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Key Points:

- Mantle xenoliths from intraplate settings have a wide range of halogen elemental ratios
- The SCLM in different localities originally had MORB-like halogen ratios, suggesting uniform halogen ratios in the convecting mantle
- Evolution rate of mantle I/Cl value is estimated using mass balance calculations

Supporting Information:

- Supporting Information S1
- Table S1
- Table S2
- Table S3

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Halogen Heterogeneity in the Lithosphere and Evolution of Mantle Halogen Abundances Inferred From Intraplate Mantle Xenoliths

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Abstract We present halogen, noble gas, and major and trace element compositions of mantle xenoliths from intraplate settings (Eifel, Kilbourne Hole, San Carlos, and Hawaii). The xenoliths show a wide range of halogen elemental ratios, which form two arrays centered on the halogen composition of mid-ocean ridge basalts. The samples on the array toward high I/Cl value have relatively low Cl concentration and low ratios of highly incompatible elements relative to heavy rare earth elements, whereas the samples on the array toward low Br/Cl value have higher Cl concentration and trace elements ratios. The detailed mechanisms to account for these signatures are equivocal at present. However, they are most likely to be related to secondary processes of volatile loss during partial melting and secondary phase formation during interaction with melts. The common primary mid-ocean ridge basalt-like halogen ratios in mantle xenoliths from different parts of the globe indicate that the mantle itself must have a relatively uniform composition over a wide scale. The mantle has maintained its halogen composition over billion year timescales without being affected by I-rich halogens being transported into the mantle. Mass balance calculations suggest that, in order to maintain the I/Cl ratio of the convecting mantle over 2 Gyr, the I/Cl ratio of the subducted halogens must be no more than several times higher than the present-day mantle value.

Plain Language Summary Elemental and isotopic compositions of volatile species such as halogens, noble gases, hydrogen, and carbon can be used to trace the evolution of these species in the Earth. Halogens are important tracers of subduction recycling of surface volatiles into the mantle; however, there is only limited understanding of halogens in the mantle. Here we provide new halogen data of mantle xenoliths from intraplate settings. The mantle xenoliths show a wide range of halogen elemental ratios, which are expected to be related to later processes after the xenoliths formed. A similar primary halogen component is present in the xenoliths sampled from different localities. This suggests that the mantle has the uniform halogen composition over a wide scale. The halogen composition in the convecting mantle is expected to have remained constant over more than 2 billion years, despite subduction of iodine-rich halogens. We used mass balance calculations to gain understanding into evolution rate of I/Cl ratio in the mantle. Calculations suggest that, in order to maintain the I/Cl ratio of the mantle over 2 Gyr, the I/Cl ratio of the subducted halogens must be no more than several times higher than the present-day mantle value.

1. Introduction

Volatiles are continuously expelled from the mantle via volcanic activity while being simultaneously transported into the mantle at subduction zones (e.g., Barnes et al., 2018; Hilton et al., 2002; Holland & Ballentine, 2006; Ito et al., 1983; Kendrick et al., 2017; Schilling et al., 1978). Since even a relatively small addition of volatiles may result in major changes to the chemical and physical properties of mantle rocks,

understanding volatile recycling processes is critical for gaining insights into mantle heterogeneity and its temporal evolution (e.g., Bolfan-Casanova, 2005; Holland & Ballentine, 2006; Kawamoto et al., 2015; Kendrick et al., 2017). However, critical questions remain over the quantity of volatiles being subducted, how they are transported, and the mechanism of their incorporation into the mantle (e.g., Barnes et al., 2018; Chavrit et al., 2016; Hilton et al., 2002; Holland & Ballentine, 2006; Ito et al., 1983; Kendrick et al., 2017; Kobayashi et al., 2017; van Keken et al., 2011).

Halogens and noble gases show highly contrasting concentrations between the surface and interior of the Earth, making them exceptionally sensitive indicators of subducted volatiles (e.g., Frezzotti & Ferrando, 2018; Hanley & Koga, 2018; Holland & Ballentine, 2006; Kendrick et al., 2017; Klemme & Stalder, 2018; Ozima & Podosek, 2002). Furthermore, these groups of elements show distinct elemental and/or isotopic compositions in different reservoirs, which can be used to reveal the origin and/or subduction path of volatiles (e.g., Broadley et al., 2016; Chavrit et al., 2016; Holland & Ballentine, 2006; John et al., 2011; Kendrick et al., 2011, 2012, 2017; Kendrick, Arculus, et al., 2014; Kendrick, Honda, et al., 2013, 2015; Kendrick, Jackson, et al., 2014, 2015; Kobayashi et al., 2017; Ozima & Podosek, 2002; Schilling et al., 1978; Sumino et al., 2010). Holland and Ballentine (2006) showed that the elemental and isotopic compositions of nonradiogenic isotopes of heavy noble gases (Ar, Kr, and Xe) in the convecting mantle are similar to those of seawater together with a sedimentary component and argued that seawater-sourced fluids are subducted into the convecting mantle. Seawater-like noble gases associated with halogens having Br/Cl and I/Cl values similar to sedimentary pore fluids (seawater trapped in the pores of marine sediments) have been found in exhumed mantle wedge peridotites (Sumino et al., 2010), mantle xenoliths from subduction zones (Kobayashi et al., 2017), and serpentinites from forearc and oceanic lithosphere (Kendrick et al., 2011; Kendrick, Honda, et al., 2013). The decomposition of I-rich organic materials in sediments results in sedimentary pore fluids that are enriched in I and leads to I/Cl ratios extending up to a few thousand times higher than the seawater value (Fehn et al., 2006; Kastner et al., 1990; Martin et al., 1993; Muramatsu et al., 2007). Sedimentary pore fluid-like halogens have also been found in mantle xenoliths from Antarctica, where they are attributed to ancient subduction enrichment processes that also contributed sediment-derived noble gases (Broadley et al., 2016).

On the basis of noble gas/H₂O and halogen/H₂O ratios of fluid inclusions in mantle xenoliths collected at volcanic fronts, Kobayashi et al. (2017) proposed that closed system processes control volatile transportation into the mantle. Volatiles derived from sedimentary pore fluid are incorporated into serpentine in a closed system formed at the slab outer rise, that is, their original compositions are preserved. Serpentine dehydration is a stepwise process accompanied by elemental fractionation of halogens (John et al., 2011; Kendrick et al., 2011); however, Kobayashi et al. (2017) argued that, although the dehydrated fluids may escape from the shallower part of subducting slabs, dehydration-hydration processes within the oceanic lithospheric mantle occur within a closed system until the final stage of serpentine dehydration, thus preserving the original sedimentary pore fluid-like compositions. Retention of this signature in the serpentine dehydration fluids trapped as fluid inclusions in the mantle xenoliths collected at volcanic fronts implies near total loss of both halogens and noble gases from the subducting slabs.

The sedimentary pore fluid-like signatures may be further transported into the mantle beyond sub-arc depths. In cold subducting slabs, serpentine transforms to hydrous high-pressure phases such as phase A (e.g., Ohtani, 2015), which are stable beyond sub-arc depth. If the noble gases can be retained during the transformation, serpentine and its high-pressure polymorphs may account for subduction of seawater-like noble gases into the convecting mantle. Serpentinites exhibit up to a few hundred times higher I/Cl ratio than the depleted mid-ocean ridge basalt (MORB) source mantle (John et al., 2011; Kendrick et al., 2011; Kendrick, Honda, et al., 2013). If seawater-like noble gases have been transported into the convecting mantle by the hydrated (serpentinized) oceanic lithospheric mantle, then I-rich halogens may have also been subducted. However, Kendrick, Jackson, et al. (2014, 2015) have reported relatively low and consistent halogen elemental ratios for MORB and oceanic island basalts (OIBs) and argued that these features can be explained if fractionation of halogens occurs during subduction, prior to being recycled and mixed into the deeper mantle. Since OIB may have sampled reservoirs >2 Ga, the similarity between MORB and OIB suggests that the halogen elemental ratios in the mantle have remained constant for at least 2 Gyr (Kendrick, Jackson, et al., 2015). As samples from the subcontinental lithospheric mantle (SCLM), diamonds exhibit a wide

range of Br/Cl and I/Cl ratios. However, Siberian diamonds have MORB-like halogen ratios and a MORB-like end-member is also present in diamonds from Canadian and African kimberlite sources, suggesting this component is widespread globally in the SCLM (Burgess et al., 2002, 2009; Johnson et al., 2000). However, the mechanisms responsible for reducing the I/Cl value of subducted fluid(s) to the MORB value and the magnitude of I recycling into the asthenospheric mantle are not well understood.

The halogen compositions of the lithospheric mantle, especially Br and I, are also not well constrained. In the lithospheric mantle, halogens are thought to be mainly stored in hydrous minerals formed by metasomatic processes such as amphibole, apatite, and phlogopite (Frezzotti & Ferrando, 2018; Klemme & Stalder, 2018). Recent studies have emphasized the importance of nominally anhydrous minerals as repositories for halogens in the lithospheric mantle (Frezzotti & Ferrando, 2018; Klemme & Stalder, 2018). However, because few analytical techniques can quantify trace amounts of halogens in mantle-derived materials, especially parts per billion or subparts per billion levels of Br and I, little is known about their abundance, behavior, and distribution including the extent of heterogeneity in the lithospheric mantle.

Here we report the compositions of heavy halogens (Cl, Br, and I), noble gases, and major and trace elements in mantle xenoliths from continental intraplate settings (Eifel, Kilbourne Hole, and San Carlos) and an oceanic intraplate setting (Hawaii). The lithospheric mantle at these localities is thought to be metasomatized by slab- and plume-derived components (section 2.1). Although the sizes of samples are limited, mantle xenoliths provide direct evidence of volatile signatures in the lithospheric mantle. The major objective of this work is to investigate the halogen characteristics of the lithospheric mantle at different localities through geochemical analyses of mantle xenoliths and to place constraints on the evolution history of the halogen compositions in intraplate settings. The evolution rate of halogen ratios in the convecting mantle is also investigated using a mass balance approach by considering the halogen subduction flux into the mantle, the outgassing flux from the mantle, and the halogen content of the mantle.

