**Subduction zone fluxes of halogens and noble gases in seafloor
and forearc serpentinites**

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Abstract. Serpentinites form by hydration of ultramafic lithologies in a range of seafloor and shallow subduction zone settings. Serpentinites are recognised as major reservoirs of fluid mobile elements and H₂O in subducting oceanic lithosphere, and together with forearc serpentinites formed in the mantle wedge, provide critical information about shallow-level volatile fluxes during subduction. The current study provides new Cl, as well as the first comprehensive Br, I and noble gas analyses, reported for seafloor and forearc chrysotile-lizardite serpentinites. The samples were recovered from IODP drilling campaigns of mid-ocean ridge, passive margin and forearc settings (n = 17), and ophiolites in the Italian Alps and Apennines (n = 10). The aims of this study were to determine the compositional variability of noble gases and halogens in serpentinites entering subduction zones and evaluate the efficiency of gas loss during the early stages of serpentinite subduction.

The chrysotile-lizardite serpentinites and serpentised peridotites contain 43 to 2300 ppm Cl and 3×10^{-13} to 2×10^{-11} mol g⁻¹ ³⁶Ar, with the concentrations of these elements broadly related to the estimated degree of serpentinisation. The serpentinites have extremely variable Br/Cl and I/Cl ratios with many samples preserving compositions similar to organic-rich sedimentary marine pore fluids. Serpentinites from the Marianas Forearc have very high I concentrations of up to 45 ppm I and I/Cl ratios of ~14,000 times the seawater value that is higher than those observed in sedimentary marine pore fluids. The serpentinites have ¹³⁰Xe/³⁶Ar and ⁸⁴Kr/³⁶Ar ratios that are mostly close to or above seawater values, and ²⁰Ne/³⁶Ar ratios that range from seawater to lower values. The serpentinites contain <10-270 ppm K and, irrespective of age (0 Ma to ~160 Ma), are characterised by ⁴⁰Ar/³⁶Ar ratios of 300-340 that are slightly higher than the seawater value of 296, thus indicating the presence of minor excess ⁴⁰Ar*. Three of six serpentinites analysed for helium also have measurable excess ⁴He contents that cannot be explained by *in situ* production. The data show that

serpentinites trap noble gases and halogens that originate from seawater, diverse crustal lithologies and organic matter.

Combined with previous analyses of metamorphosed serpentinites, the new data suggest that approximately 60-70% of the ^{36}Ar entering subduction zones in serpentinites is lost from chrysotile and/or antigorite and could potentially escape through the forearc. An additional, ~20-30 % of the ^{36}Ar entering subduction zones in serpentinites is lost during antigorite breakdown and may be cycled through the arc or back-arc, and ~1-10 % of the ^{36}Ar entering subduction zones in serpentinites may be subducted into the deeper mantle. The data demonstrate decoupling of noble gases, halogens and water during subduction and suggest that subduction-zone fluid fluxes may concentrate noble gases and iodine in newly formed forearc serpentinites. The distinctive I/Cl enrichment of forearc serpentinites suggest that halogen abundance ratios provide a plausible means for inferring the geotectonic setting of serpentinisation in ophiolite samples. The exceptional Cl, Br, I and noble gas concentrations of serpentinites, the potential subduction of the forearc serpentinites and the stability of serpentine minerals to mantle depths of >200 km, imply that serpentinites could dominate the deep recycling budgets of both the heavy halogens and atmospheric noble gases.

Keywords: serpentine, noble gases, halogens, iodine, subduction.

1. Introduction

The Earth's inventory of volatiles, including H₂O, halogens and noble gases, is overwhelmingly concentrated in the surface reservoirs of the atmosphere, seawater and sediments (e.g. Deruelle et al., 1992; Ozima and Podosek, 2002; Pyle and Mather, 2009; Rubey 1951; Schilling et al., 1978). However, volatiles are incorporated into the oceanic lithosphere by hydrothermal processes on the seafloor and there are three distinct volatile reservoirs within subducting oceanic lithosphere: i) sediments; ii) altered ocean crust (e.g. basalts and gabbros), and iii) serpentinites formed by hydration of ultramafic lithologies (e.g. Peacock, 1990; Rüpke et al., 2004; Schmidt and Poli, 1998; Ulmer and Trommsdorff, 1995). The extent to which different surface volatiles can be transported into the mantle by subduction of the oceanic lithosphere, or are recycled back to the surface through volcanic arcs, represents a fundamental uncertainty in our planets evolution (e.g. Ito et al., 1983; Parai and Mukhopadhyay, 2012; Rüpke et al., 2004; Schilling et al., 1978; Schmidt and Poli, 1998; Staudacher and Allègre, 1988).

Serpentinites are estimated to account for anywhere between 10 and 70 % of the chemically bound water entering subduction zones (e.g. Parai and Mukhopadhyay, 2012; Rüpke et al., 2004; Schmidt and Poli, 1998). However, various lines of reasoning suggest serpentinites could make a disproportionately large contribution to the deep subduction cycles of specific fluid mobile elements and water (Rüpke et al., 2004; Scambelluri et al., 2004; Scambelluri and Tonarini, 2012; Schmidt and Poli, 1998; Ulmer and Trommsdorff, 1995). Firstly, serpentinites contain higher concentrations of water (13 wt %) and many fluid mobile elements (e.g. 0.1-1 wt. % Cl) than any other major subduction zone lithology (Savov et al., 2007; Scambelluri et al., 2004; Schmidt and Poli, 1998; Sharp and Barnes, 2004). Secondly, the high pressure serpentine mineral antigorite is stable to depths of greater than ~200 km on cold geotherms and in cold slab interiors (Fig 1; Ulmer and Trommsdorff, 1995).

Thirdly, slab fluids released by compaction of sediments or dehydration of altered ocean crust at shallow depths, serpentinise and cool the forearc mantle wedge, with mass balance considerations suggesting that a portion of the serpentinised mantle wedge is entrained with the slab and subducted deeper into the mantle (Bostock et al., 2002; Savov et al., 2007). Fourthly, the chemical signature of B isotopes in arc magmas, the iodine-enrichment of back arc basin basalts, and earthquake focal depths as great as 250 km are most easily explained by volatile release from deeply subducted antigorite-serpentinites (Green II et al., 2010; Kendrick et al., 2012; Scambelluri and Tonarini, 2012). Finally, water has a high solubility in nominally anhydrous minerals like olivine under mantle pressures (Kohlstedt et al., 1996), suggesting that some of the water liberated by break down of antigorite to olivine could potentially be subducted (dissolved in olivine) to even greater depths within the mantle (e.g. Jacobsen and van der Lee, 2006).

A seawater-derived noble gas component has been unequivocally resolved within the Earth's convecting mantle, which provides strong evidence for the existence of a deep water cycle (Holland and Ballentine, 2006); however, the extent to which noble gases are decoupled from water is currently unknown. Furthermore, it is important to improve our understanding of noble gas subduction processes, because the extent to which primordial noble gas signatures, such as $^{20}\text{Ne}/^{22}\text{Ne}$, are preserved in the mantle or have been modified by subduction of atmospheric noble gases, has strong implications for discerning the nature of planetary accretion, the origin of Earth's volatiles and mantle differentiation (Holland and Ballentine, 2006; Mukhopadhyay, 2012). We demonstrated previously that fluid inclusions trapped in olivine-enstatite formed by complete breakdown of antigorite (Fig 1), are dominated by seawater-derived noble gases and halogens (Kendrick et al., 2011). However, the compositional range of noble gases and halogens in low grade chrysotile-lizardite

serpentinites on the seafloor, and the role of serpentine in the shallower part of the noble gas subduction cycle has not been investigated previously (see Fig 1).

