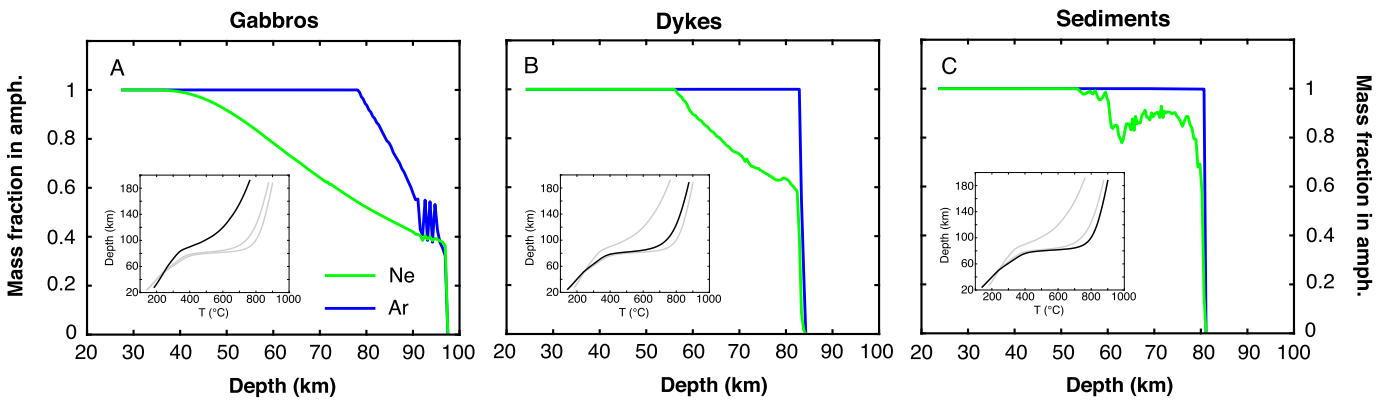

Fig. 4. Fractional release curves for Ar and Ne in the AOC. Calculations are for the Nicaraguan subduction zone. Panels **a**, **b** and **c** show release curves calculated for AOC gabbro, dyke and sediment layers, respectively. Note that uptake of Ar in panel **a** occurs in response to the increased solubility of Ar in amphibole up-pressure as amphibole crystal rims equilibrate with Ar-bearing fluids released from underlying rock volumes.

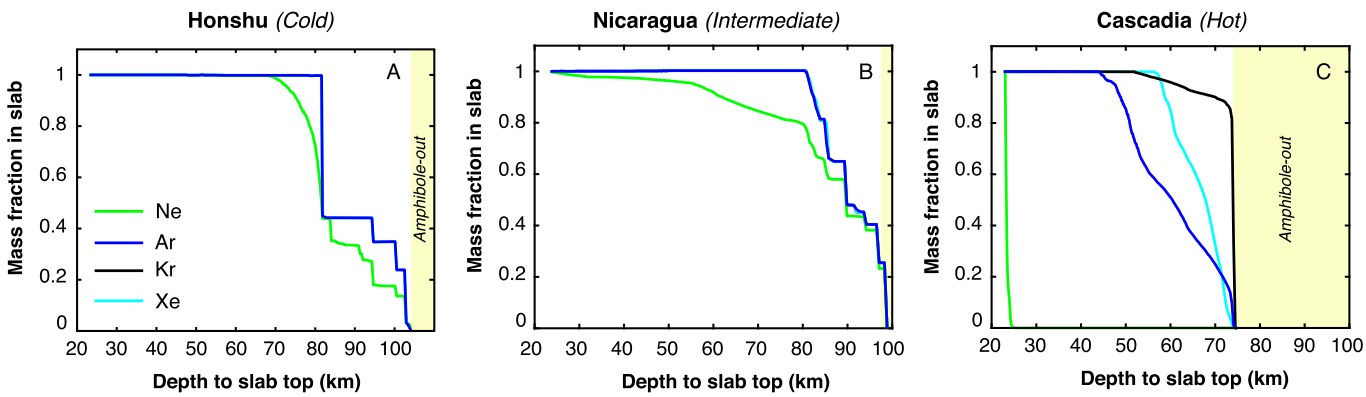

Fig. 5. Depth-dependent release of noble gases. Panels show the cumulative mass fraction of amphibole-borne Ne, Ar, Kr and Xe in the descending oceanic crust for representative cold (**a**), intermediate (**b**) and hot (**c**) subduction zones. Yellow shaded regions represent depth-intervals over which amphibole is not stable. Note that in panels **a** and **b**, curves for Kr and Xe are hidden behind the Ar curve. In panel **c**, Kr is predicted to be retained in the slab relative to Xe. The elevated diffusive mobility of Kr in amphibole permits redistribution of fluid-borne Kr during dehydration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