2. Samples

Mantle xenoliths from both continental and oceanic intraplate settings have been studied. The continental intraplate samples are from Dreiser Weiher and Meerfelder Maar in Eifel (Germany), Kilbourne Hole (New Mexico, USA), and San Carlos (Arizona, USA). The oceanic intraplate sample is from the Hualalai volcano (the Island of Hawaii, USA).

2.1. Geological Background

The continental mantle xenoliths from Eifel are hosted in Quaternary alkalic basalts. The Cenozoic European volcanic provinces including Eifel are linked to the development of an intracontinental rift (Wilson & Patterson, 2001). On the basis of Sr-Nd-Pb isotope systematics, HIMU (high μ , meaning high U/Pb)- and EM (enriched mantle)-like components have been thought to be involved in the mantle source (Wedepohl et al., 1994; Witt-Eickschen et al., 2003). Helium isotopic ratios in mantle xenoliths from Eifel are also HIMU-like, being more radiogenic than the MORB source (Buikin et al., 2005; Dunai & Baur, 1995; Gautheron et al., 2005). The homogeneous He isotopic ratios for various locations in the European volcanic provinces including Eifel led Gautheron et al. (2005) to suggest that the European SCLM is in steady state relative to in situ production of ^4He and the He influx from the asthenosphere.

The San Carlos volcanic field is a Late Tertiary to Quaternary center in the southern part of the Colorado Plateau, USA. Kilbourne Hole is a Late Pleistocene volcanic maar in the Potrillo volcanic field on the axis of the Rio Grande Rift. Subduction of the Farallon plate during the early Cenozoic metasomatized the lithospheric mantle beneath the Colorado plateau (Dixon et al., 2004; Lee, 2005). Mantle xenoliths from San Carlos have been classified into Groups I and II (Frey & Prinz, 1978). Group I xenoliths are dominated by olivine-rich peridotites that experienced partial melting (Frey & Prinz, 1978). Group II are dominated by clinopyroxenites that are interpreted to be cumulates from their host magma (Frey & Prinz, 1978). The samples studied are Group I xenoliths. Mantle xenoliths from Kilbourne Hole have been reported to be metasomatized by melt-rock interaction (Harvey et al., 2012). Urann et al. (2017) studied F and Cl in mantle xenoliths from these localities. The Cl concentrations of these mantle xenoliths are similarly low (<0.2 ppm of Cl; Urann et al., 2017). However, the relatively high F concentration in Kilbourne Hole is considered to be a consequence of interaction with hydrous slab melts from the subducted Farallon plate

Figure 1. Microphotographs of the mantle xenoliths from intraplate settings. (a) DW-07-3 from Eifel. Amphibole breaks down to fine-grained clinopyroxene (cpx), olivine, spinel, and glass. (b) MF-07-1 from Eifel. Orthopyroxene (opx) reacted with infiltrated melts. Fine-grained olivine, cpx, glass, and/or spinel were formed in grain boundaries indicated by orange circles. (c) KLB-Lhz-12 from Kilbourne Hole. Silicate glass formed during partial melting is spatially related to the host magma (basalt).

(>20 ppm of F; Urann et al., 2017). Helium isotopic ratios were reported to be MORB-like (8 ± 1 Ra, where $1 \text{ Ra} = \text{atmospheric ratio of } 1.399 \times 10^{-6}$; Moreira & Kurz, 2013; Ozima & Podosek, 2002) for mantle xenoliths from San Carlos and Kilbourne Hole (Day et al., 2015). Meisel et al. (2001) reported Re depletion model ages of the European and southwestern United States SCLM of 1.62 and 1.55 Ga, respectively.

The mantle xenolith collected at the Hualalai volcano is hosted by alkaline basalts of the 1800–1801 Kaupulehu flow (Kirby & Green, 1980). Magmatism in the Hawaiian Islands is related to a mantle plume (Wilson, 1965), and Hawaiian volcanoes have evolved through four stages: preshield, shield, postshield, and rejuvenated stages (Clague, 1987). The Hawaiian volcanoes spatially define two trends, the Loa and Kea trends, of which lavas of the shield stage have distinct geochemical signatures. The Hualalai volcano is located on the Loa trend, which contains subducted crustal and sedimentary components (e.g., Blichert-Toft et al., 1999; Hauri, 1996). Hawaiian mantle xenoliths have been reported to contain plume-derived noble gases with higher $^3\text{He}/^4\text{He}$ ratios than that of MORB (Kaneoka & Takaoka, 1978; Staudacher et al., 1986).

2.2. Sample Descriptions

Twelve mantle xenoliths were studied here: four spinel lherzolites (MF-07-1, MF-07-2, MF-07-4, and DW-07-3) and a spinel harzburgite (DW-07-4) from Eifel; four spinel lherzolites (KLB-Lhz-11, KLB-Lhz-12, KLB-Lhz-14, and KLB-Lhz-16) from Kilbourne Hole; two spinel lherzolites (SC-1 and SC-2) from San Carlos; and a dunite (Hualalai) from Hawaii. The lherzolites and harzburgite are mainly composed of olivine, orthopyroxene (opx), clinopyroxene (cpx), and spinel. The harzburgite DW-07-4 contains less cpx (about 1 vol %) than the lherzolites. The dunite is mainly composed of olivine. Hydrous minerals such as amphibole and phlogopite, which can be major reservoir for halogens in the lithospheric mantle (Frezzotti & Ferrando, 2018; Klemme & Stalder, 2018), were not found. Alteration products such as serpentine minerals and clays are also absent. However, the former presence of amphibole is evident in some Eifel samples as described below.

Eifel lherzolites show a protogranular texture, whereas the harzburgite shows porphyroclastic texture, where coarse (~10 mm in diameter) olivine and opx porphyroclasts are surrounded by a matrix of fine (~0.5 mm in diameter) recrystallized grains (olivine, opx, and cpx). The lherzolites MF-07-2, MF-07-4, and DW-07-3 include polygonal aggregates (Figure 1a), where euhedral to subhedral grains of olivine (~0.05 mm in diameter), cpx (~0.1 mm in diameter), and spinel (~0.02 mm in diameter) are embedded in clear to brown glass. The cpx grains are aligned in the same direction as the long axis of the host polygonal aggregate (Figure 1a). The size and modal abundance of the polygonal aggregates are 0.1–0.5 mm in diameter and < 1 vol %, respectively. On the basis of in situ geochemical analysis and mass balance calculations, previous studies (Shaw & Klügel, 2002; Stosch & Seck, 1980) indicated that such polygonal aggregates are a breakdown product of amphibole. As stated above, irrespective of the potential presence of amphibole, we did not observe amphibole or other hydrous mineral phases. The lherzolite MF-07-1 and harzburgite DW-07-4 include aggregates of olivine, cpx, glass, and/or spinel elongated along grain boundaries of the main constituent minerals (Figure 1b). In this aggregate, the clear glass surrounding randomly

distributed euhedral to subhedral grains of olivine (~0.2 mm in diameter), cpx (~0.3 mm in diameter), and/or spinel (~0.05 mm in diameter) is often associated with opx, at which the contact surface extends irregularly (Figure 1b). The harzburgite DW-07-4 includes a small amount of glass interstitial to the fine recrystallized grains, and it is considered that the lherzolite MF-07-1 and harzburgite DW-07-4 were metasomatized by silica-undersaturated melts at some time before eruption to the surface.

All samples from Kilbourne Hole are very fresh. Alteration and partial melt were either not observed (KLB-Lhz-11) or are present in very minor amounts (KLB-Lhz-14 and KLB-Lhz-16). Silicate glass formed during partial melting is present around spinel and spatially related to the host basalt in KLB-Lhz-12 (Figure 1c). The texture of this peridotite xenolith indicates that the xenolith was not in equilibrium with melt. This suggests that the peridotite partially melted by rapid heating most likely when the xenolith was entrained by the host magma. Alteration is also limited in San Carlos and Hawaiian samples, although small amounts of silicate glass were observed along grain boundaries. The silicate glass is most likely to have been formed by infiltration of the host magma. Secondary minerals including hydrous minerals were not observed in these samples.

Fluid and melt inclusions are present in minerals from the mantle xenoliths (Figures 2a and 2b). Although fluid inclusions were not observed in SC-1 from San Carlos, the release of noble gases during crushing experiments (section 4.2) indicates their presence. It is considered likely that the fluid inclusions are too small to be observed by optical microscopy. Raman spectra of fluid inclusions were obtained for the Eifel and some of the Kilbourne Hole samples and revealed that the fluid inclusions are mainly composed of CO₂ (Figures 2c and 2d). The presence of H₂O was not detected.

From the Raman spectra of CO₂ fluid inclusions, the depth of origin of the mantle xenoliths was estimated following the method described by Yamamoto and Kagi (2006) (supporting information). The fluid inclusions in the Eifel samples have densities of 0.7–1.1 g/cm³, except for three fluid inclusion analyses showing significantly lower density (Figure 2e and supporting information Table S1). The density of the fluid inclusions in the Kilbourne Hole sample is relatively homogeneous (0.808 ± 0.029 g/cm³). The equilibrium temperature has been estimated to be 760–1240 °C and 890–1180 °C for mantle xenoliths from Eifel and Kilbourne Hole, respectively (Harvey et al., 2012; Stosch & Seck, 1980; Witt-Eickschen et al., 2003). From the density of CO₂ and equilibrium temperature, the trapping pressures are estimated to be 0.26–1.1 GPa for Eifel and 0.40–0.52 GPa for Kilbourne Hole xenoliths (Figure 2f). The Moho discontinuities beneath Eifel and Kilbourne Hole have been reported to be about 28 km (pressure equivalent to 0.72 GPa) and about 26 km (0.66 GPa), respectively (Harvey et al., 2012; Witt-Eickschen et al., 2003). Thus, the fluid inclusion trapping pressures for Eifel and Kilbourne Hole are at, or below, the pressures equivalent to depths of the Moho discontinuities. However, as discussed later in section 4.2, mantle-derived He is dominantly present in the fluid inclusions, suggesting that shallow level contamination from a crustal component is limited.