The aim of the current study is to provide the first isotopic compositional data for noble gases, and elemental abundances of noble gases and halogens, in a range of seafloor and forearc serpentinites. Establishing the extent of variation in the ‘initial state’ of noble gases and halogens in chrysotile-lizardite serpentinites entering subduction zones, and investigating shallow-level volatile fluxes preserved in forearc serpentinites, are important steps towards re-evaluating the subduction potential of these elements (cf. Schilling et al., 1978; Staudacher and Allègre, 1988). In addition, we show that halogen relative abundance ratios (Br/Cl and I/Cl) provide a plausible method for fingerprinting the geotectonic setting of serpentinisation, which has strong implications for investigating the origin of serpentinites in the geologic record and hence the volume of serpentinites that might be subducted into the mantle.

1.2 Serpentinites and serpentinised peridotites

Pre-subduction seafloor lithologies and forearc serpentinites, with varying proportions of chrysotile-lizardite serpentine, were selected from well-characterised IODP drill cores (n = 17; Kodolányi et al., 2012) and ophiolites in the Italian Alps and Apennines (n = 10; Scambelluri et al., 1997; 2004b) (Fig 2; supplement Table S1).

Seafloor serpentinites comprising 70-99 % serpentine were selected from drill cores sampling the 15° 20' fracture zone of the Mid-Atlantic Ridge (IODP leg 209), Hess Deep on the East Pacific Rise (IODP leg 147) and the Iberian and Newfoundland passive continental margins (IODP legs 173 and 210; Fig 2; see Kodolányi et al. 2012 and supplement Table S1 for details). The passive margin serpentinites formed at temperatures of <250 °C and are

now covered by sediment (Beslier et al., 1993; Kodolányi et al. 2012; Robertson, 2007; Skelton and Valley, 2000). However, they probably formed during Cretaceous rifting (~120 Ma) and are regarded as equivalent to buried ancient mid-ocean ridge serpentinites in this study.

Forearc serpentinites comprising 65-99 % serpentine were selected from drill cores through a disturbed sequence of tectonic breccias in the Guatemala forearc (IODP leg 84; Bourgois et al., 1985), and the South Chamorro serpentine mud volcano in the Marianas Forearc (IODP leg 195; Fig 2; supplement Table S1). The South Chamorro serpentine mud volcano is located ~27 km above the subducting Pacific Plate (Savov et al., 2007) and the samples recovered from the Marianas drill cores are exhumed clasts of the hydrated mantle wedge hosted by a serpentine mud matrix (Kodolányi et al., 2012).

Ophiolite samples comprising 15-80 % serpentine (chrysotile-lizardite) were selected from the Internal and External Liguride Units (Monte Nero) of the Italian Apennines; and low strain zones at Erro Tobbio in the Italian Alps (Fig 2; supplement Table S1). These localities preserve fragments of serpentinitised lithospheric mantle from the Jurassic age Tethys ocean that have pre-Jurassic depletion ages and estimated seafloor emplacement ages of ~160 Ma (Rampone et al. 2005; Rampone and Hofmann, 2012). The External Liguride units could have formed in a setting comparable to the conjugate Iberian – Newfoundland passive margins (Rampone et al., 2005; Marroni and Pandolfi, 2007), whereas the Internal Liguride Units are interpreted as representing axial domains of a slow to ultra-slow spreading centre (Rampone and Hofmann, 2012). The samples selected from Erro Tobbio were recovered from low strain zones within the Alpine subduction collision zone; they represent a serpentinitised granular spinel peridotite (ET11/27), and plagioclase- or hornblende-bearing mylonites (ET10/05, ETPP1) that each retain low-grade lizardite and mesh-textured chrysotile acquired during a pre-subduction alteration stage (see Fig 2 of Früh-Green et al.

2001 and Hoogerduijn Strating et al., 1993; Scambelluri et al., 1997; Rampone et al., 2005). In contrast, our previous study was focused on high-grade antigorite-schists formed in overprinting high strain zones during the Alpine Orogeny (Fig 1; Kendrick et al., 2011).

The selected sample locations have been used in several previous Cl isotope and halogen studies (Barnes et al., 2008; 2009; Barnes and Sharp, 2006; Bonifacie et al., 2008; John et al., 2011; Kodolányi and Pettke, 2011; Kodolányi et al., 2012; Scambelluri et al., 2004b; Sharp and Barnes, 2004; Snyder et al., 2005). These studies demonstrated that serpentinites typically host between ~0.01 and 1 wt % Cl, and that Cl can be present in multiple locations: structurally bound Cl substitutes for the OH-group in the serpentine lattice $[(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH,Cl})_4]$; and is often present in the accessory mineral iowaite $[\text{Mg}_4\text{Fe}(\text{OH})_8\text{Cl}\cdot x\text{H}_2\text{O}]$ (Kodolányi et al., 2012). Leaching experiments have shown that more than half of the total Cl in serpentinites can be leached from powdered samples (Sharp and Barnes, 2004). However, salts have not been detected petrographically or by X-ray mapping of unwashed samples (Kodolányi et al., 2012), suggesting that the ‘water soluble Cl’ may largely reside on grain boundaries.

2. Analytical methodology

2.1 Sample preparation

The seafloor and forearc serpentinite samples were obtained from 90° sectors of 5 cm diameter drill cores by manually chipping off obvious carbonate veins, crack surfaces and outside edges that had been exposed to drilling devices or saw blades. A portion of the resulting ‘pristine’ serpentinite material was used for previous ICP-MS trace element analysis (Kodolányi et al., 2012), and 20-40 mg sized chips of this material were used in the current

study. In contrast, the previous Cl analyses of the seafloor samples were obtained from unwashed portions of the chipped off material (Kodolányi et al., 2012).

Single 20-40 mg sized chips were obtained for each sample in this study by breaking the samples in a stainless steel crushing device. The mm-sized chips were briefly washed in distilled water to remove powdered material. The washing procedure should have a negligible effect on halogen bulk concentrations because water soluble chloride would probably have been lost only from the surface layer of the samples. Most previous studies have employed similar washing procedures for uncrushed sample chips (e.g. Barnes and Sharp, 2006; John et al., 2011).

2.2 The noble gas method for halogen (Cl, Br, I) determination

Twenty seven samples were analysed for the halogens (Cl, Br and I), K, Ca and naturally occurring isotopes of Ar, Kr and Xe, using the noble gas method, which employs extended ^{40}Ar - ^{39}Ar methodology (Kendrick, 2012). The samples were irradiated for 42 hours in position 5c of the McMaster Nuclear Reactor (Canada; irradiation UM#44), to produce noble gas proxy isotopes for the halogens, K and Ca. The noble gas production ratios ($^{38}\text{Ar}_{\text{Cl}}/\text{Cl}$, $^{80}\text{Kr}_{\text{Br}}/\text{Br}$, $^{128}\text{Xe}_{\text{I}}/\text{I}$, $^{39}\text{Ar}_{\text{K}}/\text{K}$ and $^{37}\text{Ar}_{\text{Ca}}/\text{Ca}$) were monitored using Hb3Gr flux monitors (1072 Ma; Roddick, 1983) and scapolite halogen standards (SY; SP/BB1; BB2; Kendrick, 2012; supplement Fig S1). The irradiation had a mean J-value of 0.0164 ± 0.0005 (2σ), a fast neutron fluence of $\sim 3 \times 10^{18}$ neutrons cm^{-2} and a thermal neutron fluence of $\sim 8 \times 10^{18}$ neutrons cm^{-2} .

Following irradiation, the individual sample chips (20-40 mg) were placed in an ultra high vacuum furnace sample holder (without foil sample packets). The furnace was outgassed at 1600 °C and the line was baked at 150 °C for 24 hours prior to analysis. The samples

experienced temperatures of up to 90 °C during the bake out that exceed the reactor pool temperature of <38 °C experienced by the samples during the 42 hour irradiation.

