Geochemical Perspectives Letters

Published by the European Association of Geochemistry

Halogens in proto-Iceland plume basalts

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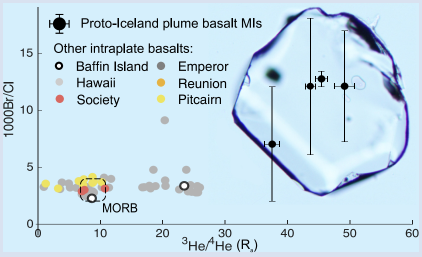
OPEN ACCESS
https://doi.org/10.7185/geochemlet.2539

Abstract



Melt inclusions in olivine phenocrysts from high $^3He/^4He$ proto-Iceland plume (PIP) basalts from Baffin Island and West Greenland have elevated Br/Cl ratios, extending to values significantly above those found in mid-ocean ridge basalt (MORB) and ocean island basalt (OIB). Chlorine isotope compositions are indistinguishable from MORB-source mantle and high Br/Cl occurs in the absence of geochemical indicators for serpentinite, altered oceanic crust or sediment. The highest Br/Cl occurs in melt inclusions from basalts with the highest $^3He/^4He$. The high Br/Cl ratios are at the high end of the range of putative Earth-source meteorites (CI- and CM-type carbonaceous chondrites). The PIP melt inclusion compositions are consistent with the addition of a small volume of halogen-rich, high Br/Cl chondritic material to halogen-depleted, low Br/Cl mantle.

Received 17 January 2025 | Accepted 1 September 2025 | Published 10 October 2025

Introduction

The halogens (F, Cl, Br, I) have proved to be valuable tracers of recycled marine sediment, altered oceanic crust and serpentinite in the Earth's mantle (Kendrick *et al.*, 2017). This recycled crustal material tends to dominate the halogen inventory of the convecting mantle (Kendrick *et al.*, 2017), likely masking the primordial halogen inventory. The relative abundances of Cl and Br in geochemically enriched intra-plate basalt glasses from Hawaii, Samoa, Society and Pitcairn are essentially indistinguishable from mid-ocean ridge basalts, implying that the convecting mantle is homogenous in terms of halogens (Kendrick *et al.*, 2014; Kendrick *et al.*, 2015; Kendrick *et al.*, 2025). However, the Earth's mantle is depleted in halogens relative to chondritic meteorites. While the depletion of F aligns with its condensation temperature, Cl and Br concentrations are an order of magnitude lower than predicted by the volatility trend (Lodders and Fegley, 1998). One possible explanation for this discrepancy is the presence of a halogen-rich reservoir in the deep Earth. The recent discovery of elevated Br/Cl in melt inclusion bearing olivine from high $^3He/^4He$ basalts from Koko and Suiko in the Emperor Seamount chain (Broadley *et al.*, 2019) provides the first indication of halogen heterogeneity in the mantle that may be associated with a deep mantle source.

The picritic flood basalts from Baffin Island (Clarke and Upton, 1971) and West Greenland (Larsen *et al.*, 1992) were erupted at around 61 Ma and are believed to be the earliest volcanic products from the Iceland plume. These proto-Iceland plume (PIP) basalts have the highest mantle-derived $^3He/^4He$ ratios recorded to date (Stuart *et al.*, 2003; Starkey *et al.*, 2009). The high $^3He/^4He$ PIP lavas have a large compositional range but tend to be geochemically depleted in terms of trace elements and radiogenic isotope compositions, with only a few enriched basalts (Starkey *et al.*, 2009; Willhite *et al.*, 2019). In this contribution, we report the F, Cl and Br compositions of melt inclusions in olivine phenocrysts from high $^3He/^4He$ basalts from Baffin Island and West Greenland in an effort to characterise the heavy halogen composition of the ^3He-rich deep mantle reservoir.

Geological Setting

The PIP basalts are subdivided into a depleted N-type (La/Sm_N < 0.7) and more enriched E-type (Kent *et al.*, 2004). Both basalt types are depleted relative to the majority of OIB with respect to Sr-Nd-Pb isotopes (Starkey *et al.*, 2009; Willhite *et al.*, 2019). Based on incompatible trace elements and Sr-Nd-Pb-Os-O isotopes, the N- and E-type magmas are not related by partial melting, fractional crystallisation or by crustal or lithospheric assimilation (Kent *et al.*, 2004). Instead, the compositional differences are attributed to melting of a heterogeneous mantle

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(Stuart *et al.*, 2003; Kent *et al.*, 2004). Herzberg and O'Hara (2002) calculate that the Baffin Island picrites formed by relatively high degrees of fractional melting of the asthenospheric mantle, around 10–11 % (depleted source) and 23–25 % (enriched source) at 120–70 km depth.

The studied samples are olivine-phyric N- and E-type basalts from Padloping Island and Cape Searle, Baffin Island, and Disko Island and Nuussuaq, West Greenland, and were previously studied by Stuart *et al.* (2003) and Starkey *et al.* (2009, 2012). They are high-Mg (MgO > 13 wt. %) picritic lavas that were selected because of their high $^3He/^4He$ (26 to 49.5 R_a), and because their bulk rock compositions are minimally affected by crustal contamination, indicated by high Nb/Th (9–14) and low K/Nb (81–331). We opted to study melt inclusions, rather than whole rock basalts, as they are more likely to record pristine volatile compositions. The host olivines are 300–500 µm diameter and have magnesian cores (100 Mg/Mg + Fe mol. 86–87), indicating equilibrium with the least fractionated PIP basalt (Starkey *et al.*, 2012).