3. Experimental Methods

3.1. Halogen and Noble Gas Analysis

The mantle xenolith samples were coarsely crushed to a grain size of 0.5–2 mm and leached with 1 M HNO₃. Halogen concentrations were determined using the neutron irradiation noble gas mass spectrometry technique (Böhlke & Irwin, 1992; Johnson et al., 2000; Kendrick, 2012; Ruzié-Hamilton et al., 2016; Turner, 1965), which enables determination of trace amounts of halogens in mantle-derived materials. Using this method, halogens (Cl, Br, and I) and some other elements (K, Ca, Ba, and U) are converted to corresponding isotopes of noble gases (³⁷Ar_{Ca}, ³⁸Ar_{Cl}, ³⁹Ar_K, ⁸⁰Kr_{Br}, ¹²⁸Xe_I, ¹³¹Xe_{Ba}, and ¹³⁴Xe_U) by neutron irradiation.

Neutron irradiation of the continental intraplate samples was carried out either in the GRICIT facilities of the TRIGA Reactor, Oregon State University, for 205.1 hr or in the SAFARI-1 reactor at Pelindaba, South Africa, for 24 hr. Noble gases in the neutron-irradiated samples (about 50 mg) were analyzed using the MS1 or ARGUS VI mass spectrometers at the University of Manchester (Ruzié-Hamilton et al., 2016). The irradiated samples were crushed in vacuo using Nupro® valve crushers (Stuart et al., 1994). Crushing facilitates preferential release of noble gases from fluid inclusions (Kurz, 1986). The noble gases extracted by crushing were analyzed using the MS1 mass spectrometer. Following crushing, the remaining powder was melted using either a Ta resistance furnace (MS1) or a CO₂ laser (CETAC Fusion CO₂; ARGUS VI).

Figure 2. (a and b) microphotographs of fluid inclusions in orthopyroxene (opx) from MF-07-1 (Eifel) and in clinopyroxene (cpx) from KLB-Lhz-11 (Kilbourne Hole), respectively. In some fluid inclusions, a vapor phase was observed in CO₂ liquid. (c and d) Representative Raman spectra of CO₂ fluid inclusions in opx from MF-07-1 and in cpx from KLB-Lhz-11, respectively. The two Raman peaks at 1,286 and 1,388 cm⁻¹ correspond to CO₂. (e) Density of the studied CO₂ fluid inclusions in the Eifel and Kilbourne Hole samples. Circles, triangles, and squares represent fluid inclusions hosted by opx, cpx, and olivine, respectively. (f) *P-T* conditions and density of the CO₂ system (Pitzer & Sterner, 1994). Contours represent the density of CO₂ in g/cm³. The *P-T* origin of the mantle xenoliths from Eifel and Kilbourne Hole is shown by the blue and green shaded areas, respectively. See text for references of the equilibrium temperature of the mantle xenoliths.

Sample weights analyzed were about 40 and 10 mg for the furnace and laser heating, respectively. The Hawaiian sample was irradiated in Japan Research Reactor-3 (JRR-3), Japan Atomic Energy Agency, for 48 hr. Noble gases were analyzed using a noble gas analysis system at the University of Tokyo, which had been modified from that described by Ebisawa et al. (2004). About 50 mg of the sample was crushed using a hydraulic press and about 30 mg of the remaining powder was melted in a W-coil furnace. The detailed analytical procedures for noble gas analysis have been described by Broadley et al. (2016), Ruzié-Hamilton et al. (2016), and Kobayashi et al. (2017).

Some samples were analyzed after Ca-derived ³⁷Ar had decayed (half-life of 35 days). For the samples from continental intraplate settings, minor interferences from Ca-derived ³⁶Ar, ³⁸Ar, and ³⁹Ar were corrected using CaO concentrations obtained by X-ray fluorescence (XRF) analysis (section 3.2). XRF data are not available for sample KLB-Lhz-12, and the CaO concentration of 1.5 wt % is assumed from the average of other Kilbourne Hole samples. The Hawaiian sample was also analyzed after ³⁷Ar had decayed; however,

interference from Ca-derived Ar was not corrected for this sample. The interference is expected to be negligible in the Hawaiian sample because it was irradiated in a neutron flux with a particularly high thermal/fast ratio (39.7 ± 2.4).

Isotopic ratios of He, Ne, and Ar were determined by analyses of unirradiated samples (0.3–2 g) using a noble gas analysis system described by Sumino et al. (2001). Noble gases in unirradiated samples were extracted by stepwise crushing using a Ni-slug moved vertically in an external magnetic field generated by solenoid coils. Prior to stepwise crushing, each sample, except for the Hawaiian sample, was heated at 800 °C for 30 min, in order to reduce the amounts of adsorbed atmospheric noble gases.

3.2. Major and Trace Element Analysis

Major and trace element compositions of the Eifel, San Carlos, and two of Kilbourne Hole samples were analyzed using XRF spectroscopy and inductively coupled plasma-mass spectrometry (ICP-MS), respectively. Whole rock samples (about 1–20 g) were washed in methanol in an ultrasonic bath, dried in an oven overnight, and ground into a powder. Using an Axios (PANalytical) XRF spectrometer at the University of Tokyo, major element compositions were determined from glass beads, which were prepared from 0.4 g of the sample powder and 4.0 g of $\text{Li}_2\text{B}_4\text{O}_7$.

The remaining powders, weighing about 110 mg, were digested in $\text{HF-HNO}_3\text{-HClO}_4$ (5:3:5) at 120 °C for 1 day. The solutions were evaporated to near dryness at 120 °C and then 4 mL of 4 M HNO_3 was added to the samples. Residues remaining in the HNO_3 solutions were further digested after decanting the HNO_3 solutions. In some samples, black residues, probably spinel, remained after the second acid treatment. Because spinel has a negligible effect on the budget of trace elements such as rare earth element (REE) and large-ion lithophile element (LILE) in peridotites (e.g., Bedini & Bodinier, 1999; Stosch & Seck, 1980), the residues were removed after being washed with 1 mL of 4 M HNO_3 . Internal standards comprising known amounts of In and Bi were added to the solutions. After dilution, the solutions were analyzed using iCAP Q ICP-MS (Thermo Fisher Scientific) at the University of Tokyo. The accuracy of trace element analysis was evaluated using JP-1, a geological reference material distributed by the Geological Survey of Japan (e.g., Shirasaka et al., 2004, and references therein).

4. Results

4.1. Halogens

The halogen compositions are presented in Table 1. The range of halogen concentrations in the intraplate mantle xenoliths are Cl = 0.086–9.6 ppm, Br = 0.56–8.6 ppb, and I = 0.042–0.752 ppb. These values are significantly lower than those of mantle peridotites from subduction zones (mostly Cl $\geq$ 10 ppm, Br $\geq$ 10 ppb, and I $\geq$ 5 ppb; Broadley et al., 2016; Kobayashi et al., 2017; Sumino et al., 2010). Urann et al. (2017) reported Cl concentration in a San Carlos harzburgite of 0.18 ppm, which is similar to those obtained in this study (0.086–0.44 ppm; Table 1). Urann et al. (2017) found a similarly low Cl concentration in a Kilbourne Hole lherzolite of 0.14 ppm; however, Beyer et al. (2012) reported that olivine separated from a Kilbourne Hole mantle xenolith contains 5.8 ppm of Cl. Although the published values vary by more than 1 order of magnitude, they span a similar range of Cl concentrations as the studied Kilbourne Hole samples (0.87–7.52 ppm; Table 1).

Some samples contain up to several parts per million of Cl in total; however, the crushing steps did not release significant amounts of halogen-derived noble gases (e.g., 0–3% of Cl; supporting information Table S2). Only CO_2 bearing inclusions were detected by Raman spectroscopy, and the low halogen release during crushing is consistent with the absence of H_2O -bearing saline fluid inclusions. The bulk of the halogens were released during furnace or laser heating, indicating they were hosted in a solid phase(s) such as the mineral lattice and melt inclusions. Repeat analysis of SC-2 from San Carlos gave halogen ratios that differed by about a factor of 2 (Table 1). Relatively large variations in halogen abundances are more likely when using small quantities ($\leq$ 50 mg) of coarsely crushed (0.5–2 mm) mineral samples, where only several grains may be present. Variations may be further amplified if the overall halogen abundances in the mineral matrix are very low or if they are dominated by halogens in minor phases such as melt inclusions that are sparsely distributed between different host mineral grains.

Table 1
Halogen Compositions of Mantle Xenoliths From Intraplate Settings

Sample	Cl (ppm)	Br (ppb)	I (ppb)	Br/Cl (10^{-3} mol/mol)	I/Cl (10^{-6} mol/mol)
<i>Eifel</i>					
MF-07-1	0.311 (63)	1.41 (11)	0.042 (20)	2.01 (44)	38 (20)
MF-07-2	9.628 (85)	4.888 (96)	0.249 (79)	0.2253 (49)	7.2 (23)
MF-07-4	6.55 (13)	5.26 (25)	0.133 (11)	0.356 (18)	5.69 (50)
DW-07-3	4.76 (23)	8.62 (39)	0.265 (34)	0.803 (53)	15.5 (21)
DW-07-4	4.847 (96)	7.55 (38)	0.204 (35)	0.692 (37)	11.8 (20)
<i>Kilbourne Hole</i>					
KLB-Lhz-11	1.22 (19)	3.97 (22)	0.478 (49)	1.44 (24)	109 (21)
KLB-Lhz-12	7.52 (15)	0.97 (36)	0.189 (17)	0.057 (21)	7.03 (64)
KLB-Lhz-14	1.04 (11)	4.47 (22)	0.330 (62)	1.92 (22)	89 (19)
KLB-Lhz-16	0.87 (18)	2.36 (13)	0.120 (20)	1.21 (26)	39 (10)
<i>San Carlos</i>					
SC-1	0.086 (63)	0.56 (11)	0.093 (31)	2.8 (21)	301 (240)
SC-2#1	0.44 (14)	3.21 (18)	0.537 (65)	3.2 (10)	341 (114)
SC-2#2	0.246 (15)	0.814 (74)	0.752 (76)	1.47 (16)	861 (102)
<i>Hawaii</i>					
Hualalai	0.173 (11)	0.626 (44)	0.215 (13)	1.60 (15)	347 (30)

Note. Errors are given as least significant figures in brackets at a 1σ level of confidence. The data are the combined total of crushing and stepwise heating. The data for individual crushing and heating steps are presented in supporting information Table S2.