To test for possible gas loss during sample preparation, five samples were analysed using 100°C heating steps of 3, 5 and 10 hour duration, or a 200 °C heating step of 20 minutes, prior to the main 20 minute heating steps of 300 and 1500 °C that were used to extract gases from all samples. The extracted noble gases were exposed to a Ti-foil getter pump during each heating step and the H₂O pressure was monitored using a Baratron manometer. Following complete breakdown of the serpentine during the 1500 °C step, the Ti-foil getter was cooled over a second 20 minutes and final gas purification was accomplished using SAES getter pumps in a third 20 minute period.

The purified noble gases were analysed for Ar, Kr and Xe isotopes in peak jumping mode using the MAP-215 noble gas mass spectrometer at the University of Melbourne. Corrections were made for small machine blanks (e.g. <1% of sample gas; electronic supplement), standard ⁴⁰Ar-³⁹Ar interference reactions, Cl-derived ³⁶Ar and U-derived ⁸⁴Kr (Kendrick, 2012). Analytical uncertainty is at the 1-2% level (internal precision); but absolute abundances have higher uncertainties determined by calibration of mass spectrometer sensitivity (~4% 2σ) and characterisation of Br and I in the scapolite standards (~10% 2σ; electronic supplement).

2.3 Helium and neon isotope analysis

Six seafloor serpentinites (non-irradiated) were analysed for He, Ne and Ar isotopes using the VG5400 noble gas mass spectrometer at the Australian National University. The preparation procedure was similar to that used at the University of Melbourne. However, noble gases were released from 60-90 mg-sized samples in a single heating step of 1500 °C, which

maximised the scarce He and Ne isotopes available for analysis. Larger samples were avoided because of difficulties involved in removing H₂O released during serpentine breakdown. The noble gas purification procedure was undertaken in two stages. The sample gas was exposed to a Ti-foil getter at 750 °C for 90 minutes and then further purified using SAES getters over a period of 30 minutes. The purified noble gases were cryogenically separated and analysed for He, Ne and Ar isotopes only. The instrument was calibrated by comparison with gas standards and (minor) Ne isotope interference corrections were made for ⁴⁰Ar⁺⁺, mass-42⁺⁺ (hydrocarbons) and CO₂⁺⁺ (Honda et al., 1993; Honda et al., 2004). The neon isotope ratios were within uncertainty of atmosphere; however, significant uncertainties in the ²⁰Ne abundances result from a substantial blank correction of 6-76% and partial ²⁰Ne loss during gas handling of samples S011 and S025; therefore the reported ²⁰Ne abundances and ²⁰Ne/³⁶Ar ratios should be considered as lower limits.

3. Results

The comprehensive dataset obtained for individual heating steps of the 27 chrysotile-lizardite samples investigated in this study is available in the electronic supplement. The systematics of noble gas release from stepped heating of chrysotile-lizardite are summarised in Fig 3, and the combined halogen and noble gas data obtained by ‘total fusion’ of the serpentinites are reported in Tables 1 and 2 and illustrated graphically in Figures 4-6.

3.1 Noble gas release systematics and total fusion data

The serpentinites exhibited variable behaviour during stepped heating. Holding samples S019, S009 and S001 at a temperature of 100 °C for periods of 3, 5 and 10 hours prior to analysis, released less than 1% of the irradiation-produced Cl-derived ³⁸Ar_{Cl} from the sample,

but 6 %, 2 % and 26 % of the naturally occurring atmospheric ^{36}Ar from the samples, respectively (Fig 3; supplementary data). Heating samples S032 and S038 to 200 °C, released less than 2% of total $^{38}\text{Ar}_{\text{Cl}}$ and 4-30% of the total ^{36}Ar within the samples (Fig 3). For the majority of samples analysed with only 300 and 1500 °C heating steps, the 300 °C step released 2 % to 46% of the total $^{38}\text{Ar}_{\text{Cl}}$, and 17 % to 92% of the total ^{36}Ar in the sample (Fig 3). In most cases, the proportion of irradiation-produced $^{80}\text{Kr}_{\text{Br}}$, $^{128}\text{Xe}_{\text{I}}$, $^{39}\text{Ar}_{\text{K}}$ and $^{37}\text{Ar}_{\text{Ca}}$, released in each step was similar to the proportion of $^{38}\text{Ar}_{\text{Cl}}$; and the proportion of atmospheric Kr and Xe was similar to the proportion of atmospheric ^{36}Ar released in each step (supplementary data).

The inefficient degassing of $^{38}\text{Ar}_{\text{Cl}}$ at temperatures of 100-200 °C (Fig 3) suggests that loss of irradiation-produced noble gas isotopes from the samples during irradiation (max. temperature ~40 °C), or *in vacuo* prior to analysis (max. temperature 90 °C), was minimal; therefore the Cl, Br, I, K and Ca concentrations obtained by the noble gas method are considered reliable. However, the serpentinites were less retentive of ‘atmospheric’ noble gas isotopes, with significant loss of ^{36}Ar from some (but not all) samples at 100-200 °C, suggesting minor loss of ^{36}Ar is more likely and could be significant for highly diffusive He isotopes. The similar release temperatures of the halogen, K and Ca derived noble gas isotopes, and the fact that the samples most retentive of irradiation-produced $^{38}\text{Ar}_{\text{Cl}}$, were also most retentive of atmospheric ^{36}Ar , suggests that gases released at 300 °C do not simply correspond to surface adsorbed atmospheric noble gases or $^{38}\text{Ar}_{\text{Cl}}$ derived from loosely bound ‘water soluble Cl’; rather, the noble gases released at 300 °C must have been partly released from structural sites. As a result, the noble gas concentrations obtained by total fusion are considered representative of the serpentinites (Table 1).

3.2 Halogens

The highly-altered seafloor and forearc serpentinites have concentrations between 420 and 2300 ppm Cl, 1.3 to 24 ppm Br and 0.02 to 45 ppm I (Table 2). The range of Cl concentrations is broadly similar for serpentinites in mid-ocean ridge settings (460-1200 ppm), passive margin settings (590-1700 ppm) and forearc settings (630-2300 ppm; Table 2). In comparison, the less strongly serpentinised peridotites from ophiolites have lower concentrations of 42-740 ppm Cl, 0.2-3.4 ppm Br and 16-2600 ppb I, with the lowest concentrations in the least-altered samples (Fig 4a).

The serpentinites and serpentinised peridotites have combined Br/Cl and I/Cl weight ratios that fall in clear groupings related to tectonic setting and cluster around the trend defined by sedimentary marine pore fluids (Fig 5). The term ‘sedimentary marine pore fluid’ is used here to describe seawater derived fluids that are hosted by pore spaces in organic-rich marine sediments and associated with gas hydrate. Sedimentary marine pore fluids define a linear relationship between Br/Cl and I/Cl (Fig 5a), that appears curved in log-log space (Fig 5b), because these fluids contain seawater derived halogens (largely Cl + Br) and halogens released with CH₄ by decomposition of organic matter present in sediments (largely Br + I; Fehn et al., 2000; 2003; 2006; 2007a; Muramatsu et al., 2001; 2007; Tomaru et al., 2007; 2009; Lu et al. 2008). Relative to seawater, organic matter contains negligible Cl, but is strongly enriched in the biophilic halogens I + Br (Fuge and Johnson, 1986; Martin et al., 1993; Muramatsu et al., 2007).

