Seawater cycled throughout Earth's mantle in partially serpentinised lithosphere

M.A. Kendrick[1]*, C. Hemond[2], V.S. Kamenetsky[3], L. Danyushevsky[3], C. Devey[4], T. Rodemann[5], M.G. Jackson[6], and M.R. Perfit[7]

*corresponding author

1 – Research School of Earth Sciences, Australian National University, 142 Mills Rd., Acton, ACT 0200, Australia

2 – Laboratoire Géosciences Océan, Institut Universitaire Europeen de la Mer, Place Nicolas Copernic, Plouzane, France.

3 - CODES and Earth Sciences, University of Tasmania, Tasmania 7001, Australia

4 – GEOMAR, Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1-3, 24148 Kiel, Germany

5 – Central Science Laboratory, The University of Tasmania, Tasmania 7001, Australia

6 – Department of Earth Science, University of California, Santa Barbara, California, USA

7 - Department of Geological Sciences, University of Florida, Gainesville, FL 32611, USA

The extent to which water and halogens have primordial origins in the Earth's mantle, or are dominated by seawater-derived components introduced by subduction, remains a matter of debate. About 90% of non-radiogenic xenon in the Earth's mantle has a subducted atmospheric origin, but the degree to which atmospheric gases and other seawater components are coupled during subduction is unclear. Here we present the concentrations of water and halogens in samples of magmatic glasses collected from global mid-ocean ridges and ocean islands. We show that water and halogen enrichment is unexpectedly associated with trace element signatures characteristic of dehydrated oceanic crust, and that the most incompatible halogens have relatively uniform abundance ratios that are different from primitive mantle values. Taken together, these results imply that Earth's mantle is highly processed and that most of its water and halogens were introduced by the subduction of serpentinised lithospheric mantle associated with dehydrated oceanic crust.

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Quantifying the global cycles of volatile elements into and out of the mantle is critical for modelling planetary evolution[1-7]. Trace elements and radiogenic isotopes provide important information about mantle heterogeneity, with many features of Ocean Island Basalts (OIB) commonly attributed to the presence of recycled subducted ocean crust (the HIMU end-member) or sediment (EM end-members) in their mantle sources (Fig 1; refs 8-10). Melts sampling EM (Enriched Mantle) reservoirs are known to be depleted in H_2O and Cl relative to lithophile elements of similar mantle incompatibility, consistent with the presence of dehydrated sediment or continental crustal material in EM sources[2,4,11-13]. However, the volatile content of the HIMU mantle end-member and the relative proportions of recycled versus primordial water in the mantle remain poorly constrained[2,4,11-15].

The current study combines new and published F, Cl, Br, I and H_2O analyses for a suite of globally distributed submarine glasses representing melts formed from all the major mantle end-member reservoirs (Figs 1 and S1, electronic supplement). The new samples include submarine HIMU glasses dredged from around St Helena Island in the southern Atlantic[9,14], and from the Foundation Seamount chain in the SE Pacific[15]. The latter samples show variable trace element and $^{206}Pb/^{204}Pb$ enrichment that result from interaction between the Foundation HIMU component and the Pacific Antarctic Ridge (Fig 1)[15,16]. New glasses were also selected from the East Pacific Rise, Mid Atlantic Ridge, Southwest and Southeast Indian Ocean Ridges, Ontong Java Plateau and Reunion Island. The previously published data include enriched MORB from Macquarie Island, HIMU-influenced MORB from the equatorial Atlantic, HIMU-type OIB from Mangaia and Tuvalu, EM-type OIB from Samoa, Society and Pitcairn, and primitive 'OIB' with high $^3He/^4He$ from Baffin Island, Samoa and the NW Lau Basin (Fig 1)[11,12,17-21]. In total we have evaluated data from ~400 glasses enabling us to define global baselines for mantle halogen and H_2O abundance ratios and elucidate previously unrecognised processes involved in the generation of HIMU and globally variable MORB mantle reservoirs.