The elemental and isotopic ($\delta^{37}Cl$) halogen compositions of PIP melt inclusions were analysed by secondary ion mass spectrometry (SIMS) (see Supplementary Information). The dataset is provided in Table S-1 and summarised in Table 1. Halogen concentrations were calibrated using a suite of natural basalt glasses. The limit of detection (LoD) was calculated using the formula LoD = 3.33σ/S, where σ is the standard deviation of the intercept and S is the slope of the calibration curve. We report uncertainties as 2σ, where σ is calculated from the standard deviations of the slope and intercept of the calibration curve. Halogen ratios were calculated for individual melt inclusions and sample averages were calculated from these ratios. The Cl and Br concentrations of MPI-DING glass StHs6/80-G are within ±10 % of the preferred values and precision for repeat analysis of F, Cl and Br in MPI-DING glass StHs6/80-G was typically ±10 %.

Halogen Composition of PIP Basalt Melt Inclusions

Average melt inclusion compositions in the PIP samples are F = 174–440 µg.g^{-1}, Cl = 78–100 µg.g^{-1} and Br = 530–1100 ng.g^{-1}. Concentrations of Cl and Br are significantly lower than those reported in enriched, EM-type and HIMU (high µ, $\mu = {}^{238}U/{}^{204}Pb$) glasses from Samoa, Society and Pitcairn (Kendrick *et al.*, 2014; Kendrick *et al.*, 2015) and are at the lower end of values reported for depleted OIB from Hawaii (Kendrick *et al.*, 2025) (Fig. 1a,b). Low halogen concentrations have previously been recorded in basaltic glasses from E-type PIP lavas from Baffin Island (Kendrick *et al.*, 2015). The PIP basalts analysed here have K/Cl of 27–62 and $^{87}Sr/^{86}Sr$ of 0.7030–0.7034 that plot at the enriched end of the MORB array (Fig. 1c).

Table 1 Average composition of PIP melt inclusions. $Emplacement information from Lass-Evans (2004) and Pedersen *et al.* (2017); *He data from Stuart *et al.* (2003) and Starkey *et al.* (2009). Uncertainties are 2σ.

Sample	CS-5	CS-6	PI-25	362077	332901
Location	Cape Searle, Baffin Island	Cape Searle, Baffin Island	Padloping, Baffin Island	Nuussuaq, West Greenland	Disko, West Greenland
Member	Anaanaa	Anaanaa	Anaanaa	Naujánguit	Ordlingassoq
Deg. N	67.22	67.22	67.18	70.50	70.38
Deg. W	62.53	62.53	62.45	53.57	53.22
Emplacement$	Dyke	Dyke	Subaerial lava flow	Submarine pillow lava	Subaerial lava flow
Olivine Fo	84.8 *(1.2)*	84.5 *(0.2)*	84.5 *(01.0)*	81.1 *(6.8)*	86.0 *(1.6)*
Type	E	E	N	N	E
$^3He/^4He$ (R/R_a)*	26.30 *(2.0)*	37.90 *(1.2)*	49.50 *(1.6)*	44.00 *(0.8)*	45.80 *(1.0)*
n	8	3	32	4	2
SiO_2 (wt. %)	51.38 *(3.30)*	49.06 *(1.81)*	49.84 *(1.51)*	49.64 *(2.13)*	52.96 *(0.51)*
Al_2O_3 (wt. %)	17.57 *(2.46)*	15.45 *(0.34)*	15.39 *(0.90)*	15.85 *(0.93)*	15.64 *(0.01)*
TiO_2 (wt. %)	1.41 *(0.27)*	1.30 *(0.05)*	1.21 *(0.36)*	1.30 *(0.10)*	1.98 *(0.17)*
FeOt (wt. %)	7.90 *(2.48)*	10.04 *(0.08)*	9.98 *(0.91)*	8.88 *(4.40)*	5.99 *(0.30)*
MnO (wt. %)	0.16 *(0.13)*	0.18 *(0.03)*	0.19 *(0.10)*	0.17 *(0.09)*	0.12 *(0.04)*
MgO (wt. %)	3.17 *(2.88)*	7.65 *(0.77)*	7.50 *(1.17)*	7.26 *(2.52)*	7.75 *(0.03)*
CaO (wt. %)	14.99 *(1.58)*	12.77 *(1.30)*	13.19 *(0.67)*	13.08 *(1.77)*	12.38 *(0.30)*
Na_2O (wt. %)	2.03 *(0.93)*	2.00 *(0.10)*	2.06 *(0.25)*	2.04 *(0.07)*	2.64 *(0.17)*
K_2O (wt. %)	0.29 *(0.14)*	0.35 *(0.18)*	0.21 *(0.10)*	0.34 *(0.11)*	0.54 *(0.01)*
Total	98.88	98.80	99.56	98.56	99.98
n F/Cl/Br	4/4/0	2/3/3	11/11/4	1/3/4	2/3/2
F (µg.g^{-1})	211 *(26)*	174 *(168)*	174 *(28)*	216 *NA*	440 *(14)*
Cl (µg.g^{-1})	100 *(22)*	78 *(17)*	85 *(32)*	98 *(31)*	83 *(42)*
Br (ng.g^{-1})	<LOD *NA*	530 *(439)*	961 *(371)*	1133 *(782)*	905 *(366)*
K/Cl	27 *(14)*	42 *(13)*	25 *(18)*	31 *(10)*	62 *(27)*
F/Cl	2.1 *(0.3)*	2.4 *(2.4)*	2.1 *(0.6)*	2.1 *NA*	5.7 *(3.8)*
1000Br/Cl	- -	6.7 *(5.0)*	11.8 *(4.9)*	11.8 *(5.9)*	12.4 *(0.7)*
n	4	1	12	-	-
$\delta^{37}Cl$ (‰)	0.60 *(0.21)*	0.04 *(0.43)*	-0.21 *0.64*	- -	- -