The seafloor serpentinites from modern mid-ocean ridges and passive margin settings have the lowest I/Cl ratios, with a minimum of 6.1×10^{-5} , that is ~20 times the seawater value of 3.1×10^{-6} , and a maximum of 1.3×10^{-3} , that is 420 times the seawater value (Fig 5). The mid-ocean ridge and passive margin serpentinites have Br/Cl ratios that vary from 2.7×10^{-3} to

5.6×10⁻³, bracketing the trend defined by sedimentary marine pore fluids and the seawater value of 3.5×10⁻³ (Fig 5). The serpentinised peridotites from the ophiolites have higher I/Cl ratios of 3.2×10⁻⁴ to 1.1×10⁻² and greater than seawater Br/Cl ratios that lie on the trend of sedimentary marine pore fluids (Fig 5). The forearc serpentinites have the highest I/Cl ratios of >1.9×10⁻³ (Fig 5); the serpentinites from the Guatemalan Forearc have combined Br/Cl and I/Cl ratios that lie on the trend of sedimentary marine pore fluids, whereas the Marianas Forearc serpentinites are enriched in I/Cl relative to sedimentary marine pore fluids (Fig 5). The maximum I/Cl ratio of 5.8×10⁻² is 14,000 times the seawater value and corresponds with an iodine concentration 45 ppm (Table 2) that is 4500 times higher than the bulk silicate Earth concentration (Deruelle et al., 1992). Organic-rich marine sediments are the only other known lithology with comparable iodine concentrations (Kennedy and Elderfield, 1987; Martin et al., 1993; Muramatsu et al., 2007).

3.3 Non-radiogenic noble gases

The serpentinites and serpentinised peridotites have extremely variable ³⁶Ar concentrations that range from a minimum of 2.6×10⁻¹³ mol g⁻¹ to a maximum of 1.9×10⁻¹¹ mol g⁻¹ (Fig 6a; Table 1), with a mean of 3×10⁻¹² mol g⁻¹. There is a broad relationship between the degree of serpentinisation and the ³⁶Ar concentration; however, there is considerable variation in ³⁶Ar concentrations even amongst serpentinites from individual localities with similar degrees of alteration (Fig 4b). For example, the Guatemalan Forearc serpentinites record both the highest and one of the lowest ³⁶Ar concentrations (Figs 4b and 6a).

The maximum ³⁶Ar concentration measured in chrysotile-lizardite (1.9×10⁻¹¹ mol g⁻¹) is ~30 % lower than the 25 °C seawater value (Fig 4b), which indicates the serpentinites have

a maximum $^{36}\text{Ar}/\text{H}_2\text{O}$ ratio of ~5 times the seawater value. In comparison, eclogite-facies antigorite-serpentinites from Erro Tobbio (Italy) and olivine-enstatite rocks formed by antigorite dehydration (Almirez, Spain), have progressively lower ^{36}Ar concentrations for higher grades of metamorphism with mean values of $\sim 10^{-12} \text{ mol g}^{-1}$ and $\sim 2 \times 10^{-13} \text{ mol g}^{-1}$, respectively (Fig 6a; Kendrick et al., 2011).

Based on the current data, which include neon isotope analyses for only six seafloor serpentinites (Table 1), the chrysotile-lizardite serpentinites have noble gas abundance ratios that range from close to seawater values, to values that are systematically enriched in $^{130}\text{Xe}/^{36}\text{Ar}$, and depleted in $^{20}\text{Ne}/^{36}\text{Ar}$ (Fig 6b). The range of $^{20}\text{Ne}/^{36}\text{Ar}$, $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$ in chrysotile-lizardite serpentinites is fairly similar to that reported for antigorite-serpentinites from Erro Tobbio, Italy and olivine-enstatite rocks formed by serpentine dehydration (Fig 6b; Kendrick et al., 2011). The serpentinites preserve slightly higher $^{20}\text{Ne}/^{36}\text{Ar}$ than the limited number of analyses currently available for marine sediments and altered oceanic basalts (Fig 6b; Matsuda and Nagao, 1986; Staudacher and Allègre, 1988). In comparison, variable noble gas abundance ratios, including much higher $^{20}\text{Ne}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$, have been reported for shales (Fig 6b; Podosek et al., 1980).

3.3.1 'Excess' radiogenic $^{40}\text{Ar}^*$ and ^4He

Irrespective of age, the serpentinites all have similar $^{40}\text{Ar}/^{36}\text{Ar}$ values of between 304 ± 3 and 342 ± 9 (2σ), that are slightly elevated relative to the atmospheric or seawater value of 296 (Table 3). The presence of non-atmospheric ^{40}Ar cannot be explained by decay of ^{40}K within any of the samples. The seafloor serpentinites and ~160 Ma ophiolite samples, with measurable K (Table 2), are calculated to contain an *in situ* radiogenic ^{40}Ar component of less than 0.1-1.5 %, which is often smaller than the analytical uncertainty of the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio

(Table 1; supplementary data). The high concentrations of ^{36}Ar and low concentrations of K in these serpentinised rocks indicate that serpentinites will retain $^{40}\text{Ar}/^{36}\text{Ar}$ signatures of close to their initial atmospheric values for hundreds of millions of years (Table 1).

Based on the U and Th abundances of up to 700 ppb U and 3 ppb Th previously reported for the six seafloor serpentinites analysed for neon and helium (Kodolányi et al., 2012), samples S015, S020 and S025 are estimated to contain less ^4He than would have been produced by *in situ* decay of U and Th (supplementary data). In contrast, *in situ* production is calculated to contribute <0.5% of the total ^4He in sample S011 from a modern mid-ocean ridge, ~6% of the total ^4He in sample S032 from the Marianas Forearc and ~50% of the ^4He in the sample S008 from the Iberian passive margin (supplementary data). These data indicate that half the serpentinites investigated contain excess ^4He and have age-corrected $^4\text{He}/^{36}\text{Ar}$ ratios of much greater than seawater (Fig 6b).

Excess $^{40}\text{Ar}^*$ and ^4He have two possible sources in seafloor serpentinites: 1) mantle-derived rocks with $^{40}\text{Ar}/^{36}\text{Ar}$ of up to ~30,000 and $^3\text{He}/^4\text{He}$ of ~8 Ra (where Ra is the atmospheric $^3\text{He}/^4\text{He}$ ratio of 1.4×10^{-6} ; Graham, 2002); and, 2) marine sediments, which typically have $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of between 296 and ~1500, and $^3\text{He}/^4\text{He}$ ratios ranging from crustal values of ~0.02 Ra near continental margins to values of ~170 Ra in sediments that host Interplanetary Dust Particles (e.g. Marcantonio et al., 2009; Matsuda and Nagao, 1986; Podosek et al., 1980; Staudacher and Allègre, 1988).

4. Discussion

4.1 Incorporating halogens into serpentinites

The relative compatibilities of Cl, Br and I in serpentine have not been investigated experimentally. However, the high concentrations of up to 24 ppm Br and 45 ppm I

determined for chrysotile-lizardite serpentinites in this, and previous studies (Table 2; John et al., 2011; Snyder et al., 2005), suggests that either both Br and I (like Cl) can substitute for the OH group in the serpentine lattice, or that these elements are efficiently trapped interstitially.

The seafloor serpentinites from modern mid-ocean ridges and passive margins, that are thought to have formed from seawater (in the absence of abundant sedimentary material), have I/Cl ratios of up to 420 times seawater and variable Br/Cl ratios (Fig 5). These data could indicate that seawater-derived halogens are fractionated during trapping in serpentine, with iodine trapped preferentially relative to Br and Cl. Alternatively, the halogen signatures could be representative of serpentinising fluids that circulated through diverse crustal lithologies. Unaltered peridotites would have been a negligible source of halogens in the serpentinites because the depleted mantle contains <1 ppb I (Dereulle et al., 1992) and probably <20 ppb Br, compared to 60 ppb I and ~66 ppm Br in seawater (Table 2). However, much higher I and Br abundances could be present in serpentinised peridotites or crustal lithologies if organic matter is introduced by microbes that metabolise the gases (CH₄ and H₂) produced by serpentinisation (e.g. Bach and Fröh-Green, 2010).