Identifying mantle volatiles

Previous studies have shown that shallow-level assimilation of seawater-derived fluids or altered ocean crust can lead to contamination of MORB and OIB melts with seawater-derived Cl and H_2O (e.g. refs 11,17,22,23). To ensure we focused on samples dominated by only mantle-derived halogens and water, we filtered out samples with anomalous Cl enrichments that lie on mixing trends towards typically higher than seawater Br/Cl and I/Cl and very low K/Cl and H_2O/Cl ratios that are characteristic of high salinity brines (exemplified by Ontong Java Plateau glasses; Fig 2)[17]. This procedure avoids making assumptions about the K/Cl of the mantle, and the combination of K/Cl, Br/Cl and I/Cl ratios is uniquely sensitive to Cl assimilation[17,24]. MORB and OIB glasses which pass this filter have overlapping and narrow ranges of Br/Cl [$(2.8 \pm 0.8)\times10^{-3}$] and I/Cl [$(60 \pm 30)\times10^{-6}$] and K/Cl of between ~7 and 50 that are considered representative of the mantle (Fig 2; cf. refs. 4,22,25,26). Literature data are screened for contamination based on K/Cl and H_2O/Cl alone and are shown as small symbols in our figures (electronic supplement Fig S3). Note that K/Cl is used in Fig 2 to provide all ratios with a common denominator, however, we follow the convention of discussing volatile/lithophile ratios (e.g. Cl/K) below.

Elements with similar mantle incompatibility like Cl, Br, I and K (or Nb) are not easily fractionated by mantle melting, so if assimilation processes are shown to be minor (Fig 2), the relative abundances of these elements in a mantle melt can be considered representative of the mantle source[4,13,17-20,23,25]. The similarity of these elements relative mantle incompatibilities is illustrated for the silicate melts investigated in Fig 3 (see also Fig S3, electronic supplement)[4,23,27]. This figure also shows that F, which has a significantly higher compatibility, is more similar to Pr than to Nd, which has been widely used for comparison with F previously[11,18,19,26] (Fig 3). The scatter of element pairs around the log-log slopes indicated by the coefficients of determination (r^2) in Fig 3 is highly variable. We attribute the exceptionally strong correlation between Br and Cl to the similar behaviour of these fluid mobile halogens during both mantle melting and subduction. In contrast, other element pairs that are suggested to have similar incompatibility during melting (e.g. H_2O/Ce, Cl/K, F/Pr, Nb/U and Ce/Pb; e.g. Figs 3, S3 and S4 and refs. 8,28,29) exhibit systematic covariations as a result of fractionation during subduction-related processes involving aqueous fluids and hydrous minerals.

The importance of subducted oceanic lithosphere

The HIMU lavas from the Foundation Seamount chain have H_2O/Ce ratios of 155-230, comparable with recent analyses of HIMU melt inclusions and submarine glasses from the Mangaia[18] and Tuvalu[19] Islands in Polynesia and overlapping the MORB range of 150-300 (Fig 4a)[28,29]. A particularly interesting feature of these lavas is that their H_2O/Ce ratios are positively correlated with $^{208}Pb/^{207}Pb$ ($r^2 = 0.67$; Fig 4a), implying that the HIMU component in the Foundation source is actually enriched in H_2O relative to similarly incompatible elements in the surrounding MORB mantle (Fig 4a). The HIMU influenced MORB from the equatorial Atlantic are even more enriched in H_2O, with H_2O/Ce of up to ~400 that is significantly higher than the usual MORB range (Fig 4a)[20,28,29]. The suggested H_2O enrichment of these reservoirs contrasts with the low H_2O/Ce of 115 obtained for the St Helena HIMU lava, that is typical of EM lavas that are depleted in H_2O and halogens relative to MORB (cf. Fig 4)[2,11,12]. We cannot preclude the possibility that H_2O has been lost from the St Helena sample by degassing, however, we note that the measured value is only slightly lower than the range of 130-240 in Mangaia melt inclusions, which have not experienced H_2O loss (Fig 4a). Relatively little H_2O is lost during open system degassing of CO_2 from submarine lavas, and multiple lines of evidence suggest that the majority of samples we are studying have not suffered significant H_2O loss (see below, electronic supplement and refs. 11,12,18-20). Given that H_2O/Ce is broadly correlated with trace element ratios that are not affected by degassing

(Fig 4), and H_2O/Ce behaves similarly to F/Pr (Figs 4d and 4e), it therefore appears that the majority of samples retain H_2O/Ce representative of their mantle source.