Elemental ratios of halogens are shown in Figure 3. The intraplate samples show a wide range of I/Cl and Br/Cl ratios (Figure 3a). Two samples (MF-07-1 from Eifel and KLB-Lhz-16 from Kilbourne Hole) show halogen ratios consistent with MORB and OIB within 1σ uncertainties. Samples from San Carlos, Kilbourne Hole (except for KLB-Lhz-12), and Hawaii form an array extending from MORB/OIB values toward higher I/Cl values as found in sedimentary pore fluids and serpentinites. Irrespective of metasomatic type (section 2.2), the Eifel samples show a linear relationship between MORB/OIB-like and low Br/Cl similar to altered oceanic crust (AOC)-like halogen ratios (Figure 3a). One Kilbourne Hole sample (KLB-Lhz-12) shows low Br/Cl ratio comparable to the Eifel samples. Chlorine concentrations of the samples having lower Br/Cl than MORB and OIB are higher than 4 ppm, whereas other samples have about 1 ppm or less (Figure 3b).

4.2. Noble Gases

The noble gas compositions are presented in Table 2. $^3\text{He}/^4\text{He}$ ratios obtained during stepwise crushing are relatively constant in each sample except for San Carlos, where He levels were equivalent to blank and could not be determined (Figure 4a and supporting information Table S3). The $^3\text{He}/^4\text{He}$ ratios of Eifel samples are 6.17–6.74 Ra (1 Ra = atmospheric ratio of 1.399×10^{-6} ; Ozima & Podosek, 2002). These values are consistent with those of previous studies on Eifel and other mantle xenoliths from the European SCLM (Buikin et al., 2005; Dunai & Baur, 1995; Gautheron et al., 2005). The $^3\text{He}/^4\text{He}$ ratios of Kilbourne Hole samples (7.92–8.10 Ra) are slightly lower than 9.08 ± 0.09 Ra reported previously for a mantle xenolith from same locality (Day et al., 2015). However, these values are within the range of the MORB source mantle (8 ± 1 Ra; Moreira & Kurz, 2013). The Hawaiian samples have $^3\text{He}/^4\text{He}$ ratios consistent with previously determined values obtained by fusion of mantle xenoliths (8.2–10.6 Ra; Kaneoka & Takaoka, 1978). $^4\text{He}/^{40}\text{Ar}^*$ ratios ($^{40}\text{Ar}^* = \{(^{40}\text{Ar}/^{36}\text{Ar})_{\text{measured}} - (^{40}\text{Ar}/^{36}\text{Ar})_{\text{air}}\} \times ^{36}\text{Ar}$) from all localities are 0.27–2.09 (supporting information Table S3) and mostly below the $^4\text{He}/^{40}\text{Ar}^*$ production ratio in the MORB source mantle of 1.6–4.2 (Graham, 2002). Lower $^4\text{He}/^{40}\text{Ar}^*$ ratios are often observed in mantle xenoliths including those from the studied localities (Buikin et al., 2005; Gautheron et al., 2005). These signatures imply that mantle-derived noble gases are preserved in the CO_2 inclusions present in the studied samples.

$^{40}\text{Ar}/^{36}\text{Ar}$ ratios ($<6,200$; supporting information Table S3) are lower than the MORB value ($\sim 30,000$; Moreira & Kurz, 2013), suggesting significant contribution from an atmospheric component. An atmospheric component also contributes to the Ne isotopic ratios (Table 2). Matsumoto et al. (2001) argued that a positive correlation between concentrations of ^3He and ^{36}Ar released during crushing is strong evidence

Figure 3. Halogen compositions of the mantle xenoliths from intraplate settings. (a) I/Cl versus Br/Cl. The black area is the range of MORB and OIB samples. The area enclosed by the dashed line represents the range of sedimentary pore fluids. The green dashed line represents linear regression for the Eifel samples using least squares fitting ($r^2 = 0.98$). (b) Br/Cl versus the inverse of Cl concentration. The black area is the range for the MORB source mantle. Data for sample SC-1 are not shown because of large uncertainties. Errors are 1σ . Data sources: MORB and OIB (Kendrick et al., 2012; Kendrick, Jackson, et al., 2014, 2015; Kendrick et al., 2017), sedimentary pore fluids (Fehn et al., 2006; Kastner et al., 1990; Martin et al., 1993; Muramatsu et al., 2007), seawater (Bruland & Lohan, 2014), serpentinites from the oceanic lithosphere (John et al., 2011; Kendrick et al., 2011; Kendrick, Honda, et al., 2013), AOC (Chavrit et al., 2016; Kendrick, Honda, et al., 2015), and MORB source mantle (Burgess et al., 2002; Jambon et al., 1995; Kendrick et al., 2012, 2017; Kendrick, Jackson, et al., 2014, 2015; Saal et al., 2002; Salters & Stracke, 2004). The halogen ratios reported by Kendrick et al. (2011, 2012) and Kendrick, Honda, et al. (2013) were recalculated using revised values for scapolite monitors (Kendrick, Arculus, et al., 2013). MORB = mid-ocean ridge basalt; OIB = oceanic island basalt; AOC = altered oceanic crust.

that the ^{36}Ar was present in the mantle source and not derived from shallow level contamination. This is because ^3He can be regarded as a mantle-derived component. DW-07-4 from Eifel shows a linear correlation between ^3He and ^{36}Ar (Figure 4b), which may indicate that its $^{40}\text{Ar}/^{36}\text{Ar}$ ratio reflects addition of a subducted atmospheric component. However, a linear correlation between ^3He and ^{36}Ar is not observed during multiple crushing steps of the other Eifel samples (Figure 4b), indicating that the atmospheric component in these samples was most likely introduced by shallow level contamination.

$^{132}\text{Xe}/^{36}\text{Ar}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of DW-07-4 from Eifel also show a linear correlation, which offsets to lower slope than the air-mantle mixing line in Figure 4c. However, most of other samples do not show a linear correlation and are relatively enriched in ^{132}Xe (Figure 4c). The Kilbourne Hole and San Carlos samples are also enriched in ^{132}Xe relative to ^{36}Ar (Figure 4c). The relative ^{132}Xe enrichment was observed for noble gases released during the heating step prior to crushing (supporting information Table S3). Despite attempts to reduce levels of adsorbed noble gases by heating samples at 800°C prior to crushing, it is considered that adsorption of atmospheric gases on the surface of sample grains explains the poor correlation between ^3He and ^{36}Ar and relative enrichment of ^{132}Xe . Furthermore, the poor correlation between $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{132}\text{Xe}/^{36}\text{Ar}$ ratios (Figure 4c) prevents any additional insight from air-mantle mixing relationships in the fluid inclusions.

No systematic difference in noble gas composition is observed between the low Br/Cl and high I/Cl samples (Table 2). This implies that noble gases and halogens are decoupled from each other in the sampled regions of the SCLM. Noble gases are thought to be retained mainly by fluid inclusions and were released from the samples using crushing extraction. However, halogens are present in a solid phase(s) and are predominantly released during heating experiments (section 4.1). The different sites for noble gases and halogens account for their decoupled signatures. The predominantly atmospheric isotopic compositions of Ne and Ar and the elementally fractionated heavy noble gas ratios in most of the samples do not provide any additional insights into the mantle sources of halogens and are not considered further from hereon.

4.3. Major and Trace Elements

The major and trace element concentrations are presented in Table 3. No systematic difference in major element composition is observed between samples showing different halogen signatures. However, the trace element patterns are distinct. The primitive mantle (PM)-normalized patterns of trace elements and REE of the high I/Cl samples (San Carlos and Kilbourne Hole) are relatively flat (Figures 5a and 5b). The PM-normalized patterns of MF-07-1 from Eifel, which has MORB/OIB-like halogens, are indistinguishable from those of the high I/Cl samples (Figures 5a and 5b). The patterns of the low Br/Cl samples (Eifel except for MF-07-1) are distinct from other samples (Figures 5c and 5d). In particular, the ratios of LILE and light REE (LREE) to heavy REE (HREE) of high I/Cl samples are lower and relatively constant compared to the low Br/Cl samples and in the latter these ratios increase with lower Br/Cl values (Figure 6). The LREE enrichment relative to HREE is consistent with previous findings for Eifel mantle xenoliths that contain metasomatic products formed by the breakdown of amphibole (Stosch & Seck,