is relatively less diffusive in amphibole (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 mineral breakdown minimizes elemental fractionations. This behavior is expected for all minerals that retain noble gases up to their *P–T* stability limit.

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

The extent and depth of dehydration in the oceanic crust is diverse among global subduction zones and depends strongly on thermal structure (Fig. 2; van Keken et al., 2011). Whereas cold slabs, such as Honshu, only begin to lose H_2O when they contact the hot overlying mantle wedge at depths >80 km, hot slabs, such as Cascadia, lose a significant fraction of the trench input H_2O flux beneath the fore arc. Fig. 5 shows depth-dependent release curves calculated for Ne, Ar, Kr and Xe in cold, intermediate and hot slabs, respectively. Each curve represents the cumulative amount of noble gas residing in amphibole within the oceanic crust as a function of depth to the slab top.

Our results show that the noble gas composition near the depth of amphibole-out in cold and intermediate subduction zones (Fig. 5a and 5b) is essentially unfractionated and that loss is dominated by dissolution or breakdown reactions. Diffusive release of Ne is predicted to occur throughout the entire depth interval of amphibole stability in hot slabs and throughout a shallower depth interval in intermediate slabs. All noble gases are diffusively mobile in hot slabs before amphibole breakdown, maximizing elemental fractionations. The effects of sluggish diffusion and pressure-enhanced solubility in amphibole are apparent for Kr and Xe in hot slabs. Calculations for Cascadia predict that Kr is effectively redistributed from amphibole in deep portions to shallow portions of the slab by vertically-ascending fluids (Fig. 5c). The continuous dehydration of hot slabs, such as Cascadia, enables mineral-hosted noble gases to diffuse into the grain boundary, resulting in kinetic fractionations. In contrast, cold slabs, such as Honshu, dehydrate discontinuously, resulting in a pulse-like release of non-fractionated noble gases during hydrous mineral breakdown.

Calculated heavy noble gas fractionation trends for bulk AOC undergoing cold and hot subduction are shown in Fig. 6. Starting AOC values for $^{84}Kr/^{36}Ar$ and $^{130}Xe/^{36}Ar$ are calculated from log-normal average concentrations of the mineral data shown in Fig. 1. Comparison between the calculated AOC fractionation trends (gray lines, Fig. 6) and the composition of the MORB mantle (star, Fig. 6) allows us to assess the importance of the thermal grade of subduction to the mantle heavy noble gas composition. The magnitude of Ar–Kr–Xe fractionation associated with hot subduction of AOC means that such recycled material cannot dominate the heavy noble gas flux into the MORB mantle. Rather, the MORB mantle heavy noble gas pattern is consistent with addition of Ar–Kr–Xe along