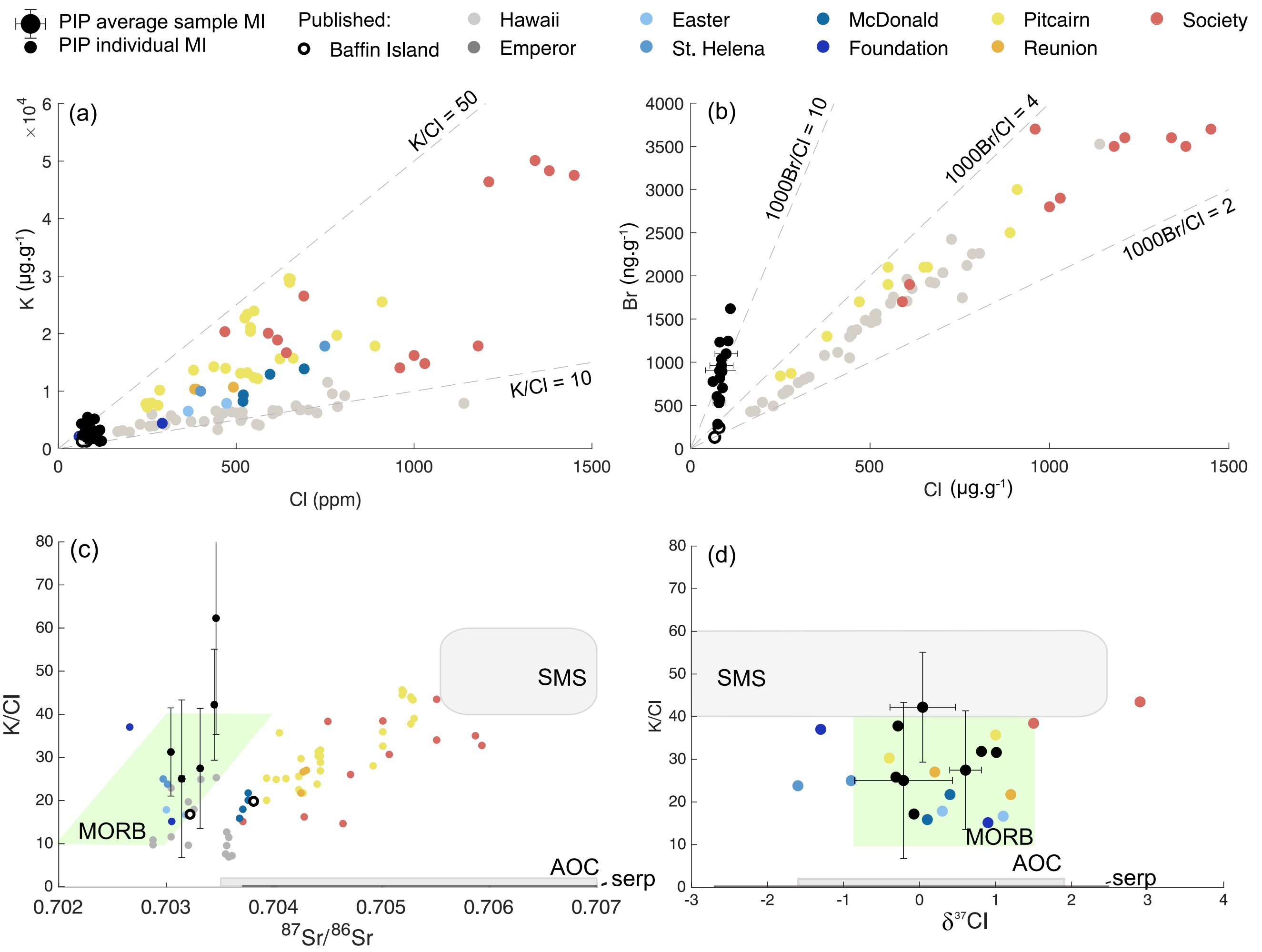

Figure 1 Compositions of the melt inclusions in PIP basalt olivine compared to glasses from depleted (grey; Broadley *et al.*, 2019; Kendrick *et al.*, 2025), EM-type (warm colours; Stroncik and Haase, 2004; John *et al.*, 2010) and HIMU (blues; Stroncik and Haase, 2004; John *et al.*, 2010; Kendrick *et al.*, 2014) basalts. MORB (green field) is from Kendrick *et al.* (2017). Data sources for average SMS (subducted marine sediments), AOC (altered oceanic crust) and serpentinite fields are provided in Table S-4.