Table 2
Noble Gas Compositions of Mantle Xenoliths From Intraplate Settings

Sample	$^3\text{He}/^4\text{He}$ (Ra)	^4He (10^{-8})	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$	^{20}Ne (10^{-12})	$^{38}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{Ar}/^{36}\text{Ar}$	^{40}Ar (10^{-8})	^{84}Kr (10^{-12})	^{132}Xe (10^{-12})
<i>Eifel</i>										
MF-07-1	6.22 (15)	1.606 (61)	10.38 (18)	0.0347 (22)	7.54 (32)	0.1892 (13)	2912 (15)	4.61 (18)	0.538 (33)	0.0762 (81)
MF-07-2	6.262 (80)	8.68 (21)	10.105 (54)	0.03291 (75)	48.7 (1.2)	0.18841 (64)	1949 (11)	20.68 (49)	3.05 (10)	0.402 (25)
MF-07-4	6.17 (12)	2.759 (70)	10.19 (10)	0.0362 (16)	13.91 (37)	0.18850 (73)	1914.2 (8.6)	11.57 (29)	1.898 (63)	0.287 (14)
DW-07-3	6.48 (13)	2.543 (81)	9.640 (82)	0.0295 (12)	12.36 (40)	0.18833 (65)	1081.0 (6.0)	4.84 (15)	1.210 (40)	0.1129 (70)
DW-07-4	6.740 (58)	16.49 (41)	11.015 (99)	0.0432 (13)	30.78 (78)	0.1891 (11)	4882 (18)	43.3 (1.1)	2.642 (95)	0.358 (32)
<i>Kilbourne Hole</i>										
KLB-Lhz-11	8.10 (28)	1.213 (50)	9.81 (10)	0.0324 (12)	14.96 (65)	0.18798 (80)	1013.1 (25)	4.79 (19)	1.462 (66)	0.343 (20)
KLB-Lhz-12	7.95 (44)	0.527 (21)	9.789 (49)	0.02896 (42)	67.0 (3.2)	0.18808 (93)	343.6 (12)	6.48 (30)	4.93 (26)	0.422 (31)
KLB-Lhz-14	7.92 (26)	1.440 (61)	9.63 (15)	0.0300 (17)	12.90 (56)	0.18770 (82)	692.3 (21)	3.50 (14)	1.699 (75)	0.437 (29)
KLB-Lhz-16	8.09 (82)	0.278 (16)	9.68 (22)	0.0300 (39)	6.29 (33)	0.1883 (13)	620.3 (15)	1.613 (81)	0.979 (61)	0.277 (25)
<i>San Carlos</i>										
SC-1	b.l.	b.l.	9.56 (37)	0.0285 (38)	1.242 (64)	0.1875 (15)	337.2 (10)	0.313 (14)	0.343 (22)	0.0743 (55)
SC-2	b.l.	b.l.	9.81 (24)	0.0312 (27)	3.05 (16)	0.18761 (96)	749.4 (14)	0.919 (40)	0.352 (21)	0.0500 (38)
<i>Hawaii</i>										
Hualalai#1	9.51 (16)	44.7 (22)	10.61 (16)	0.0321 (16)	96.6 (4.8)	0.19010 (63)	2376 (72)	24.4 (1.2)	2.26 (11)	0.1430 (72)
Hualalai#2	9.00 (18) ^a	25.0 (13) ^a	10.35 (16)	0.0321 (19)	72.0 (7.2)	0.18740 (63)	2791.7 (9.5) ^a	27.8 (1.4) ^a	2.68 (13)	0.295 (15)
Air	1		9.8	0.029		0.188	296			
MORB	8		12.6	0.060		0.188	~30,000			

Note. Errors are given as least significant figures in brackets at a 1σ level of confidence. Units of noble gas concentrations are ccSTP/g. Ra: atmospheric $^3\text{He}/^4\text{He} = 1.399 \times 10^{-6}$ (Ozima & Podosek, 2002). b.l.: equivalent to static blank level (1.4×10^{-10} ccSTP for ^4He). The data are the combined total of all stepwise crushing steps. The data for individual crushing steps and heating prior to crushing are presented in supporting information Table S3. MORB = mid-ocean ridge basalt.

^aFrom Fischer et al. (2005). Data sources: air (Ozima & Podosek, 2002) and MORB (Moreira & Kurz, 2013).

1980). It should be noted that, due to limited sample availability, it was not possible to analyze abundances of trace elements in KLB-Lhz-12, which shows a low Br/Cl ratio (Figure 3a). This means the trace element features displayed by the low Br/Cl samples may be restricted to the single locality of Eifel.

Some samples showed relative enrichment or depletion of Nb and Ta, or a positive spike at Pb (Figures 5a and 5c). Removal of spinel residue after acid treatment (section 3.2) might cause the depletion of these elements in some samples. However, the origin of the positive Pb anomaly is unclear at present.

5. Discussion

5.1. Halogens in Intraplate Settings

The intraplate mantle xenoliths show a wide range of halogen compositions both in concentrations and ratios, which is also apparent at the locality scale at Eifel and Kilbourne Hole (Figure 3). The two halogen arrays formed by the samples shown in Figure 3 are centered on the MORB/OIB halogen composition, implying a common mantle end-member for the two arrays. On the basis of the two arrays, from hereon samples are grouped into either a high I/Cl group (San Carlos, Hawaii, and Kilbourne Hole except for KLB-Lhz-12) or a low Br/Cl group (Eifel and KLB-Lhz-12).

5.1.1. High I/Cl Group

The San Carlos and Hawaiian samples have the highest I/Cl ratio ($>300 \times 10^{-6}$ mol/mol; Table 1) and their halogen elemental ratios (I/Cl and Br/Cl ratios) are similar to those of sedimentary pore fluids and serpentinites (Figure 3a). At first sight, this may imply mixing with a subducted component in the mantle source. However, these samples have Cl concentrations lower than that of the depleted mantle (0.5–6 ppm; Burgess et al., 2002; Jambon et al., 1995; Kendrick et al., 2017; Saal et al., 2002; Salters & Stracke, 2004), which is the opposite from what would be expected for incorporation of such halogen-rich fluids. This is consistent with the findings of Urann et al. (2017), who previously argued against percolation of Cl-rich fluids in San Carlos as evidenced by the low Cl concentration. Furthermore, the relatively low concentrations of trace elements and low LILE/HREE and LREE/HREE ratios of San Carlos (Figures 5a and 5b) do not support the presence of a slab-derived fluid and/or melt added by subduction. San Carlos and Hawaiian samples contain small amounts of silicate glass associated with grain boundaries, which were most likely formed by infiltration

Figure 4. Noble gas compositions of the mantle xenoliths from intraplate settings. (a) $^3\text{He}/^4\text{He}$ versus the inverse of ^4He concentration. The dashed line is $^3\text{He}/^4\text{He}$ ratio of air. The shaded areas represent the range of $^3\text{He}/^4\text{He}$ ratios of the MORB source mantle (8 ± 1 Ra) and European SCLM (6.3 ± 0.4 Ra). (b) ^3He concentration versus ^{36}Ar concentration. (c) $^{40}\text{Ar}/^{36}\text{Ar}$ versus $^{132}\text{Xe}/^{36}\text{Ar}$. The dotted line represents linear mixing between the noble gas compositions of the convecting mantle and unfractionated air. Errors are 1σ . Data sources: He and Ar of Hualalai#2 (Fischer et al., 2005), Eifel (B05,G05) (Buikin et al., 2005; Gautheron et al., 2005), Kilbourne Hole and San Carlos (D15) (Day et al., 2015), MORB source mantle (Moreira & Kurz, 2013), European SCLM (Gautheron et al., 2005), air and seawater at 0 °C (Ozima & Podosek, 2002), and convecting mantle (Holland & Ballentine, 2006). SCLM = subcontinental lithospheric mantle; MORB = mid-ocean ridge basalt.

of the host magma (section 2.2). Although the halogen composition of the silicate glass is unknown, the concentration may be higher than that in mantle minerals. However, the low Cl concentration and low LILE/HREE and LREE/HREE ratios of these samples suggest that the bulk samples do not contain enough amount of silicate glass to explain their high I/Cl ratios.

San Carlos samples show K/Cl ratios (>170 mol/mol; supporting information Table S2) several times higher than samples from Kilbourne Hole and Eifel (4–37 mol/mol) and the mantle value (6–45 mol/mol; Kendrick et al., 2017). Given the similar incompatibilities of Cl and K, such high K/Cl ratios associated with low halogen contents imply that the halogen signatures are more likely to be related to the selective loss of volatiles rather than addition. However, it is unlikely that the xenoliths have experienced degassing in the same way as erupted melts. Elemental fractionation among heavy halogens (Cl, Br, and I) is not apparent in MORB and OIB (Kendrick, Jackson, et al., 2014, 2015; Kendrick et al., 2017). However, heavy halogens are highly incompatible; therefore, residual peridotites containing much lower halogen concentrations than MORB and OIB may be more sensitive to minor halogen fractionation effects. The fractionation of the K/Cl ratios might also be amplified in the residual peridotites and occurs during partial melting of peridotites. Although the detailed mechanism is equivocal, the high K/Cl ratio and relatively low Cl concentration may indicate that the San Carlos samples experienced a volatile loss event.

Similar inferences are not readily possible based on the K/Cl value of the Hawaiian sample. The Hawaiian sample was irradiated in the JRR-3 (section 3.1), where the fast neutron flux was too low to generate sufficient $^{39}\text{Ar}_\text{K}$, such that the K content could not be determined. An upper limit estimate based on the blank

Table 3
Major (wt %) and Trace Element (ppm) Compositions of Mantle Xenoliths From Continental Intraplate Settings