The broad correlations between H_2O/Ce, F/Pr, Cl/K, Ce/Pb and Nb/U in global OIB and MORB (Fig 4) can be explained if: i) subducted HIMU-like components (with high Nb/U and Ce/Pb) and EM-like components (with low Nb/U and Ce/Pb) contribute to the global variation of trace element abundances throughout the entire mantle (see also refs. 26,30,31); and ii) EM sources have systematically lower H_2O/Ce, Cl/K and F/Pr ratios than HIMU sources (Fig 4). The correlations in Fig 4 cannot be explained by either preferential degassing of EM lavas or melting and crystallisation processes, because: F, Cl and lithophile elements all have high solubilities in submarine lavas, and the plotted ratios involve elements of similar mantle incompatibility that do not vary as a function of melt enrichment (Figs 3, S4 and S5, supplementary data).

The implied water- and halogen-enrichment of some HIMU sources is at odds with these sources, which are depleted in most fluid mobile elements and characterised by high Nb/U and Ce/Pb (Fig 4c), being generated solely by dehydration of subducted oceanic crust (ref. 8). This apparent contradiction can, however, be easily resolved if subducted oceanic crust is closely associated with variable amounts of serpentinised lithospheric mantle.

The involvement of serpentinised mantle in HIMU reservoirs has not been apparent from conventional trace element geochemistry because serpentinites are strongly depleted in most incompatible trace elements[32]; however, serpentinites have higher H_2O and halogen contents than any other major subduction zone lithology[27,32,33]. Furthermore, thermal models of subducted slabs predict that the oceanic crust and lithosphere are progressively dehydrated with increasing depth, with the deepest and therefore coldest core of the slab (e.g. serpentinised lithospheric mantle) sometimes transported beyond the arc and backarc environments before complete dehydration[33]. As a result, the characteristically high Nb/U, Ce/Pb and U/Pb of HIMU reservoirs (Fig 4c) could be generated by variable loss of fluid mobile elements from dehydrated oceanic crust[8], and H_2O and halogens could still be carried into the deeper mantle by the underlying serpentinised lithosphere. Recent studies have shown that water (and probably halogens) released from serpentine at great depths, could then be re-trapped in high density hydrous aluminosilicate minerals that are most likely to form in the Al-rich crustal section of the slab[34]. Alternatively, the involvement of partially serpentinised lithosphere in the generation of HIMU is consistent with recent proposals for melting lithosphere (peridotite) as well as crust (pyroxenite) during HIMU generation[35,36].

The subducted and partially dehydrated-crust and serpentine composite created by these processes could have highly variable trace element, H_2O and halogen concentrations, so the proportion of serpentinised lithosphere required to generate HIMU signatures is not well defined. However, the highest Nb/U (65-70), H_2O/Ce (280-400) and Cl/K (0.12-0.16) of the HIMU influenced reservoirs in Fig 4 could be generated from a subducted slab comprising a ~7 km thick crustal section in which the uppermost kilometre was intensely altered and then almost completely dehydrated during subduction and an underlying lithospheric mantle in which the uppermost 10 km preserved 1-2% serpentine (Table S2; electronic supplement). The values used in this calculation are, of course, not unique but serve to illustrate that the association of H_2O and halogen enrichment with depletion of other fluid mobile trace elements in the mantle (Fig 4d-f) can be regarded as a fingerprint for serpentinite subduction. Furthermore, variations in the i) proportions of serpentinised lithospheric mantle and dehydrated oceanic crust, ii) the halogen content of serpentine, and iii) the degree of slab dehydration could all shape the complex nature of the geochemical correlations in Fig 4.

Primitive mantle halogen abundances

In contrast to previous studies, our filtered dataset (Fig 2 and electronic supplement) suggests there are systematic variations in mantle halogen and H_2O content that are unrelated to melt extraction (Fig 4). Importantly, Cl/K encompasses similar ranges in OIB and MORB as well as in both depleted and enriched MORB (Figs 3-4 and Table S1, electronic supplement). Therefore, even though low Cl/K ratios are common in depleted MORB, the total variation in mantle Cl/K cannot be attributed to the melt extraction history (cf. refs. 22,26). Rather the Cl/K, F/Pr and H_2O/Ce ratios of mantle sources are largely inherited from previously subducted materials including variably dehydrated sediment, crust and serpentinised lithospheric mantle. These components are then mixed with depleted mantle in different proportions to produce characteristic ranges of Nb/U, H_2O/Ce, Cl/K and F/Pr in different MORB and OIB reservoirs, with the highest absolute concentrations of volatiles and other recycled trace elements in OIB sources (Figs 3 and 4)[30,31].