The majority of the serpentinised peridotites from ophiolites, and the Guatemalan Forearc serpentinites, have combined Br/Cl and I/Cl ratios that lie on the trend defined by sedimentary marine pore fluids (shown as grey dots in Fig 5). This suggests the halogens (Cl, Br, I) might have fairly similar compatibilities in serpentine and that sedimentary marine pore fluids were probably involved in serpentinisation in these localities. It seems unlikely that a range of serpentinite Br/Cl and I/Cl compositions similar to sedimentary marine pore fluids would be produced by preferentially trapping seawater-derived halogens on the order I>Br>Cl in these samples and not in the mid-ocean ridge serpentinites (Fig 5). Furthermore, the strong I-enrichment of these samples would be difficult to generate from seawater which

contains very little iodine (Table 2), and Guatemala Forearc serpentinites have negative $\delta^{37}\text{Cl}$ that has previously been attributed to the involvement of sedimentary marine pore fluids released from a subducting slab during sediment compaction (Barnes and Sharp, 2006).

In contrast to Guatemala serpentinites, the Marianas Forearc serpentinites are strongly enriched in I/Cl relative to sedimentary marine pore fluids and have near zero $\delta^{37}\text{Cl}$ (Fig 5; Barnes et al., 2008). The fractionated I/Cl signature of the Marianas Forearc serpentinites, could indicate serpentinisation by slab fluids released by dehydration of I-rich slab lithologies. The only two lithologies known to have sufficiently high iodine contents, that they could potentially produce voluminous fluids with very high I/Cl ratios, are organic-rich marine sediments (e.g. Martin et al., 1993; Muramatsu et al., 2001; 2007) and serpentinites (Table 2). The near zero $\delta^{37}\text{Cl}$ of the Marianas serpentinites was previously ascribed to the involvement of Cl released from subducted-serpentinites undergoing the chrysotile to antigorite transition (cf. Barnes et al., 2008). The antigorite-serpentinites from Erro Tobbio have lower I/Cl ratios than the chrysotile-bearing peridotites from Erro Tobbio (Fig 5; Kendrick et al., 2011), potentially indicating that fluids with elevated I/Cl could be generated during prograde transformation of chrysotile to antigorite (Fig 1). However, among the seafloor serpentinites investigated here, the Marianas Forearc serpentinites record the most prominent LILE enrichment (Kodolányi et al., 2012; Savov et al., 2007), that supports the possible involvement of fluids derived from sedimentary units. Given the Marianas arc is sediment starved (Savov et al., 2007), this indicates serpentinites can efficiently inherit very strong iodine enrichment from relatively small volumes of sediment.

4.1.1 Halogens in tectonic reconstructions?

Based on the current data and interpreted mechanisms for halogen incorporation in serpentinite (section 4.1), it seems plausible that halogen abundance ratios can be used to make useful inferences about the tectonic setting of serpentinisation.

Serpentinites that form at spreading centres without sediment are likely to have low (MORB-like) I/Cl ratios (Fig 5b). Serpentinites that form from sedimentary marine pore fluids in settings with abundant sedimentary cover (including slab-bend zones and forearcs; Bostock et al., 2002; Ranero et al., 2003), or that re-equilibrate with sediments later in their history, are more likely to have elevated I/Cl ratios, and combined Br/Cl and I/Cl ratios similar to sedimentary marine pore fluids (e.g. Guatemala; Fig 5b). Finally, forearc serpentinites related to slab fluids, can have fractionated halogen signatures with extreme I/Cl enrichment (e.g. Marianas; Fig 5b).

The serpentinised peridotites from all of the ophiolites investigated have higher than MORB I/Cl ratios, and Br/Cl similar to sedimentary marine pore fluids (Fig 5b), suggesting serpentinisation did not occur exclusively within sediment-starved mid-ocean ridge settings. The very strong I/Cl enrichment of samples from the External Ligurides (Monte Nero), is similar to the Guatemala and Marianas Forearc serpentinites (Fig 5b). The External Liguride unit is an olistolith hosted by Alpine Flysch, meaning it is possible that part of the iodine enrichment occurred after the initial serpentinisation of these samples. However, in situ iodine analyses could be used to clarify the timing of iodine enrichment, and if it is an original feature of the serpentinisation it would contribute to understanding the tectonic setting of serpentinisation in this locality, because the I/Cl enrichment is unlikely to have formed at a slow spreading centre (cf. Rampone and Hofmann, 2012).

4.2 Incorporating noble gases into serpentinites

Serpentinites have highly variable noble gas concentrations that partly reflect the degree of serpentinisation (Fig 4), and define a broad trend of decreasing concentration with increasing metamorphic grade (Fig 6a). This systematic behaviour suggests that measured ^{36}Ar concentrations are fairly representative of serpentinites and have not been unduly affected by gas loss or adsorption processes during sample preparation or analysis. Given noble gases cannot chemically substitute for any component within the serpentine lattice, the noble gases must be trapped interstitially or within voids in the serpentine lattice, because fluid inclusions are not visible in any of the samples.

Experimental data obtained for synthetic serpentine at 340 °C and 1 Kbar indicate that the heaviest noble gases have the highest solubilities in serpentine and noble gas partition coefficients (K_i) were estimated as 0.0004-0.0012 (where $K_i = [\text{mol/g serpentine}]/[\text{mol/g water}]$; Zaikowski and Schaeffer, 1979). Based on these figures, the observed ^{36}Ar concentrations in the Cl-rich serpentinites of this study are considerably higher than can be explained by seawater serpentinisation. The discrepancy could be explained because fluids with ^{36}Ar concentrations at least an order of magnitude higher than seawater could occur in hydrothermal and metamorphic environments (e.g. Kendrick et al., 2011; Kendrick and Burnard, 2013). Furthermore, the partition coefficient of ^{36}Ar in serpentine could be increased significantly by the presence of impurities such as Cl, which increase structural disordering and lattice defects (Deer et al., 1992), thus increasing the ability of serpentine to trap noble gas. The broad correlation between serpentinite Cl and ^{36}Ar concentrations (Fig 4c) is partly related to the degree of alteration (Fig 4ab), but is also consistent with noble gases having an enhanced solubility in Cl-rich serpentine.

The variation in noble gas abundance ratios (Fig 6b) is expected given the complex process of serpentinisation by seawater-derived fluids that have variably equilibrated with seafloor lithologies which would fractionate noble gases by adsorption/desorption and

diffusion processes. Moreover, noble gas fractionation will occur during serpentinisation, if for example, serpentinising fluids with noble gas abundance ratios similar to seawater were consumed during serpentinisation, the earliest generations of serpentine would have low $^{20}\text{Ne}/^{36}\text{Ar}$ and high $^{130}\text{Xe}/^{36}\text{Ar}$ ratios. However, the concentrations of light noble gases would increase in the residual fluid more quickly than the concentrations of heavy noble gases; therefore later generations of serpentine would have progressively higher noble gas concentrations and higher $^{20}\text{Ne}/^{36}\text{Ar}$ ratios (cf. Fig 6b). If the fluid was entirely consumed by serpentinisation reactions, then the average noble gas abundance ratios and $^{36}\text{Ar}/\text{H}_2\text{O}$ of ‘multi-generation’ serpentine would be identical to seawater.

4.3 Preserving halogens and noble gases during subduction

Noble gases trapped interstitially or in defect structures within serpentine, could potentially be lost during subduction as a result of diffusion, independently of mineral transformations in the serpentine system (Fig 1). However, noble gas loss will only occur by diffusion, if fluids are present to advect the ‘lost’ noble gases out of the rock unit and maintain a diffusion gradient. The heavy halogens (Br + I) probably exhibit similar behaviour to Cl and are at least partly incorporated in the serpentine lattice; therefore it is likely that significant halogen loss only occurs during transformation of chrysotile/lizardite to antigorite and antigorite breakdown (see Fig 1). However, the efficient loss of halogens (as well as other trace elements) and noble gases, probably only occurs during the chrysotile to antigorite transition if external fluids are present (Kodolányi and Pettke, 2011), because this transition liberates <1 wt. % H_2O , the liberated water could react with incompletely serpentinised peridotites to form new antigorite, meaning it would be preserved within the rock unit.