Chlorine isotopes can be used as tracers of recycled chlorine in the mantle (John *et al.*, 2010). The chlorine isotope composition (δ^{37}Cl) of three PIP basalt melt inclusions range from −0.2 to +0.6 ‰ (SMOC). This range overlaps the mantle value (−0.2 ± 0.5 ‰ (1σ); Sharp *et al.*, 2007) (Fig. 1d) and is lower than EM-type basalts which have more positive δ^{37}Cl (John *et al.*, 2010).

A key observation is that N- and E-type PIP melt inclusions in samples have 1000Br/Cl ratios (6.7 to 12.4) that are significantly higher than recorded by MORB and OIB (2.8 ± 0.8; Kendrick *et al.*, 2017). These are also higher than Br/Cl ratios recorded in low ^{3}He/^{4}He E-type basalts from Baffin Island (Kendrick *et al.*, 2015) (Fig. 2a,b). The highest values are outside of uncertainty of MORB mantle value at 2σ. Importantly, the samples with the highest ^{3}He/^{4}He have the highest Br/Cl ratios, although any correlation is obscured by the large uncertainty (Fig. 2c).

Contamination

The Br/Cl ratio of basaltic melt can increase during interaction with seawater-derived brines in the crust, either before emplacement within the magma chamber or after emplacement during alteration (Kendrick *et al.*, 2013a). However, only one of the studied basalts was emplaced in a submarine setting, the others being subaerial or hypabyssal (Table 1). In addition, the PIP melt inclusions do not show the low K/Cl and F/Cl ratios and the negative correlations of these ratios with Br/Cl that characterise mixing with saline brine (Kendrick *et al.*, 2013a) (Fig. 2a).

The PIP basalt sequence was erupted through continental lithosphere and high grade crustal basement (Robillard *et al.*, 1992), and the high Br/Cl ratios may have been generated during interaction of the melts with the lithosphere and/or crust during ascent. Peridotite xenoliths from the lithospheric mantle have high Br/Cl ratios, a feature that has been attributed to metasomatism by subduction-related fluids (Broadley *et al.*, 2016). Similarly, while lower continental crust has low halogen concentrations and low Br/Cl, organic matter within upper continental crust has elevated Br/Cl (Han *et al.*, 2023). Assimilation of metasomatised lithosphere or organic-rich upper continental crust could impart high Br/Cl ratios to the basaltic melts. However, the PIP basalts in this study lack the elevated LILE/HREE ratios, HFSE depletions and radiogenic Sr isotope compositions that are indicative of incorporation of altered oceanic crust and lithosphere (Fig. 1c). Furthermore, it is difficult to explain the co-occurrence of high Br/Cl and high ^{3}He/^{4}He by reactivation of subducted or crustal halogens. Therefore, we suggest that the

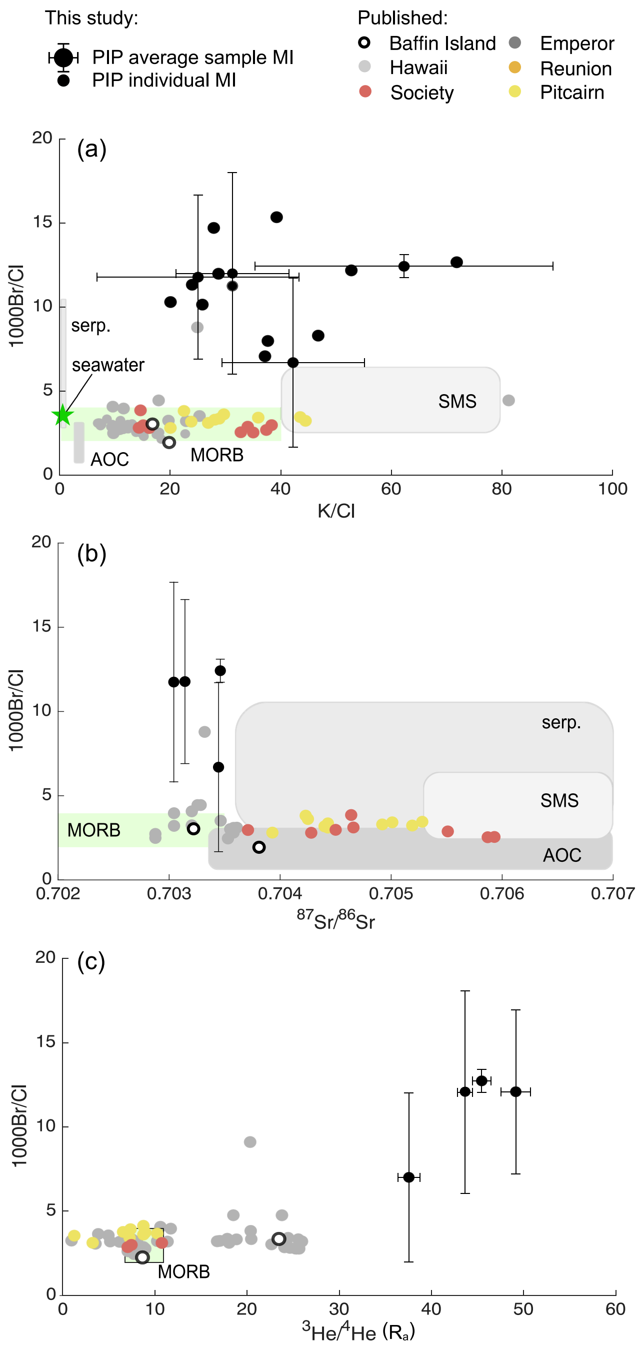

Figure 2 Composition of melt inclusions in PIP olivines compared to depleted (grey), EM-type (warm colours) and HIMU (blues) OIB and to MORB (green field). Date sources as in Figure 1.

high Br/Cl ratios are likely to be characteristic of the high $^3He/^4He$ PIP source.