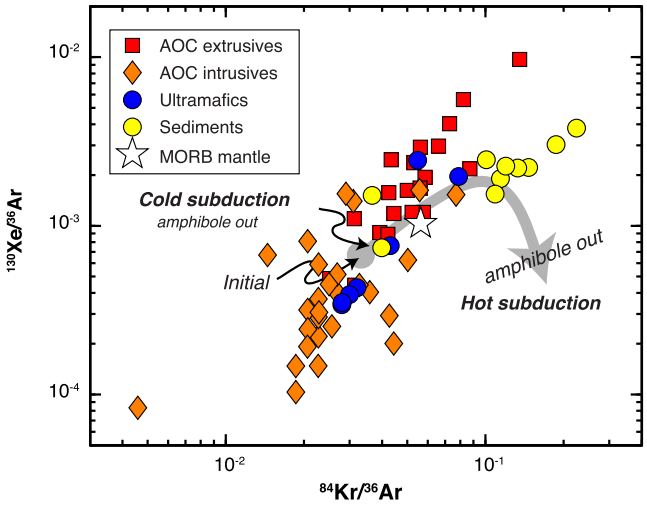

Fig. 6. Heavy noble gas fractionation trends for hot and cold slabs. $^{130}Xe/^{36}Ar$–$^{84}Kr/^{36}Ar$ three element plot showing the cumulative composition of AOC undergoing subduction along hot (gray arrow points down-P) and cold subduction zones. AOC mineral and MORB mantle compositions shown for comparison. Note the negligible fractionation for cold slabs. AOC analyses are the same as presented in Fig. 1; MORB mantle composition from Holland and Ballentine (2006).

cold subduction zones. We note that the mantle composition plots along our calculated fractionation trend for hot subduction. This implies that minor Ar–Kr–Xe fractionations occur within cold slabs at depths in excess of amphibole out. Critically, these results show that the magnitude of noble gas elemental fractionation in amphibole of the oceanic crust is strongly correlated with the thermal grade of subduction and, therefore, with the depth-dependent flux of H_2O from the slab.

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, or other lower pressure AOC minerals, 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; Kelley, 2002; 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.% H_2O, 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 H_2O.

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, but incomplete, atmosphere–mantle mixing over Earth history. The elemental pattern of heavy noble gases input into subduction zones, as constrained by analyses of altered sections of slab (Chavrit et al., 2016; Kendrick et al., 2013, 2015, 2011; Staudacher and Allègre, 1988), is similar to the elemental pattern of heavy noble gases in the mantle (Fig. 1). We note that the elemental pattern of the mantle is currently defined by two samples that are in agreement (Bravo Dome, Holland and Ballentine, 2006 and Popping Rock, Moreira et al., 1998). More analyses of the MORB mantle heavy noble gas pattern are needed to better constrain the magnitude of fractionation that occurs during subduction of atmospheric noble gases. Nevertheless, at face value, the similarity of recycled and MORB mantle heavy noble gas patterns implies that there is minimal elemental fractionation over the time-integrated subduction flux of noble gases into the mantle. Our modeling shows that noble gas fractionations are minimized along cold and intermediate subduction zones; hotter slabs preferentially lose He–Ne–Ar relative to Kr–Xe at shallow depths, transporting an elementally fractionated signature to the deeper mantle (Figs. 5, 6).

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 (O'Nions and Tolstikhin, 1996; Porcelli and Wasserburg, 1995a, 1995b), demands a subduction flux of $^{36}Ar \sim 7 \times 10^{26}$ atoms/yr (calculated using a ^{3}He flux of 3.2×10^{26} atoms/yr from Bianchi et al., 2010, and a value of 0.44 for the $^{3}He/^{36}Ar$ ratio of popping rock from Moreira et al., 1998, assuming a value of 12.5 for $^{20}Ne/^{22}Ne$ Ballentine et al., 2005). 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. This estimate is predicated on the assumption that atmospheric noble gases are not subducted in the mantle portion of the descending slab. Given that the initial noble gas concentration of the mantle is expected to correlate with degree of hydration, this assumption represents an end-member case of a dry mantle lithosphere (i.e. zero slab serpentinization; Hacker, 2008; van Keken et al., 2011). 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. S4), an order