Taken together, the mean ^{36}Ar concentration of chrysotile-lizardite serpentinites in this study ($\sim 3 \times 10^{-12} \text{ mol g}^{-1}$) and antigorite-serpentinites from Erro Tobbio ($\sim 10^{-12} \text{ mol g}^{-1}$; Kendrick et al., 2011) suggests that as much as two thirds of the ^{36}Ar entering subduction zones is lost from chrysotile and/or antigorite to external fluids and could be lost through the forearc. In comparison, serpentine loses only $\sim 1/13^{\text{th}}$ of its water content during the chrysotile-antigorite transition, demonstrating that noble gases and water are decoupled during the early part of the subduction cycle. It is possible that iodine is lost preferentially relative to Br and Cl during the chrysotile-to-antigorite transition (section 4.1). The decoupling of noble gases and halogens from each other and water means it is possible that external fluids could acquire elevated concentrations of both noble gases and iodine during the chrysotile to antigorite transition. Migration of these external slab fluids into higher parts of the forearc could then generate the very high ^{36}Ar and iodine concentrations observed in forearc serpentinites (Figs 4-6; sections 4.1 and 4.2).

The cycle could repeat itself multiple times with the most incompatible volatiles being concentrated in forearc serpentinites to the greatest extent (Bostock et al., 2002; Savov et al., 2007). Partial subduction of the forearc serpentinites might generate successive generations of slab fluids, that migrate and generate forearc serpentinites, with progressively higher ^{36}Ar and iodine concentrations. Despite the possibility that iodine is lost preferentially relative to Cl during the chrysotile to antigorite transition (section 4.1), the antigorite-serpentinites from Erro Tobbio retain much higher I/Cl ratios than igneous amphibole or mica (Fig 5a; Kendrick et al., 2011). Furthermore, it is possible that much higher I/Cl ratios could be preserved in antigorite-serpentinites formed from very iodine-rich chrysotile-serpentinites (cf. Fig 5). Together with the stability of antigorite to depths exceeding 200 km (Ulmer and Tromsdorff, 1995), the strong I and Br enrichment of serpentinites (Fig 5), suggest that serpentinites may represent the dominant pathway for deep Br and I subduction (Snyder et al., 2005).

Based on the mean ^{36}Ar concentrations of chrysotile-lizardite serpentinites ($\sim 3 \times 10^{-12}$ mol g^{-1}) and olivine-enstatite rocks formed by antigorite breakdown ($\sim 2 \times 10^{-13}$ mol g^{-1} ; Kendrick et al., 2011), we can estimate an average gas loss efficiency at >90-95 % during serpentine breakdown (Fig 6a). Depending on exactly how it is calculated, the data suggest that approximately ~60-70 % of the ^{36}Ar entering subduction zones is lost through the forearc, during the chrysotile to antigorite transition; ~20-30% of noble gases entering subduction zones are lost during antigorite breakdown, and could potentially escape through the arc or back arc; and ~1-10 % of the noble gas entering subduction zones in serpentinites could be subducted in olivine-enstatite dehydration residues further into the mantle (Kendrick et al., 2011). This small percentage is highly significant because the mean ^{36}Ar concentration of olivine-enstatite rocks from Almirez remains 60 times greater than the estimated mantle concentration of 2.5×10^{-15} mol g^{-1} (Fig 6a; Kendrick et al., 2011).

4.4 Implications for subduction recycling

Iodine and the noble gases are highly incompatible elements that are strongly concentrated in Earth's surface reservoirs and have previously been regarded as difficult to subduct (cf. Deruelle et al., 1992; Muramatsu et al., 2001; Muramatsu and Wedepohl, 1998; Schilling et al., 1978; Staudacher and Allègre, 1988). However, the high iodine and noble gas contents of the serpentinites documented in this study reveal a possible pathway for the deep subduction of these elements. This interpretation explains most of the recent observations: firstly ^{129}I studies have demonstrated that despite I-loss from organic matter in the forearc (Muramatsu et al., 2001), iodine in crater lakes above magmatic arcs has a subduction origin (Fehn et al., 2007b; Snyder and Fehn, 2002); wedge fluids exhumed from 100 km in the Higashi-Akaishi peridotite of Japan have seawater-derived noble gas signatures

and high I/Cl ratios that are within the range of serpentinites and not sedimentary marine pore fluids (Fig 5b; Sumino et al., 2010); back arc basin basalts are Cl-enriched and have I/Cl ratios of up to five times the MORB value, consistent with serpentinites recycling Cl and minor iodine to the deeper mantle (Kendrick et al., 2012); and the convecting mantle contains resolvable components of seawater-derived Ar, Kr and Xe (Holland and Ballentine, 2006).

There are now several lines of evidence for subduction of the heavy noble gases and halogens (including I), and there is a clear mechanism by which subduction of these elements can occur (sections 4.1-4.3; Kendrick et al., 2011). However, the extent to which Ne and He can be subducted into the mantle is still an open question. If ^{36}Ar has a dominantly subducted origin in the mantle (Holland and Ballentine, 2006), and subduction zone minerals preserve seawater-like $^{20}\text{Ne}/^{36}\text{Ar}$ ratios, then mass balance requires that at least 10-15% of mantle Ne has a subducted origin (Kendrick et al., 2011). The serpentinite samples in this study, and the antigorite and olivine-enstatite rocks formed by serpentine breakdown encompass a range of $^{20}\text{Ne}/^{36}\text{Ar}$ ratios both above and below seawater (Fig 6b). An even greater range of $^{20}\text{Ne}/^{36}\text{Ar}$ has been reported for unconsolidated sediments and shales (Matsuda and Nagao, 1986; Podosek et al., 1980; Staudacher and Allègre, 1988). Further analyses are therefore required to obtain meaningful average $^{20}\text{Ne}/^{36}\text{Ar}$ ratios for serpentinite and sediment; however, the current data allow the possibility that ^{20}Ne subduction explains the non-solar $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of the mantle (Kendrick et al., 2011).

The current serpentinite data indicate significant excess ^4He was preserved in half of the serpentinites analysed (Fig 7; Table 1; section 4.3.1). This demonstrates that ^4He can be trapped in serpentine; however, excess helium is probably only significant in samples with low ppb-level U concentrations (supplementary data). Furthermore, it is possible that He is retained in seafloor serpentinites much less efficiently than the heavier noble gases (Ne, Ar, Kr and Xe).

5. Summary and conclusions

Chrysotile-lizardite serpentinites trap variable and elevated concentrations of atmospheric noble gases (Fig. 6). Noble gas relative abundance ratios are fractionated from seawater values by fluid-mineral partitioning behaviour. Serpentinites provide efficient pathways for the subduction of atmospheric Xe, Kr, Ar and probably allow for significant Ne subduction. In contrast, helium is probably not efficiently trapped or retained in serpentine.

Unlike noble gases, the halogens (Cl, Br, I) appear to have similarly high compatibilities in chrysotile-lizardite serpentinites. The majority of serpentinites analysed have halogen compositions similar to sedimentary marine pore fluids. However, deviations from this trend occur in mid-ocean ridge and forearc settings, raising the possibility that halogen abundance ratios can help identify geotectonic setting and the sources of fluids involved in serpentinisation (Fig 5).

The ability of serpentine to incorporate ppm levels of Br and I, its high concentrations of atmospheric noble gas (low concentrations of K, Th and U), and the stability of antigorite to depths exceeding 200 km (Ulmer and Trommsdorff, 1995), indicate that seafloor and forearc serpentinites could dominate the deep-subduction cycles of both the halogens (Cl, Br and I) and atmospheric noble gases.