The median Cl/K of the OIB and MORB investigated, which we consider fairly representative of the entire mantle, is 0.06 ± 0.01. This value is ~6 times higher than the value previously adopted as representative of depleted MORB unaffected by seawater assimilation[37], which has been used to estimate unrealistically low concentrations of Cl and Br in the primitive mantle[38]. The use of mantle Cl/lithophile ratios to constrain primitive mantle Cl concentration is subject to large uncertainty because, as we have shown, Cl and H_2O are fractionated from lithophile elements in surface reservoirs and during subduction. Halogen and H_2O concentrations of the terrestrial primitive mantle can therefore be determined most reliably by summing the estimated abundances in the main terrestrial geochemical reservoirs: seawater, evaporites, marine sediments, brines, the crust and mantle (Table 1)[1,39].

The abundances of halogens in the surface reservoirs can be estimated with varying levels of confidence and Cl, which is concentrated in ocean water and evaporites, can be quantified with much greater precision than Br or I (Table 1). We estimate average concentrations of halogens in a single processed mantle domain that has been affected by melt extraction and subduction input based on the median values of F/Pr, Cl/K, Br/Cl and I/Cl ratios in the MORB and OIB investigated (Figs 2-4; Table 1, electronic supplement). We assume that the processed mantle domain encompasses 70 ± 20 % of the total mantle based on the rarity of OIB with high $^3He/^4He$ ratios[40] and the minimum of 50% defined by the inventory of atmospheric ^{40}Ar (ref. 41). Summing the reservoirs and weighting them according to their size yields primitive mantle concentrations of 17 ± 5 ppm F, 26 ± 8 ppm Cl, 76 ± 25 ppb Br, 7 ± 4 ppb I and 800 ± 300 ppm H_2O (Table 1) and enables us to estimate that about 80% of H_2O and heavy halogens are currently stored in Earth's surface reservoirs (Table S2). The primitive mantle concentrations include estimates of uncertainty that are realistic for our model based on only two mantle domains and they are consistent with several previous estimates for each halogen and H_2O (e.g. refs. 1,25,39,42). However, the primitive mantle abundances of these elements could be even higher if a significant part of the mantle transition zone forms a third mantle domain with elevated H_2O and halogen abundances (see for example refs. 43,44).

The combined data give a primitive mantle I/Cl ratio of $(270 \pm 120)\times10^{-6}$, which excludes uncertainty in the volume of processed mantle, and is significantly higher than the median mantle value of $(63 \pm 5)\times10^{-6}$ (2σ) estimated from MORB and OIB (Fig 2). Given that chlorine and iodine have indistinguishable incompatibility in the mantle (Fig 3), this difference is probably explained by preferential subduction of Cl relative to I, which is suggested by the relative abundances of these halogens in amphibolites[24] and antigorite-serpentinites[45].

Subduction fluxes

Isotopic data indicate that ~85-90% of the non-radiogenic Kr and Xe and a large proportion of the N in the mantle sources of both OIB and MORB have a subducted atmospheric origin[5-7,46]. Given that halogens and H_2O are more easily incorporated into mineral phases within the subducting slab than noble gases, the presence of subducted halogens and water in the mantle is to be expected.

The deep subduction fluxes of halogens and H_2O are loosely constrained by the constancy of continental freeboard, which requires that the amount of water at Earth's surface remains relatively constant and therefore that H_2O subduction has been roughly balanced with mantle outputs since the Archaean[3]. Mantle outputs of H_2O and Cl in MORB and OIB are estimated as $(0.6\text{-}2.1)\times10^{11}$ kg H_2O yr^{-1} and $(2\text{-}5)\times10^{9}$ kg Cl yr^{-1} (Table 2)[1,3,47]. As sediments and oceanic crust are likely to be largely (e.g. 95%) dehydrated during subduction, they cannot carry enough H_2O or Cl into the deep mantle to balance the outputs (Table 2). However, the discrepancy can be balanced, if in accordance with our analysis, 1-2% of the uppermost 10 km of subducting oceanic lithospheric mantle is serpentinised (Table 2). The emphasis on serpentinised lithosphere is further supported by the observation that the dominant δ^{37}Cl signature of the mantle is similar to seawater and serpentinites[48]. At current rates of subduction and magmatism the entire mantle inventories of Cl and H_2O could be subducted into the mantle, and equivalent amounts transferred to the surface reservoirs, in about 4 Ga (Table 2)[1]. The limited variations in Br/Cl and I/Cl in the mantle (Fig 2) indicate similar cycling of Br and I, with the relative abundances of Cl, Br and I in the mantle probably controlled by slab mineralogy. In contrast, the greater compatibility of F in common mineral structures (Fig 3) means that it has been preferentially retained in the mantle and continental crust and has been less strongly cycled through the oceans and back into the mantle. The suggested flux of serpentinised lithosphere in this model (Table 2) also provides a viable pathway for subduction of the mantle's inventory of non-radiogenic Ar, Kr and Xe, based on the reported concentration ranges of noble gases in serpentinites[27].