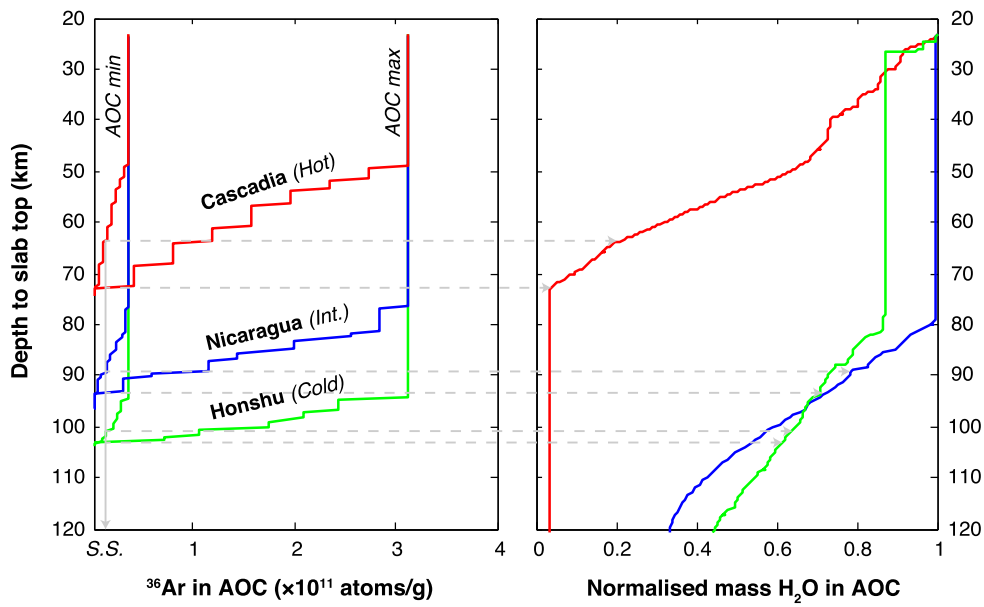

Fig. 7. Concentrations of ^{36}Ar and mineral-bound H_2O in AOC. Vertical arrow in left panel represents the steady-state (SS) AOC ^{36}Ar concentration. Horizontal arrows connect maximum and minimum AOC ^{36}Ar concentrations with respective mineral-bound H_2O concentrations.

of magnitude larger than the steady-state subduction flux. This implies that on a globally averaged basis ∼90% of ^{36}Ar is extracted from subducting AOC prior to closure of the slab. Taking into account the standard deviation on the average ^{36}Ar concentration within AOC translates to 65–95% extraction. We acknowledge that this estimate is based on the assumption that the concentration of ^{36}Ar within the MORB mantle is in steady state. This end-member assumption is supported by short (∼1 Ga) residence times of incompatible elements within the upper-mantle (Galer and O'Nions, 1985; Kellogg and Wasserburg, 1990; O'Nions and McKenzie, 1993; White, 1993) and implies that any primordial ^{36}Ar originally present within the MORB mantle has been degassed and that the present-day ^{36}Ar inventory is derived from the lower-mantle or the atmosphere.

Cold and intermediate slabs dominate the modern H_2O 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 (∼100 km, Figs. 5 and 7). At 100 km depth, 40–20% of the initial H_2O within AOC has also been extracted (Fig. 7). Assuming Ar and H_2O closure are synchronous implies that the subduction efficiency of H_2O past the depth of amphibole-out within cooler subduction zones is 60–80%. 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 serpentine group minerals, or a MORB mantle that is experiencing net outgassing of ^{36}Ar will serve to increase the depth of Ar closure, and correspondingly, decrease estimates of H_2O subduction efficiency within AOC.

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. This implies that subduction cycling of atmospheric noble gases into the convecting mantle has reduced the magnitude of primordial noble gas isotopic anomalies over time (Moreira and Raquin, 2007; Porcelli and Wasserburg, 1995a, 1995b). 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).

6. Conclusions

We have modeled the kinetic fractionation of noble gases hosted in amphibole during subduction of hydrous oceanic crust. Model results show that the fractionation of light (Ne) from heavy (Ar–Kr–Xe) noble gases is primarily controlled by the availability of a free grain-boundary fluid phase, which, in turn, is controlled by the thermal grade of subduction. All noble gases are diffusively mobile in amphibole along the P–T paths associated with hot subduction zones, promoting elemental fractionations within the noble gases; fractionation of noble gases is minimal along cold subduction zones because gas release from amphibole occurs by mineral breakdown and not diffusion. Interpreted in the context of this finding, the MORB mantle Ar–Kr–Xe pattern is consistent with the input of noble gases and, by inference, other major volatile phases, through cold and intermediate subduction zones. Finally, we have only considered the role of amphibole as a noble gas carrier phase, but the findings of our study are applicable to other minerals. Specifically, if noble gases are diffusively mobile through a mineral lattice at temperatures cooler than the thermal limit of the mineral's stability field, then elemental fractionations are expected to occur. This provides an impetus to understand noble gas kinetics in other potential carrier phases, including phengite, chlorite, lawsonite and antigorite.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2017.04.046.

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