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Table 1: Summary of % serpentinitisation and noble gas data (2 σ analytical uncertainty)

Sample	Protolith	% serp.	^{36}Ar mol g $^{-1}$ $\times 10^{-12}$	$^4\text{He}_\text{E}/^{36}\text{Ar}$	$^{20}\text{Ne}/^{36}\text{Ar}$	$^{84}\text{Kr}/^{36}\text{Ar}$	$^{130}\text{Xe}/^{36}\text{Ar}$	$^3\text{He}/^4\text{He}$ R/Ra	$^{40}\text{Ar}/^{36}\text{Ar}$
<i>15°20'N Fracture Zone, Mid-Atlantic Ridge</i>									
S011	Harz	96	1.4	2.3 $\pm$ 0.7	0.10 $\pm$ 0.07	0.032 $\pm$ 0.002	0.00043 $\pm$ 0.00003	nd	304 $\pm$ 3
S001	Harz	70	0.30	nd	nd	0.043 $\pm$ 0.004	0.00076 $\pm$ 0.00008	nd	333 $\pm$ 13
S009	Harz	80	6.9	nd	nd	0.030 $\pm$ 0.002	0.00039 $\pm$ 0.00002	nd	311 $\pm$ 2
S002	Harz	85	1.4	nd	nd	0.028 $\pm$ 0.003	0.00034 $\pm$ 0.00003	nd	332 $\pm$ 3
<i>Hess Deep, East Pacific Rise</i>									
S025	Harz	70	4.6	nd	0.10 $\pm$ 0.04	0.028 $\pm$ 0.003	0.00035 $\pm$ 0.00002	10 $\pm$ 16	307 $\pm$ 2
<i>Iberian passive margin</i>									
S016	Harz	99	0.60	nd	nd	0.040 $\pm$ 0.003	0.00071 $\pm$ 0.00005	nd	310 $\pm$ 5
S008	Harz	93	0.34	7 $\pm$ 2	0.02 $\pm$ 0.02	0.047 $\pm$ 0.006	0.00085 $\pm$ 0.00007	7 $\pm$ 7	312 $\pm$ 9
<i>Newfoundland passive margin</i>									
S015	Dun	88	0.82	nd	0.09 $\pm$ 0.02	0.038 $\pm$ 0.003	0.00077 $\pm$ 0.00005	0.2 $\pm$ 1.2	313 $\pm$ 4
S013	Dun	97	0.86	nd	nd	0.037 $\pm$ 0.003	0.00069 $\pm$ 0.00005	nd	339 $\pm$ 8
<i>Mariana forearc</i>									
S030	Harz	87	0.66	nd	nd	0.027 $\pm$ 0.002	0.00040 $\pm$ 0.00004	nd	334 $\pm$ 16
S038	Harz	80	1.5	nd	nd	0.034 $\pm$ 0.003	0.00049 $\pm$ 0.00005	nd	314 $\pm$ 7
S032	Harz	96	5.5	0.8 $\pm$ 0.1	0.13 $\pm$ 0.01	0.041 $\pm$ 0.003	0.00078 $\pm$ 0.00003	nd	306 $\pm$ 4
S035	Harz	65	0.82	nd	nd	0.029 $\pm$ 0.003	0.0001 $\pm$ 0.0001	nd	322 $\pm$ 27
<i>Guatemala forearc</i>									
S020	Harz	93	19	nd	0.19 $\pm$ 0.02	0.034 $\pm$ 0.002	0.00068 $\pm$ 0.00005	37 $\pm$ 62	308 $\pm$ 2
S019	Harz	95	0.32	nd	nd	0.035 $\pm$ 0.003	0.00060 $\pm$ 0.00004	nd	331 $\pm$ 11
S018	Dun	98	13	nd	nd	0.039 $\pm$ 0.002	0.00094 $\pm$ 0.00006	nd	312 $\pm$ 2
S017	Dun	99	18	nd	nd	0.039 $\pm$ 0.003	0.00083 $\pm$ 0.00004	nd	309 $\pm$ 3
<i>Internal Ligurides, Apennines</i>									
LBAR15	Harz	50	0.39	nd	nd	0.029 $\pm$ 0.003	0.00035 $\pm$ 0.00004	nd	305 $\pm$ 16
LBAR18	Lherz	20	0.22	nd	nd	0.039 $\pm$ 0.004	0.00051 $\pm$ 0.00006	nd	327 $\pm$ 25
LBR4V	Lherz	15	0.46	nd	nd	0.025 $\pm$ 0.002	0.00024 $\pm$ 0.00004	nd	341 $\pm$ 21
<i>External Ligurides (Monte Nero), Apennines</i>									
MN1	Lherz	80	0.32	nd	nd	0.023 $\pm$ 0.002	0.00022 $\pm$ 0.00003	nd	322 $\pm$ 13
MNS2	Lherz	80	0.44	nd	nd	0.026 $\pm$ 0.002	0.00023 $\pm$ 0.00003	nd	320 $\pm$ 10
MNS4	Lherz	50	0.34	nd	nd	0.031 $\pm$ 0.002	0.00042 $\pm$ 0.00005	nd	309 $\pm$ 11
MN5	Lherz	50	0.18	nd	nd	0.018 $\pm$ 0.003	0.00021 $\pm$ 0.00006	nd	313 $\pm$ 36
<i>Erro Tobbio, Western Alps</i>									
ET11/27	Lherz	60	1.7	nd	nd	0.029 $\pm$ 0.003	0.00033 $\pm$ 0.00002	nd	318 $\pm$ 4
ETPP1	Lherz	50	0.86	nd	nd	0.026 $\pm$ 0.002	0.00030 $\pm$ 0.00003	nd	317 $\pm$ 11
ET10/5	Lherz	20	0.90	nd	nd	0.025 $\pm$ 0.002	0.00025 $\pm$ 0.00002	nd	322 $\pm$ 8
Seawater (25 °C) ¹			34	0.049	0.17	0.036	0.00035	1	296

¹ Reference values from Ozima and Podosek (2002). The $^3\text{He}/^4\text{He}$ ratio is normalised to the atmospheric (Ra) of 1.4×10^{-6} . The $^4\text{He}_\text{E}/^{36}\text{Ar}$ value has been corrected for *in situ* production of ^4He based on previously reported U and Th abundances (see Kodolányi et al. (2012) or datasheet 2 of the supplementary information).

Abbreviations: Harz = harzburgite; Dun = dunite; Lherz = Lherzolite; bas = basalt; gab = gabbro; serp = serpentinite. Additional sample information is in Table S1 of the supplement.