Halogen Composition of the Proto-Iceland Plume Mantle Source Region

The composition of the N-type and E-type mantle sources were estimated by accumulated fractional melt modelling assuming modal melting (see Supplementary Information). We use the composition of melt inclusions in samples PI-25 and CS-6 to represent melts from the depleted and enriched asthenospheric mantle, respectively, and assume melt fractions of 0.1 for the depleted melt and 0.25 for the enriched melt, as appropriate for melting of the PIP source (Herzberg and O'Hara, 2002). We use partition coefficients D_F and D_{Cl} from Joachim *et al.* (2015) and consider Br and Cl to be similarly incompatible. The calculated halogen composition of the source mantle is shown in Figure 3 and Table S-6, and the 1000Br/Cl ratio is 11.3 (PI-25) and 6.8 (CS-6).

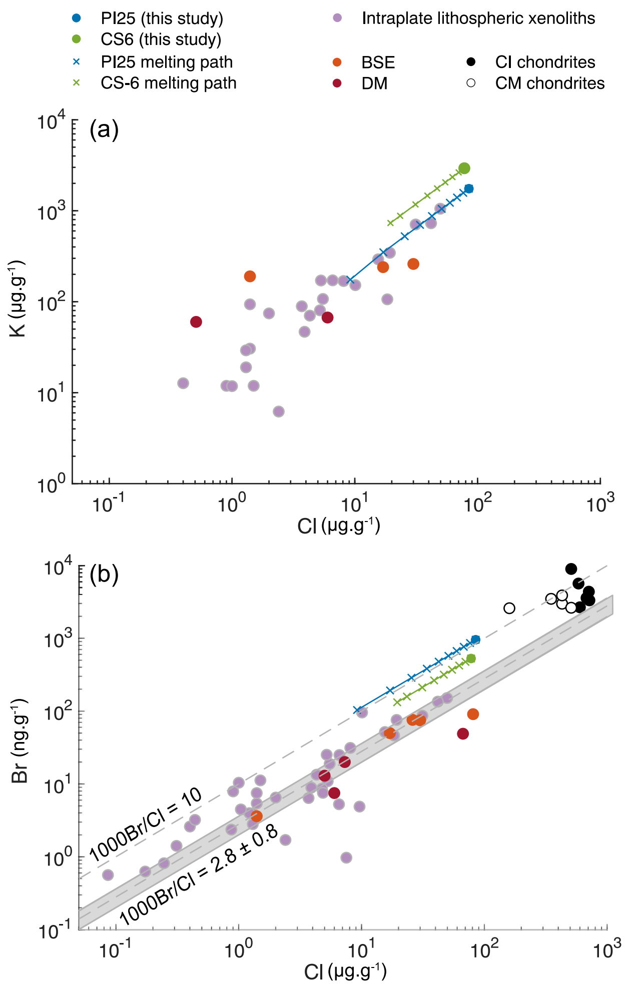

Figure 3 Calculated accumulated fractional melting path yielding the melt seen in N-type (PI-25), and E-type (CS-6) PIP basalts, shown in increments of F = 0.1 from 0.1 (PI-25) and 0.25 (CS-6). Compared to estimates for DM, BSE and to peridotite xenoliths from intraplate settings and to CI- and CM-chondrites (Table S-6).

The halogen compositions of bulk silicate Earth (BSE) and depleted mantle (DM) are estimated from the currently available OIB and MORB data (Table S-6). The calculated K, F and Cl contents of the mantle source of the N-type and E-type PIP basalts are broadly within range of most estimates of DM and BSE. However, the calculated Br content of the PIP sources is significantly higher than DM and BSE (Fig. 3), resulting in Br/Cl ratios that are 2–4 times higher than DM and BSE.

Scenario 1: Addition of Recycled Halogens to the Iceland Mantle Plume Source

Subducted sediments can have elevated average Br/Cl ratios of 4.9 ± 1.5 but with individual analyses extending to ~100 (Han *et al.*, 2023). The $\delta^{37}Cl$ composition of subducted sediment ranges from −3.7 to +2.4 ‰ (Barnes and Sharp, 2017), and thus overlaps the mantle-like chlorine isotope composition of the PIP basalt melt inclusions and cannot exclude subducted sediment as the source of the high Br/Cl ratios. However, the PIP basalts are depleted and lack the elevated $^{87}Sr/^{86}Sr$ signatures typically associated with subducted sediment (Fig. 1c, Fig. 2b). Therefore, a recycled sediment origin for the higher Br/Cl ratios is only possible if the halogens are decoupled from lithophile trace elements during sediment devolatilisation; however, Cl is known to enhance the solubility of trace elements, including Sr, *via* chloride complexing such that Sr is compatible in saline fluid (*e.g.*, Keppler, 2017). In addition, volcanic glasses that do have radiogenic $^{87}Sr/^{86}Sr$ compositions associated with the presence of recycled sediment do not have elevated Br/Cl contents (Kendrick *et al.*, 2017).