	Eifel					Kilbourne Hole		San Carlos	
	MF-07-1	MF-07-2	MF-07-4	DW-07-3	DW-07-4	KLB-Lhz-11	KLB-Lhz-16	SC-1	SC-2
<i>wt %</i>									
SiO ₂	43.52	45.19	44.33	44.25	42.54	43.72	44.53	45.57	44.47
TiO ₂	0.06	0.04	0.04	0.05	0.05	0.12	0.05	0.05	0.10
Al ₂ O ₃	1.99	2.31	2.15	1.26	1.19	3.23	1.35	1.99	5.05
FeO	7.91	8.16	8.32	7.80	7.37	8.71	8.66	8.04	8.49
MnO	0.12	0.13	0.13	0.12	0.11	0.13	0.13	0.13	0.13
MgO	45.28	43.48	43.2	47.06	48.35	41.31	46.11	44.15	39.31
CaO	1.56	2.2	2.2	1.17	0.77	2.7	0.71	1.23	2.09
Na ₂ O	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	0.08
K ₂ O	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.07
P ₂ O ₅	0.03	0.03	0.03	0.04	0.03	0.03	0.03	0.02	0.03
Total	100.47	101.54	100.40	101.76	100.41	100.01	101.57	101.18	99.82
<i>ppm</i>									
Sc	11	15	13	13	8.9	15	8.7	13.4	25
V	82	114	102	64	81	112	108	93	149
Rb	0.047	0.27	0.23	0.32	0.35	0.14	0.15	0.044	0.58
Sr	4.6	30	16	22	6.0	7.0	2.6	5.8	16
Y	0.96	0.97	1.0	0.74	0.39	2.5	0.47	0.63	1.8
Zr	1.4	0.76	1.2	3.3	1.8	3.4	1.3	1.4	5.8
Nb	0.23	0.69	0.65	4.9	0.84	0.23	0.29	0.28	1.7
Cs	0.0019	0.0036	0.0046	0.0045	0.0060	0.0068	0.0039	0.0035	0.0073
Ba	3.3	10.6	9.7	10.0	10.8	3.3	1.8	0.30	8.1
La	0.18	3.5	2.2	1.4	0.61	0.22	0.13	0.32	0.83
Ce	0.42	5.4	2.9	4.0	1.1	0.52	0.29	0.76	1.6
Pr	0.059	0.37	0.30	0.54	0.12	0.087	0.032	0.087	0.18
Nd	0.29	0.85	1.1	2.2	0.48	0.52	0.15	0.36	0.74
Sm	0.089	0.070	0.18	0.37	0.090	0.23	0.037	0.090	0.17
Eu	0.034	0.025	0.049	0.11	0.030	0.090	0.013	0.032	0.066
Gd	0.12	0.14	0.18	0.30	0.096	0.33	0.050	0.10	0.23
Tb	0.024	0.020	0.027	0.036	0.014	0.067	0.0093	0.017	0.043
Dy	0.18	0.16	0.18	0.19	0.080	0.48	0.075	0.12	0.32
Ho	0.040	0.040	0.041	0.033	0.017	0.11	0.019	0.026	0.073
Er	0.13	0.14	0.13	0.086	0.053	0.33	0.069	0.087	0.24
Tm	0.020	0.022	0.022	0.012	0.0081	0.049	0.012	0.015	0.038
Yb	0.14	0.16	0.16	0.073	0.060	0.33	0.096	0.11	0.28
Lu	0.023	0.027	0.026	0.012	0.010	0.053	0.018	0.020	0.045
Hf	0.054	0.029	0.019	0.066	0.048	0.14	0.038	0.030	0.15
Ta	0.011	0.021	0.016	0.29	0.041	0.011	0.010	0.019	0.11
Pb	0.082	0.24	0.28	0.12	0.087	0.26	0.064	0.13	0.12
Th	0.024	0.59	0.34	0.15	0.090	0.025	0.027	0.013	0.13
U	0.011	0.11	0.11	0.031	0.026	0.0088	0.0069	0.0044	0.046

level of ³⁹Ar_K yields K/Cl <230 mol/mol, which does not exclude a similar volatile loss process as inferred for San Carlos. The K/Cl ratios of the Kilbourne Hole samples are within the range of the mantle value. These samples also show less deviation of halogen ratios from the mantle range and may not have experienced the same level of volatile loss relative to San Carlos samples.

5.1.2. Low Br/Cl Group

The Eifel samples show a linear relationship between I/Cl and Br/Cl ratios (Figure 3a), suggesting that the halogen signatures reflect a mixing between two components. The Br/Cl ratios of Eifel samples decrease with increasing Cl concentrations and LILE/HREE and LREE/HREE ratios (Figures 3b and 6). Breakdown products in some samples attest to the former presence of amphibole (MF-07-2, MF-07-4, and DW-07-3; section 2.2). Amphibole is known to have relatively high Cl concentration and low Br/Cl (and I/Cl) ratio (Chavrit et al., 2016; Kendrick, 2012; Kendrick, Honda, et al., 2015; Kobayashi et al., 2017). If the halogens in amphibole are retained in its breakdown products, the low Br/Cl trend for the Eifel samples extending from MORB/OIB values can be explained by the former presence of amphibole in the peridotites.

Figure 5. (a) Primitive mantle-normalized incompatible trace element and (b) rare earth element patterns of the samples with high I/Cl ratios and those with MORB-like halogen ratios (Figure 3a). (c) Primitive mantle-normalized incompatible trace element and (d) rare earth element patterns of the samples with low Br/Cl ratios (Figure 3a). Normalizing values after McDonough and Sun (1995). MORB = mid-ocean ridge basalt.

Relative enrichment of LREE to HREE, which was observed in Eifel mantle xenoliths containing breakdown products of amphibole (Stosch & Seck, 1980), and correlation between Br/Cl and LREE/HREE ratios (Figure 6) support the suggestion that these signatures are controlled by the former presence of amphibole.

Sample DW-07-4, which was metasomatized by melt infiltration, plots on the same trend as other Eifel samples (Figure 3a); however, the breakdown products of amphibole were not found in the studied section (section 2.2). Instead, this sample contains silicate glass formed by melt infiltration, where a substantial amount of halogens may be present. On the basis of Sr-Nd-Pb isotope systematics, HIMU- and EM-like components have been thought to be involved in the plume beneath Eifel (Wedepohl et al., 1994; Witt-Eickschen et al., 2003). OIB that has EM and HIMU components has been reported to have MORB-like halogen elemental ratios (Kendrick, Jackson, et al., 2014, 2015; Kendrick et al., 2017). Amphibole in mantle xenoliths from Eifel is thought to be formed by reaction between anhydrous peridotites and a hydrous fluid or melt (Stosch & Seck, 1980). Thus, addition of this fluid or melt may be responsible for the halogen ratios in DW-07-4, resulting in it plotting on a trend formed by former amphibole.

The halogen signatures in the Eifel samples can be explained by a mixing between MORB/OIB-like halogens and those in former amphibole and/or silicate glass. MF-07-1, which has the least metasomatized texture, has halogen ratios consistent with MORB and OIB within uncertainties. Melt inclusions, which might be trapped just prior to eruption, may be the main host of the MORB/OIB-like halogens. Halogen concentrations in melt inclusions are expected to be relatively high compared to those in mineral lattice. However, the Cl concentration in MF-07-1 is low (0.311 ± 0.063 ppm; Table 1) and consistent with those obtained by in situ analyses of mantle minerals (Urann et al., 2017), suggesting that the mineral lattice is the major host of halogens, at least for Cl. Even if melt inclusions having MORB/OIB-like halogen ratios contribute to the halogen budget, they do not overwhelm those present in the lattice. This suggests that the mineral lattice of MF-07-1 has halogen elemental ratios similar to MORB and OIB. Therefore, because the least

Figure 6. Br/Cl versus (a) U/Yb and (b) La/Yb. Errors are 1σ . Br/Cl ratio of the depleted mantle is defined by MORB (and OIB). Data sources: U/Yb and La/Yb of the depleted mantle (Salters & Stracke, 2004) and Br/Cl ratios of MORB and OIB (Kendrick et al., 2012; Kendrick, Jackson, et al., 2014, 2015; Kendrick et al., 2017). The Br/Cl ratio reported by Kendrick et al. (2012) was recalculated using revised values for scapolite monitors (Kendrick, Arculus, et al., 2013). MORB = mid-ocean ridge basalt; OIB = oceanic island basalt.

metasomatized xenolith has MORB/OIB-like halogen ratios, the SCLM beneath Eifel is expected to have had halogen ratios consistent with MORB and OIB before amphibole and silicate glass were formed.

The $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$ ratios of the fluid inclusions are consistent with mantle origin: however, the depth of origin of the Eifel samples, which is estimated from density of CO_2 in fluid inclusions, extends up to the base of the crust (Figure 2b). Fluid inclusions hosted by omphacite in eclogites from the Norwegian Caledonides have been reported to have high Br/Cl ratios up to 14×10^{-3} mol/mol (Svensen et al., 1999, 2001). These extreme ratios were explained by Cl incorporation into hydrous minerals during lower crustal hydration leaving residual fluids with high Br/Cl values. If halogens in such hydrous minerals were incorporated into the xenoliths, then the Br/Cl ratio would decrease. However, a deep crustal origin is not consistent with the noble gases present in fluid inclusions (section 4.2) and, as discussed above, the geochemical signatures of the Eifel samples are entirely consistent with the MORB/OIB-like halogens, which are observed in the least metasomatized sample (MF-07-1), and addition of amphibole- and/or silicate glass-derived halogens to some samples.

KLB-Lhz-12 from Kilbourne Hole shows similar halogen signatures to those from Eifel (Figure 3). This sample contains silicate glass around spinel, which was formed during partial melting and is spatially related to the host basalt (Figure 1c). The partial melting is expected to have occurred when the xenolith was entrained by the host magma (section 2.2). Although the timescale for interaction with the host magma may be limited, it is possible that the xenolith acquired halogens from the magma. Urann et al. (2017) argued that a slab melt derived from the subducted Farallon plate was responsible for the relatively high F concentration in a Kilbourne Hole mantle xenolith. It is also possible that the low Br/Cl halogens, which are similar to AOC (Figure 3a; Chavrit et al., 2016; Kendrick, Honda, et al., 2015), were also derived from a slab melt. This process indicates that the low Br/Cl component is secondary. Although other Kilbourne Hole samples are classified in the high I/Cl group (section 5.1.1), their halogen elemental ratios plot around those of MORB and OIB (Figure 3a). As argued earlier, the low halogen concentrations suggest that the mineral lattice is the major host of halogens in the Kilbourne Hole samples in the high I/Cl group. This indicates that the

halogen ratios in the SCLM beneath Kilbourne Hole can be explained by three processes: (i) an original MORB/OIB-like halogen compositions, (ii) a small amount of volatile loss from KLB-Lhz-11 and KLB-Lhz-14, and (iii) minor addition of slab melts to KLB-Lhz-12.

5.1.3. The SCLM as a Volatile Reservoir

Kendrick, Jackson, et al. (2014, 2015) and Kendrick et al. (2017) noted the uniformity of halogen ratios in the present-day mantle on the basis of the similarity between MORB and OIB. Hereafter, we refer to the halogen elemental ratios in the present-day mantle as those obtained from MORB and OIB, $\text{Br/Cl} = (1.2 \pm 0.4) \times 10^{-3}$, and $\text{I/Cl} = (17 \pm 8) \times 10^{-6}$ mol/mol (Kendrick et al., 2017). The mantle Br/Cl and I/Cl ratios and the Cl concentration in the depleted mantle (0.5–6 ppm; Burgess et al., 2002; Jambon et al., 1995; Kendrick et al., 2017; Saal et al., 2002; Salters & Stracke, 2004) yield Br and I concentrations in the depleted mantle of 1.4–16 and 0.03–0.4 ppb, respectively.