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Table 2: Serpentinite halogen, K and Ca data (2 σ analytical uncertainty)²

Sample	K	Ca	Cl	Br	I	K/Cl	Br/Cl ($\times 10^{-3}$)	I/Cl ($\times 10^{-6}$)	Cl/ ^{36} Ar ($\times 10^6$)
	ppm	wt. %	ppm	ppm	ppm	Weight ratios			molar
<i>15°20'N Fracture Zone, Mid-Atlantic Ridge</i>									
S011	10	nd	1100	5.2	0.056	0.009 ± 0.004	4.7 ± 0.2	52 ± 2	22.5 ± 0.3
S001	nd	2.2	460	1.3	0.58	nd	2.7 ± 0.1	1260 ± 70	44 ± 2
S009	74	0.64	1200	6.8	0.085	0.06 ± 0.02	5.5 ± 0.1	69 ± 8	5.0 ± 0.1
S002	60	0.28	800	4.5	0.043	0.08 ± 0.01	5.6 ± 1.0	54 ± 3	15.8 ± 0.2
<i>Hess Deep, East Pacific Rise</i>									
S025	nd	0.85	1200	6.0	0.074	nd	5.1 ± 0.1	63 ± 5	7.23 ± 0.08
<i>Iberian passive margin</i>									
S016	71	0.20	1400	5.1	0.18	0.050 ± 0.005	3.6 ± 0.1	127 ± 5	66 ± 1
S008	4	0.14	590	1.6	0.017	0.008 ± 0.004	2.8 ± 0.5	28 ± 1	49 ± 1
<i>Newfoundland passive margin</i>									
S015	nd	2.2	1200	3.8	0.053	nd	3.3 ± 0.1	46 ± 2	40 ± 1
S013	nd	6.1	1700	5.5	0.50	nd	3.2 ± 0.1	290 ± 20	56 ± 1
<i>Mariana forearc</i>									
S030	128	0.33	420	2.7	6.2	0.31 ± 0.03	6.4 ± 0.2	14,800 ± 600	18 ± 1
S038	167	0.17	1000	8.2	45	0.16 ± 0.02	7.9 ± 0.2	43,300 ± 1800	19.6 ± 0.4
S032	163	0.32	1200	8.2	35	0.13 ± 0.02	6.8 ± 0.2	28,800 ± 1500	6.2 ± 0.1
S035	152	0.39	630	5.1	18	0.24 ± 0.05	8.2 ± 0.2	28,300 ± 1600	21 ± 1
<i>Guatemala forearc</i>									
S020	159	0.52	2300	24	9.4	0.07 ± 0.05	10.4 ± 0.3	4100 ± 200	3.43 ± 0.04
S019	13	0.17	1100	5.7	2.1	0.012 ± 0.005	5.3 ± 0.1	1950 ± 70	95 ± 3
S018	205	0.34	1100	8.4	5.2	0.18 ± 0.06	7.4 ± 0.2	4600 ± 300	2.37 ± 0.02
S017	268	0.54	990	7.2	6.9	0.3 ± 0.1	7.2 ± 0.1	6900 ± 300	1.56 ± 0.02
<i>Internal Ligurides, Apennines</i>									
LBAR15	nd	0.19	42	0.19	0.041	nd	4.5 ± 0.2	970 ± 40	3.1 ± 0.2
LBAR18	nd	1.1	42	0.16	0.016	nd	3.8 ± 0.2	370 ± 20	5.4 ± 0.4
LBR4V	nd	2.9	530	1.8	0.17	nd	3.4 ± 0.1	320 ± 20	33 ± 2
<i>External Ligurides (Monte Nero), Apennines</i>									
MN1	nd	1.4	300	1.8	2.1	nd	5.9 ± 0.3	6900 ± 400	26 ± 1
MNS2	nd	1.1	140	1.0	1.6	nd	6.9 ± 0.3	11,300 ± 600	9.0 ± 0.3
MNS4	nd	0.24	270	1.8	2.6	nd	6.6 ± 0.3	9500 ± 400	23 ± 1
MN5	34	0.37	300	1.9	2.5	0.11 ± 0.06	6.3 ± 0.3	8400 ± 500	46 ± 5
<i>Erro Tobbio, Western Alps</i>									
ET11/27	nd	0.77	740	3.4	1.3	nd	4.6 ± 0.2	1800 ± 100	12.0 ± 0.2
ETPP1	37	0.37	560	2.4	0.49	0.07 ± 0.04	4.3 ± 0.2	870 ± 50	18 ± 1
ET10/5	nd	2.4	330	1.3	0.64	nd	3.8 ± 0.2	1900 ± 100	10.5 ± 0.3
Seawater (25 °C)	380	400	19,400	66	0.06	0.02	3.47	3.08	16

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² Analytical uncertainty does not include uncertainty in the reference materials (Kendrick, 2012). The total uncertainty for Br/Cl and I/Cl ratios is ~10 % (2 σ). The full data set is reported comprehensively in the electronic supplementary datasheets.

Fig 1 (Kendrick et al., 2012)

Fig 1. Phase diagram showing the stability fields of serpentine minerals and the relationship of the low-grade chrysotile-lizardite serpentinites of this study (1) to eclogite facies antigorite-serpentinites from Erro Tobbio, Italy (2) and olivine-enstatite rocks from Almirez, Spain (3) (Kendrick et al., 2011). The subduction zone PT paths shown were modelled by Peacock (1990). Mineral stabilities are from Bromiley and Pawley (2003) and Ulmer and Trommsdorf (1995) additional references are provided in Kendrick et al.(2011).

Fig 2 (Kendrick et al., 2012)

Fig 2. Excerpt from the World Ocean Floor map of Heezen and Tharp (1977) showing the approximate positions of the IODP drill holes and ophiolites sampled in this study: MAR = Mid-Atlantic Ridge 15° 20' N Fracture Zone; H = Hess Deep on the East Pacific Rise; I = 'peridotite ridge' on the Iberian passive margin; N = 'Mauzy Ridge' on the Newfoundland passive margin; G = Guatemala forearc; M = South Chamorro seamount, Marianas forearc; and A = Italian ophiolites (Alps and Apennines). References to sample locations and drill core are given in supplement Table S1.

Fig 3 (Kendrick et al., 2012)

Fig 3. Noble gas release systematics of six samples with contrasting degassing behaviour, showing the % gas released versus temperature of the heating step. Significant release of irradiation-produced noble gases only occurs at temperatures of ≥ 300 °. Samples that are more retentive of irradiation-produced $^{38}\text{Ar}_{\text{Cl}}$ tend to be more retentive of atmospheric ^{36}Ar .

Fig 4 (Kendrick et al., 2012)

Fig 4. The relationship between the degree of serpentinisation a) Cl concentration (ppm), and b) ^{36}Ar concentration (mol g⁻¹). c) log-log plot showing the broad relationship between Cl and ^{36}Ar concentration in variably serpentinised peridotites.

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Fig 5 (Kendrick et al., 2012)

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Fig 5. Linear (a) and log-log (b) Br/Cl versus I/Cl three element plots showing the chrysotile-lizardite serpentinites of this study and the average of Erro Tobbio (ET) antigorite-serpentinites (Ant. ET; Kendrick et al., 2011). Reference fields include: the compositional range of gas hydrate and sedimentary marine pore fluids (grey dots; Fehn et al., 2000; 2003; 2006; 2007ab; Muramatsu et al., 2001; 2007; Tomaru et al., 2007; 2009; Lu et al., 2008); MORB glasses (Jambon et al., 1995; Kendrick et al., 2012 – supplementary data); mica/amphibole (Kendrick, 2012); and the composition of 'wedge fluids' exhumed from 100 km (Sumino et al., 2010). Note Br*/I indicates the seawater-corrected Br/I ratio where $Br^* = Br - 0.0035 \times Cl$.

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Fig 6 (Kendrick et al., 2012)

Fig 6. Noble gases in chrysotile-lizardite serpentinites and other subduction zone lithologies. a) The ^{36}Ar concentrations of serpentinites and rocks formed by serpentine breakdown are highlighted in the grey box. Seawater and the upper mantle are shown for reference. b) Spidergram showing serpentinite noble gas (Ng) abundance ratios ($^4\text{He}/^{36}\text{Ar}$, $^{20}\text{Ne}/^{36}\text{Ar}$, $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$) normalised to air (Air = 1). The compositions of seawater, the upper mantle, and fields for sedimentary rocks and altered basalts are shown for reference. Serpentinite analyses are shown with the same symbols as in part a, and averages are shown for antigorite and olivine-enstatite. Data sources include: Holland and Ballentine (2006); Kendrick et al. (2011), Matsuda and Nagao (1986), Moreira et al. (1998), Podosek et al., (1980), Staudacher and Allègre (1988). Note that the ^4He abundances are corrected for in situ production in this study but not in the literature data, meaning the ^4He enrichment depends on age.