Elevated Br/Cl ratios like those in the PIP melt inclusions are found in sedimentary marine pore fluids and in serpentinite (Kendrick *et al.*, 2013b) (Fig. 2). Sedimentary pore fluids extend from mantle-like compositions to strongly negative $\delta^{37}Cl$ values of −8 ‰, with most of the available data sitting to the negative side of the terrestrial value (Barnes and Sharp, 2017). This means that sedimentary pore fluids are a possible, but less likely source of high Br/Cl in the PIP melt inclusions. Serpentinite is a more plausible candidate because the $\delta^{37}Cl$ averages −0.1 ‰. Broadley *et al.* (2019) report high Br/Cl in crushed olivine from high $^{3}He/^{4}He$ basalts from Suiko and Koko in the Emperor seamounts chain, where the halogens were inferred to reside in fluid and/or melt inclusions. They attribute high Br/Cl to incorporation of altered oceanic crust and dehydrated serpentinite into the high $^{3}He/^{4}He$ Hawaii plume source. However, serpentinites are characterised by strongly radiogenic $^{87}Sr/^{86}Sr$ compositions and low K/Cl that are not seen in the PIP basalts (Fig. 1c). Furthermore, the PIP basalts lack elevated Fe/Mn and depleted Ca associated with the presence of eclogite or pyroxenite and have primitive Nd isotope compositions, consistent with an absence of recycled oceanic crust (Jackson *et al.*, 2010). Therefore, while serpentinite may be the source of the high Br/Cl ratios in the PIP melt inclusions, its contribution to the lithophile element inventory was minimal.

Scenario 2: High Br/Cl Mantle

An alternative interpretation is that elevated Br/Cl ratios are intrinsic to the deep mantle. In this scenario, the low halogen content of the convecting mantle is due to depletion during crust formation, while the lower Br/Cl is due to incorporation of low Br/Cl recycled material. One option is that the deep mantle source of the PIP lavas is a heavy halogen-poor, high Br/Cl lower mantle reservoir. Such a source must be heterogeneous to account for the presence of both N- and E-type PIP basalts both with high $^{3}He/^{4}He$ and high Br/Cl. Therefore, the PIP melts may be more easily explained by addition of a small volume of heavy halogen-rich, high Br/Cl deep mantle to halogen-poor mantle.

Current estimates for BSE suggest that the mantle is depleted in Cl and Br relative to chondritic meteorites. In addition, although Cl and Br have similar condensation temperatures, the limited available data suggest that chondritic meteorites have higher Br/Cl ratios than BSE, with most estimates being close to the average solar system value of 4.7 (Lodders and Fegley, 1998). The Br/Cl ratio of the PIP melt inclusions is within range but at the upper end of compositions reported for CI- and CM-type carbonaceous chondrites (Fig. 3b), the subtypes of carbonaceous chondrites that most closely resemble the source of volatile elements delivered to the Earth (Alexander *et al.*, 2012). Together, this implies that the primordial mantle may have been more halogen-rich and had higher Br/Cl ratios than the convecting mantle, and so incorporation of a small vestige of primitive mantle material into depleted/enriched mantle at the core mantle boundary could explain the unusual halogen composition of the PIP melts. Alternatively, the halogen-rich, high Br/Cl PIP source may reflect a deep mantle heterogeneity, perhaps related to the Earth's accretion and degassing history.

Scenario 3: Addition of Heavy Halogens From the Core

The low chlorine content of BSE may be reconciled with the composition of chondritic meteorites if the core is a significant reservoir for the heavy halogens (Yuan and Steinle-Neumann, 2024). Halogens may reside in the core if they partitioned into liquid metal during core formation. Quantum mechanical calculations indicate that Cl shows lithophile to mildly compatible behaviour (Yuan and Steinle-Neumann, 2024). Bromine partitioning behaviour at high pressure is unknown; however, if halogens become more compatible in metal with increasing atomic number, then the core could potentially have a high Br/Cl ratio. However, if Br is mildly compatible in the core, it would be difficult to explain why Br would be transferred out of the core into PIP source.

Conclusions and Implications

Melt inclusions in olivine from high $^{3}He/^{4}He$ PIP basalts are halogen-poor and have high Br/Cl ratios relative to MORB and the majority of OIB. The absence of elemental and radiogenic isotope evidence for recycled crustal material in the PIP basalt source, and the absence of elevated Br/Cl in OIB where recycled material is thought to be present, suggest that recycled halogens may not be the source of the elevated Br/Cl ratios in the PIP melt inclusions.

The high Br/Cl ratios are within range of those of chondritic meteorites that may have delivered volatiles to the early Earth. The PIP melt inclusion compositions are consistent with the addition of a small vestige of halogen-rich, high Br/Cl chondritic material to halogen-poor, low Br/Cl mantle. The presence of a halogen-rich, high Br/Cl chondritic reservoir in deep Earth could explain the apparent deficit of heavy halogens in the Earth relative to chondritic meteorites. Alternatively, the halogen-rich, high Br/Cl mantle source may reflect heterogeneity related to the Earth's accretion history.