Although the studied samples experienced metasomatic events, the Br and I concentrations of most of the continental samples are within the ranges of the depleted mantle concentrations (Table 1). Chlorine concentrations are within a factor of 2 for all samples except for San Carlos SC-1, which has an unusually low Cl concentration (0.086 ± 0.063 ppm, Table 1). This indicates that the studied SCLM has halogen

concentrations that are not very different from the depleted mantle. The lithospheric mantle beneath the continental margin subduction zones is, however, enriched in halogens, especially I, because of slab-derived halogens (Broadley et al., 2016). Therefore, the global average of halogen concentrations in the SCLM is expected to be higher than those in the depleted mantle, indicating the SCLM is an important reservoir of halogens (Broadley et al., 2016, 2018).

5.2. The Evolution of Mantle Halogen Content

5.2.1. Mantle Halogen Content and Subduction of Halogens

The wide range of halogen compositions in the studied mantle xenoliths (Figure 3) reflects secondary processes in the lithospheric mantle, which has modified the original signature. Despite these halogen heterogeneities, the mantle xenoliths from different parts of the globe (Europe and North America) show relatively consistent primary halogen ratios, which are in the range of MORB and OIB. The simplest explanation for common MORB/OIB-like halogens is that the halogen compositions in the convecting mantle have been relatively uniform, and the SCLM has preserved its halogen compositions since its isolation from the convecting mantle. However, given the complex metasomatic history in the studied localities (section 2.2), it is also possible that the MORB/OIB-like halogens were introduced in a subsequent stage via asthenospheric melts and/or fluids. Because the common MORB/OIB-like halogens are found in different parts of the globe, this process also suggests that the mantle itself must have a relatively uniform composition over a wide scale. This is consistent with arguments based on MORB, OIB, and diamond samples (Burgess et al., 2002; Kendrick, Jackson, et al., 2014, 2015; Kendrick et al., 2017).

An important issue to assess is the timescale over which the mantle maintained its uniform MORB-like halogen ratios. Meisel et al. (2001) have investigated the Re-Os system of mantle xenoliths including those from the localities studied here and reported Re depletion model ages of the SCLM in Europe and southwestern United States of 1.62 and 1.55 Ga, respectively. If it is assumed that the primary (present-day MORB-like) halogen composition in the studied samples has been retained since these ages, then it is suggested that the halogen composition in the convecting mantle has remained constant for ≥ 1.62 Ga. However, because the Re-Os system is relatively robust against subsequent processing in the mantle (e.g., Walker et al., 1989), the Re depletion model ages might not be reset during the metasomatic events, in which the MORB-like halogens may be introduced. A common MORB-like end-member has been found in diamonds from Africa and Siberia and as a component in Canadian diamonds showing a large range of fractionated halogen ratios (Burgess et al., 2002, 2009; Johnson et al., 2000). The eruption ages of host kimberlites of the diamonds are up to about 380 Ma (Burgess et al., 2002, 2009; Johnson et al., 2000). The slightly higher I/Cl ratios of African diamonds relative to the modern MORB value (Burgess et al., 2002; Johnson et al., 2000) may indicate that the mantle I/Cl value was higher in the past, although equally it may reflect a relatively minor level of mantle heterogeneity. Separate from diamonds, it has been argued that the mantle has maintained its halogen composition over billion year timescales. Because OIB may have sampled ancient reservoirs >2 Ga in age, the similarity between MORB and OIB halogen compositions has been used as evidence that the convecting mantle has maintained a uniform and constant halogen compositions over this timescale (Kendrick, Jackson, et al., 2015).

Having established that the MORB mantle halogen composition has remained stable for 2 Gyr, we first consider likely subduction components and then place constraints on halogen subduction over this timescale by modeling net fluxes to the deeper mantle. On the basis of relationships between lithophile trace elements and halogens in MORB and OIB, it has been argued that halogens in the mantle are being added by subduction (Kendrick et al., 2017). Serpentinites from the oceanic lithospheric mantle show relatively limited variation in Br/Cl ratios ($1\text{--}3 \times 10^{-3}$ mol/mol), whereas their I/Cl ratios vary from $<10 \times 10^{-6}$ to $>3,000 \times 10^{-6}$ mol/mol (John et al., 2011; Kendrick et al., 2011; Kendrick, Honda, et al., 2013). More than 80% of the reported I/Cl ratios of serpentinites are higher than the mantle value (John et al., 2011; Kendrick et al., 2011; Kendrick, Honda, et al., 2013). Mantle peridotites from subduction zones have sedimentary pore fluid-like halogens with high I/Cl ratios ($\geq 200 \times 10^{-6}$ mol/mol), which are thought to be transported by the hydrated (serpentinized) oceanic lithospheric mantle (Broadley et al., 2016; Kobayashi et al., 2017; Sumino et al., 2010). Thus, it is most likely that the I/Cl ratio of halogens transported by the hydrated oceanic lithospheric mantle is higher than the mantle value.

Figure 7. Cartoon showing calculation model about I/Cl evolution in the mantle. Italics are assumptions to simplify the calculation.

Kendrick, Jackson, et al. (2015) accounted for the uniform and relatively low I/Cl ratio of the mantle by suggesting that addition of the hydrated oceanic lithospheric mantle with high I/Cl ratio is balanced either by subduction of Cl-rich materials such as AOC (Chavrit et al., 2016; Kendrick, Honda, et al., 2015) or by the preferential loss of I from subducting slabs at relatively shallow depths (John et al., 2011; Kendrick et al., 2011; Pagé et al., 2016). However, there is support for I-rich halogen subduction beneath and beyond sub-arc depth. (i) Halogen signatures in mantle peridotites from subduction zones show that fractionation of halogens is limited at least until sub-arc depths (Kobayashi et al., 2017; Sumino et al., 2010). Kobayashi et al. (2017) proposed that the dehydration-hydration processes operating in the oceanic lithospheric mantle preserve the original sedimentary pore fluid-like signatures at least until sub-arc depth. (ii)

Mantle peridotite xenoliths from the Western Antarctic Rift are strongly enriched in I relative to Cl, with I/Cl ratio up to 1 order of magnitude higher than marine sedimentary pore fluids (Broadley et al., 2016). The I enrichment is attributed to accumulation of fractionated sedimentary pore fluid-like halogens, which were subducted during Paleozoic subduction along the margin of Gondwana (Broadley et al., 2016). (iii) Serpentine-derived I-rich halogens have been also found in back-arc basin basalts, again suggesting that the I-rich halogens are transported beyond sub-arc depth (Kendrick, Arculus, et al., 2014). These observations suggest that sedimentary pore fluid-like halogen ratios are preserved until sub-arc depth and that I-rich signatures can be potentially further transported.

5.2.2. Mass Balance Constraints on the Asthenospheric Mantle Halogen Composition

In order to consider evolution of the mantle halogen contents, it is necessary to consider the mass balance among input and output fluxes and the halogen contents in the mantle. The presence of seawater-like noble gases in the convecting mantle (Holland & Ballentine, 2006), which were added via serpentine subduction, raises the potential for a corresponding addition of serpentine-derived I-rich halogens. However, the subduction flux of noble gases into the deep mantle is not well constrained, which limits our ability to understand the storage capacity of the mantle for subducted I-rich halogens. Here we use a mass balance approach to evaluate how much I can be subducted and mixed into the convecting mantle in order to maintain the mantle I/Cl value at a constant value. The approach uses mass balance among the halogen subduction flux into the mantle, the outgassing flux from the mantle, and the halogen content of the mantle (Figure 7). The subduction flux is considered to be the fraction of halogens that are subducted beyond arcs (deep subduction input into the mantle), and the outgassing flux is considered to be the amount of halogens released from mid-ocean ridges and oceanic islands.

While halogen elemental ratios are uniform in the mantle (Kendrick, Jackson, et al., 2014, 2015; Kendrick et al., 2017), their abundances may be heterogeneous. High-pressure and high-temperature experiments have suggested that Cl abundance in the OIB source mantle may be several times higher than that in the MORB source mantle (Joachim et al., 2015, 2017). However, the uniform halogen elemental ratios in the mantle make it possible to evaluate the evolution rate of I/Cl ratio in the convecting mantle using a ratio of average concentrations of Cl and I in the whole mantle.

In order to simplify the calculation, we assume that (i) the I/Cl ratio is uniform in the whole mantle; (ii) the subduction and outgassing fluxes of Cl are completely balanced, that is, the Cl abundance of the mantle is at steady state; (iii) the halogen subduction flux and I/Cl ratio of subducting halogens are constant; (iv) I in the oceanic crust is negligible, that is, I is transported only by the hydrated (serpentinized) oceanic lithospheric mantle; and (v) the outgassing flux of I is proportional to its average concentration (I/Cl ratio) in the whole mantle. Under these assumptions, we estimate the range of I/Cl ratios for subducting halogens that can maintain the mantle I/Cl value for 2 Gyr.

The uniform I/Cl ratio observed in MORB and OIB (Kendrick, Jackson, et al., 2014, 2015; Kendrick et al., 2017) supports the first assumption. Kendrick et al. (2017) estimated that the subduction and outgassing fluxes are well balanced at present, which is consistent with the second assumption. The third assumption may not be valid for the geological past because the subduction fluxes of volatiles are expected to be lower in the past relative to present day as a result of hotter geotherms in ancient subduction zones (e.g., van

Keken et al., 2011). Given this uncertainty, our calculation should be considered a maximum estimate for the I/Cl evolution rate in the convecting mantle. The fourth assumption is supported by the order of magnitude lower flux of I trapped within the AOC entering subduction zones compared to the hydrated oceanic lithospheric mantle (Chavrit et al., 2016).

Serpentine transforms to hydrous high-pressure phases such as phase A in cold subducting slabs (e.g., Ohtani, 2015). If halogens are retained during this phase transformation, substantial amounts of I-rich halogens can be transported into the deep mantle. Kendrick et al. (2018) reported that even secondary peridotites formed by the final breakdown of serpentine retain halogens with concentrations up to 1 order of magnitude higher than the depleted mantle. The hydrated oceanic lithospheric mantle is often invoked to account for subduction of volatiles and fluid-mobile elements into the deep mantle. Using thermal and petrological modeling, van Keken et al. (2011) argued that significant amount of water is transported into the deep mantle by the hydrated oceanic lithospheric mantle. The recycling of the hydrated oceanic lithospheric mantle into the deep mantle may explain a wide range of B isotopic ratio observed in OIB (Harvey et al., 2014). This highlights the potential importance of the hydrated oceanic lithospheric mantle as a carrier of halogens into the deep mantle.

The I/Cl ratio of the convecting mantle at any given time t ($I/Cl_{Mantle}(t)$) is calculated from equations (1)–(3):

$$I/Cl_{Mantle}(t + \Delta t) = [I/Cl_{Mantle}(t) \times Cl_{Mantle} + \{F_{Sub,I} - F_{Out,I}(t)\} \times \Delta t / M_{Mantle}] / Cl_{Mantle} \quad (1)$$

$$F_{Sub,I} = I/Cl_{Serp.} \times F_{Serp.,Cl} \quad (2)$$

$$F_{Out,I}(t) = I/Cl_{Mantle}(t) \times F_{Out,Cl} \quad (3)$$

where Cl_{Mantle} is the average Cl concentration in the whole mantle, M_{Mantle} is mass of the whole mantle, $F_{Sub,I}$ is subduction flux of I, $F_{Serp.,Cl}$ is subduction flux of Cl transported by the hydrated (serpentinized) oceanic lithospheric mantle, $I/Cl_{Serp.}$ is the I/Cl ratio of halogens transported by the hydrated oceanic lithospheric mantle, and $F_{Out,X}$ is the outgassing flux of halogen X from the mantle. As stated in assumptions (ii) and (iii) above, Cl_{Mantle} , $F_{Serp.,Cl}$, $I/Cl_{Serp.}$, and $F_{Out,Cl}$ are constant. The quantity of each parameter used in equations (1)–(3) is given in Table 4. The evolution rate of the mantle I/Cl ratio is calculated for given Cl_{Mantle} and $I/Cl_{Serp.}$. Because we assume that subduction and outgassing fluxes of Cl are balanced, we calculate for $F_{Out,Cl} \geq F_{Serp.,Cl}$.

The evolution rate of I/Cl ratio in the convecting mantle over the past 2 Gyr is shown in Figure 8. Our calculations show that subduction of the I-rich halogens ($I/Cl_{Serp.} \geq 200 \times 10^{-6}$ mol/mol) cannot maintain the I/Cl ratio in the convecting mantle, which originally had a depleted mantle concentration of halogens (Figures 8a and 8b). Subduction of halogens with $I/Cl_{Serp.} = 500 \times 10^{-6}$ mol/mol doubles I/Cl ratio in the convecting mantle within only <0.2 and <0.6 Gyr in the mantle containing 1 and 5 ppm of Cl, respectively. Even if a much higher primitive mantle Cl concentration is assumed (30 ppm of Cl; Palme & O'Neil, 2014), subduction of halogens with $I/Cl_{Serp.} \geq 500 \times 10^{-6}$ mol/mol will lead to a higher than present-day mantle I/Cl value over 2 Gyr (Figure 8d).

As stated earlier, although the elemental ratios are uniform (Kendrick, Jackson, et al., 2014, 2015; Kendrick et al., 2017), the halogen concentrations in the mantle are heterogeneous (Joachim et al., 2015, 2017). The OIB source mantle is expected to be relatively halogen rich compared to the depleted MORB source mantle (Joachim et al., 2015, 2017). The depleted domain in the mantle can be assumed to be about 70% of the whole mantle on the basis of the rarity of OIB with high (primitive) $^3\text{He}/^4\text{He}$ ratio (e.g., Graham, 2002). Assuming the mantle composes 70% of depleted mantle and 30% of primitive mantle, the average Cl concentration in the whole mantle is about 10 ppm.

The mass balance model suggests that, if the I/Cl ratio of the subducting oceanic lithospheric mantle is up to about 4–9.5 times higher than the mantle value ($I/Cl_{Serp.} = (65\text{--}160) \times 10^{-6}$ mol/mol), then the I/Cl ratio in

Table 4
Parameters Used in the Mass Balance Calculation

Symbol	Meaning	Value
Cl_{Mantle}	Cl concentration in the mantle	0.5–6 ppm (depleted mantle) 30 ppm (primitive mantle)
$I/Cl_{Mantle}(0)$	I/Cl ratio in the mantle of at $t = 0$	$(17 \pm 8) \times 10^{-6} \text{ mol/mol}^a$
M_{Mantle}	Mass of the whole mantle	$4.1 \times 10^{24} \text{ kg}$
$F_{Serp.,Cl}$	Deep subduction flux of Cl transported by the hydrated (serpentinized) oceanic lithospheric mantle	$4.5\text{--}9.9 \times 10^{10} \text{ mol/year}$
$F_{Out,Cl}$	Outgassing flux of Cl from mid-ocean ridges and oceanic islands	$6.8\text{--}14 \times 10^{10} \text{ mol/year}$

^aObtained from present-day mid-ocean ridge basalt and oceanic island basalt. Data sources: Cl concentration in the depleted mantle (Burgess et al., 2002; Jambon et al., 1995; Kendrick et al., 2017; Saal et al., 2002; Salters & Stracke, 2004), Cl concentration in the primitive mantle (Palme & O'Neil, 2014), I/Cl ratios in mid-ocean ridge basalt and oceanic island basalt (Kendrick et al., 2017), and subduction and outgassing fluxes of Cl (Ito et al., 1983; Kendrick et al., 2017; Schilling et al., 1978).

the convecting mantle, which has 10 ppm of Cl, can be maintained over 2 Gyr within uncertainties. However, the I/Cl ratio of halogens transported by the hydrated oceanic lithospheric mantle is expected to be more than 1 order of magnitude higher than the mantle value. Assuming halogens are subducted beyond sub-arc depth with an average serpentinite I/Cl ratio of $500 \times 10^{-6} \text{ mol/mol}$ (John et al., 2011; Kendrick et al., 2011; Kendrick, Honda, et al., 2013), then a maximum of about 15–30% of the serpentinite-related I transported beyond sub-arc depths can be further subducted into the deep mantle.

Figure 8. Evolution of I/Cl ratio in the convecting mantle over the last 2 Gyr shown for the range of possible mantle Cl concentrations (see Table 4 for details): (a) 1, (b) 5, (c) 10, and (d) 30 ppm. Each colored area represents the I/Cl ratio at the time of t at given I/Cl ratio of subducting halogens with uncertainties that reflect those of the subduction and outgassing fluxes. Gray area enclosed by dashed lines is the range of the present-day mantle I/Cl ratio, $(17 \pm 8) \times 10^{-6} \text{ mol/mol}$ (Table 4).

This corresponds to deep subduction flux of about 7×10^6 mol/year of I. Although it is noted that halogen fluxes into the trench via the oceanic lithospheric mantle depend on the depth considered, the estimated maximum deep I subduction flux of 7×10^6 mol/year corresponds to about 60% of I flux entering the trench via 300 m of the uppermost part of the hydrated oceanic lithospheric mantle (1.1×10^7 mol/year; Barnes & Straub, 2010; Chavrit et al., 2016; John et al., 2011; Kendrick, Honda, et al., 2013). It is uncertain where the major fraction of I lost from the subducting slabs currently resides. Potential long-term storage sites for halogens have been suggested to be within the SCLM in subduction zones (Broadley et al., 2016) and/or cratonic lithosphere (Broadley et al., 2018; Weiss et al., 2015).

The evolution of the mantle Br/Cl ratio can also be estimated by using the same mass balance approach. The results of this modeling (not shown) show that the present-day mantle Br/Cl value, $(1.2 \pm 0.4) \times 10^{-3}$ mol/mol, can be maintained by subduction of halogens with $\text{Br/Cl} \leq 9 \times 10^{-3}$ mol/mol within uncertainties. This range covers that of natural serpentinites from oceanic lithosphere (about $(1-3) \times 10^{-3}$ mol/mol; John et al., 2011; Kendrick et al., 2011; Kendrick, Honda, et al., 2013). Bromine transported by the oceanic crust, which is more significant than crustal I, is not considered in this calculation. However, because of the limited variation of Br/Cl ratio in geochemical samples compared to I/Cl ratio, the mantle Br/Cl value can be maintained even without preferential loss of Br.

6. Conclusions

Intraplate mantle xenoliths from Eifel, Kilbourne Hole, San Carlos, and Hawaii show a wide range of halogen compositions that are also apparent at the locality scale. The halogen elemental ratios form two arrays centered on the MORB/OIB halogen composition. One array extends toward high I/Cl value and the other extends toward low Br/Cl value. The mantle xenoliths having low Br/Cl ratios show higher Cl concentrations and higher LILE/HREE and LREE/HREE ratios, whereas other xenoliths show relatively low Cl concentrations and low LILE/HREE and LREE/HREE ratios. The Eifel samples show a linear relationship between Br/Cl and I/Cl ratios, and their Br/Cl ratios decrease with increasing Cl concentration and LILE/HREE and LREE/HREE ratios. The San Carlos samples, which show the highest I/Cl values, show K/Cl ratios several times higher than other samples and the mantle value.

The detailed mechanisms to explain the high I/Cl halogen signatures remain unclear: however, a volatile loss process during partial melting may explain the signatures of the high I/Cl group samples. The low Br/Cl group can be explained by the former presence of amphibole and/or silicate glass having a low Br/Cl ratio and high LILE/HREE and LREE/HREE ratios. Although the halogen compositions in the studied localities are heterogeneous, the presence of a common MORB-like end-member in the mantle xenoliths from different parts of the globe (Europe and North America) indicates that the mantle itself must have relatively uniform halogen ratios over a wide scale.

Halogen compositions in the mantle have been argued to have remained constant over billion year time-scales (Kendrick, Jackson, et al., 2015): however, halogens with I/Cl ratios more than 1 order of magnitude higher than the mantle value may be transported into the mantle at least beyond sub-arc depth. Mass balance calculations involving the subducting flux into the mantle, the outgassing flux from the mantle, and the halogen content in the mantle indicate that, in order to maintain the I/Cl ratio of the convecting mantle over 2 Gyr, the I/Cl ratio of the subducted halogens must be no more than several times higher than the present-day mantle value.

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