The occurrence of these high Br/Cl melts has implications for our understanding of the cycling and homogenisation of halogens in the mantle, as well as the halogen composition and degassing history of the Earth. The high Br/Cl component may be easier to detect in depleted OIB magmas, where the signature is less strongly overprinted by recycled halogens.

Acknowledgements

The authors thank the handling editor Romain Tartèse and Mark Kendrick and Ray Burgess for constructive and thoughtful reviews. This research was funded by SFI grant 15/ERC/B3131 'Halogen' to ELT. The iCRAG laboratory was supported by SFI/RI/3227. ER-K acknowledges SYSTER-INSU-CNRS "Halogens history". Professor J. Godfrey Fitton is thanked for supplying samples collected in 1996 by Ian Snape, Coleen Cole and Sally Brown during an Edinburgh University expedition to Baffin Island supported by the Laidlaw-Hall Trust.

Editor: Romain Tartèse

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2539.

Cite this letter as: Tomlinson, E.L., Rose-Koga, E.F., Bouvier, A.-S., O'Farrell, D., Caulfield, J.T., Jackson, M.G., Moussallam, Y., Stuart, F.M., Villeneuve, J. (2025) Halogens in proto-Iceland plume basalts. *Geochem. Persp. Let.* 37, 12–17. https://doi.org/10.7185/geochemlet.2539

References

Alexander, C.M.O'D., Bowden, R., Fogel, M.L., Howard, K.T., Herd, C.D.K., Nittler, L.R. (2012) The Provenances of Asteroids, and Their Contributions to the Volatile Inventories of the Terrestrial Planets. *Science* 337, 721–723. https://doi.org/10.1126/science.1223474

Barnes, J.D., Sharp, Z.D. (2017) Chlorine Isotope Geochemistry. *Reviews in Mineralogy and Geochemistry* 82, 345–378. https://doi.org/10.2138/rmg.2017.82.9

Broadley, M.W., Ballentine, C.J., Chavrit, D., Dallai, L., Burgess, R. (2016) Sedimentary halogens and noble gases within Western Antarctic xenoliths: Implications of extensive volatile recycling to the sub continental lithospheric mantle. *Geochimica et Cosmochimica Acta* 176, 139–156. https://doi.org/10.1016/j.gca.2015.12.013

Broadley, M.W., Sumino, H., Graham, D.W., Burgess, R., Ballentine, C.J. (2019) Recycled components in mantle plumes deduced from variations in halogens (Cl, Br, and I), trace elements, and ^{3}He/^{4}He along the Hawaiian-Emperor seamount chain. *Geochemistry, Geophysics, Geosystems* 20, 277–294. https://doi.org/10.1029/2018GC007959

Clarke, D.B., Upton, B.G.J. (1971) Tertiary Basalts of Baffin Island: Field Relations and Tectonic Setting. *Canadian Journal of Earth Sciences* 8, 248–258. https://doi.org/10.1139/e71-025

Han, P.-Y., Rudnick, R.L., He, T., Marks, M.A.W., Wang, S.-J., Gaschnig, R.M., Hu, Z.-C. (2023) Halogen (F, Cl, Br, and I) concentrations of the upper continental crust through time as recorded in ancient glacial diamictite composites. *Geochimica et Cosmochimica Acta* 341, 28–45. https://doi.org/10.1016/j.gca.2022.11.012

Herzberg, C., O'Hara, M.J. (2002) Plume-associated ultramafic magmas of phanerozoic age. *Journal of Petrology* 43, 1857–1883. https://doi.org/10.1093/petrology/43.10.1857

Jackson, M.G., Carlson, R.W., Kurz, M.D., Kempton, P.D., Francis, D., Blusztajn, J. (2010) Evidence for the survival of the oldest terrestrial mantle reservoir. *Nature* 466, 853–856. https://doi.org/10.1038/nature09287

Joachim, B., Pawley, A., Lyon, I.C., Marquardt, K., Henkel, T., Clay, P.L., Ruzie, L., Burgess, R., Ballentine, C.J. (2015) Experimental partitioning of F and Cl between olivine, orthopyroxene and silicate melt at Earth's mantle conditions. *Chemical Geology* 416, 65–78. https://doi.org/10.1016/j.chemgeo.2015.08.012

John, T., Layne, G.D., Haase, K.M., Barnes, J.D. (2010) Chlorine isotope evidence for crustal recycling into the Earth's mantle. *Earth and Planetary Science Letters* 298, 175–182. https://doi.org/10.1016/j.epsl.2010.07.039

Kendrick, M.A., Arculus, R., Burnard, P., Honda, M. (2013a) Quantifying brine assimilation by submarine magmas: Examples from the Galapagos Spreading Centre and Lau Basin. *Geochimica et Cosmochimica Acta* 123, 150–165. https://doi.org/10.1016/j.gca.2013.09.012

Kendrick, M.A., Honda, M., Pettke, T., Scambelluri, M., Phillips, D., Giuliani, A. (2013b) Subduction zone fluxes of halogens and noble gases in seafloor and forearc serpentinites. *Earth and Planetary Science Letters* 365, 86–96. https://doi.org/10.1016/j.epsl.2013.01.006

Kendrick, M.A., Jackson, M.G., Kent, A.J.R., Hauri, E.H., Wallace, P.J., Woodhead, J. (2014) Contrasting behaviours of CO_2, S, H_2O and halogens (F, Cl, Br, and I) in enriched-mantle melts from Pitcairn and Society seamounts. *Chemical Geology* 370, 69–81. https://doi.org/10.1016/j.chemgeo.2014.01.019

Kendrick, M.A., Jackson, M.G., Hauri, E.H., Phillips, D. (2015) The halogen (F, Cl, Br, I) and H_2O systematics of Samoan lavas: Assimilated-seawater, EM2 and high-^{3}He/^{4}He components. *Earth and Planetary Science Letters* 410, 197–209. https://doi.org/10.1016/j.epsl.2014.11.026

Kendrick, M.A., Hémond, C., Kamenetsky, V.S., Danyushevsky, L., Devey, C.W., Rodemann, T., Jackson, M.G., Perfit, M.R. (2017) Seawater cycled throughout Earth's mantle in partially serpentinized lithosphere. *Nature Geoscience* 10, 222–228. https://doi.org/10.1038/ngeo2902

Kendrick, M.A., Nebel, O., Hanyu, T., Maunder, B.L., Maas, R. (2025) Earth's early differentiation recorded by halogen abundance ratios in Hawaiian lavas. *Geochimica et Cosmochimica Acta* 393, 196–207. https://doi.org/10.1016/j.gca.2025.01.019

Kent, A.J.R., Stolper, E.M., Francis, D., Woodhead, J., Frei, R., Eiler, J. (2004) Mantle heterogeneity during the formation of the North Atlantic Igneous Province: Constraints from trace element and Sr-Nd-Os-O isotope systematics of Baffin Island picrites. *Geochemistry, Geophysics, Geosystems* 5, Q11004. https://doi.org/10.1029/2004GC000743

Keppler, H. (2017) Fluids and trace element transport in subduction zones. *American Mineralogist* 102, 5–20. https://doi.org/10.2138/am-2017-5716

Larsen, L.M., Pedersen, A.K., Pedersen, G.K., Piasecki, S. (1992) Timing and duration of Early Tertiary volcanism in the North Atlantic: new evidence from West Greenland. *Geological Society, London, Special Publications* 68, 321–333. https://doi.org/10.1144/GSL.SP.1992.068.01.20

Lass-Evans, S. (2004) *Anatomy of the ancestral Iceland plume a chemical and isotopic study of the tertiary basalts and picrites from Baffin Island*. PhD thesis, University of Edinburgh. https://era.ed.ac.uk/handle/1842/11034

Lodders, K., Fegley, B. (1998) *The Planetary Scientist's Companion*. Oxford University Press, Oxford. https://doi.org/10.1093/oso/9780195116946.001.0001

Pedersen, A.K., Larsen, L.M., Pedersen, G.K. (2017) Lithostratigraphy, geology and geochemistry of the volcanic rocks of the Vaigat Formation on Disko and Nuussuaq, Paleocene of West Greenland. *GEUS Bulletin* 39, 1–244. https://doi.org/10.34194/geusb.v39.4354

Robillard, I., Francis, D., Ludden, J.N. (1992) The relationship between E- and N-type magmas in the Baffin Bay Lavas. *Contributions to Mineralogy and Petrology* 112, 230–241. https://doi.org/10.1007/BF00310457

Sharp, Z.D., Barnes, J.D., Brearley, A.J., Chaussidon, M., Fischer, T.P., Kamenetsky, V.S. (2007) Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. *Nature* 446, 1062–1065. https://doi.org/10.1038/nature05748

Starkey, N.A., Stuart, F.M., Ellam, R.M., Fitton, J.G., Basu, S., Larsen, L.M. (2009) Helium isotopes in early Iceland plume picrites: Constraints on the composition of high ^{3}He/^{4}He mantle. *Earth and Planetary Science Letters* 277, 91–100. https://doi.org/10.1016/j.epsl.2008.10.007

Starkey, N.A., Fitton, J.G., Stuart, F.M., Larsen, L.M. (2012) Melt inclusions in olivines from early Iceland plume picrites support high ^{3}He/ ^{4}He in both enriched and depleted mantle. *Chemical Geology* 306–307, 54–62. https://doi.org/10.1016/j.chemgeo.2012.02.022

Stroncik, N.A., Haase, K.M. (2004) Chlorine in oceanic intraplate basalts: Constraints on mantle sources and recycling processes. *Geology* 32, 945–948. https://doi.org/10.1130/G21027.1

Stuart, F.M., Lass-Evans, S., Fitton, J.G., Ellam, R.M. (2003) High ^{3}He/^{4}He ratios in picritic basalts from Baffin Island and the role of a mixed reservoir in mantle plumes. *Nature* 424, 57–59. https://doi.org/10.1038/nature01711

Willhite, L.N., Jackson, M.G., Blichert-Toft, J., Bindeman, I., Kurz, M.D., Halldorsson, S.A., Hardardottir, S., Gazel, E., Price, A.A., Byerly, B.L. (2019) Hot and Heterogenous High-^{3}He/^{4}He Components: New Constraints From Proto-Iceland Plume Lavas From Baffin Island. *Geochemistry, Geophysics, Geosystems* 20, 5939–5967. https://doi.org/10.1029/2019GC008654

Yuan, I., Steinle-Neumann, G. (2024) Earth's "missing" chlorine may be in the core. *Journal of Geophysical Research: Solid Earth* 129, e2023JB027731. https://doi.org/10.1029/2023JB027731