Numerous studies have demonstrated the potential importance of serpentinites for volatile transport during subduction[3,45,49,50], however, the mantle-scale association of H_2O and halogen enrichment with fluid-mobile trace element depletion shown here provides one of the first lines of evidence for the actual impact of serpentinite subduction on mantle volatile budgets. The implied flux of seawater-derived volatiles into the mantle reconciles the behaviours of water and halogens with noble gases[5-7] and challenges traditional views of planetary evolution. The suggested exchange of halogens and H_2O between the surface and mantle reservoirs (Table 2) means that it should no longer be assumed that the atmospheres and oceans were produced by outgassing of the mantle[1]. Rather scenarios in which the atmosphere and oceans were partly derived from a veneer of late accreted volatile-rich materials and volatiles were then gradually mixed into the Earth's mantle by plate tectonic processes are equally plausible[7].

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Author Contributions

MAK conceived the project and undertook the majority of analyses. CH measured radiogenic isotopes in Foundation and St Helena samples at PSO-Brest and TR measured water by FTIR at UTAS. CH, VSK, CD, LD, MGJ and MRP provided sample material and LD and VSK provided major and/or trace element data associated with their samples. MAK wrote the initial manuscript and incorporated comments from VSK, MGJ, CD, LD, MRP and CH into the final version.

Additional information

Supplementary information is available in the online version of this paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.A.K. at mark.kendrick@anu.edu.au

Fig 1. $^{206}Pb/^{204}Pb$ versus $^{87}Sr/^{86}Sr$ diagram for glasses included in this study. The principle mantle end-members are depleted MORB mantle (DMM), enriched mantle 1 and 2 (EM1 and EM2), high-μ meaning high U/Pb (HIMU) and the Focus zone (FOZO) which is characterised by elevated $^{3}He/^{4}He$ and is thought to represent primitive mantle. Data sources are given in the electronic supplement. Abbreviations: Mac. Is. – Macquarie Island. EQ-MAR = equatorial Mid Atlantic Ridge.

Fig 2. The relative abundances of halogens and H_2O in OIB and MORB glasses. Samples that have assimilated seawater are shown as grey symbols. a) I/Cl versus Br/Cl showing seawater (black star) and the composition of brines in amphibole- and quartz-hosted fluid inclusions[24]. b) K/Cl versus H_2O/Cl with equivalent salinities (wt. % salts) based on seawater salt. Samples free of seawater assimilation indicate the mantle has Br/Cl of $(2.8 \pm 0.8)\times10^{-3}$, I/Cl of $(60 \pm 30)\times10^{-6}$ and K/Cl of ~7-50 (n ~ 160; Table S1). Abbrev.: f.c. = fractional crystallisation.

Fig 3. Log-log concentration plots showing the relative compatibilities of Cl and F. Elements with log-log slopes of 0.95-1.05 are regarded as having indistinguishable compatibilities. The glasses investigated have ~20-2000 ppm Cl, and ~85-2000 ppm F. The scatter around each slope as indicated by the coefficients of determination (r^2), could result from different behaviours of elements in subduction zones. All concentrations are log ppm except for P which is log wt. %. Additional elements are included in Figs S3 and S4.

Fig 4. The volatile, isotope and trace element systematics of the mantle. a,b) The glasses H_2O/Ce is shown as a function of $^{208}Pb/^{207}Pb$ and $^{87}Sr/^{86}Sr$ enrichment ($^{208}Pb/^{207}Pb$ is used to enable plotting of Tuvalu and Mangaia data[18,19]). c) Nb/U-Ce/Pb plot separating HIMU (high Nb/U and Ce/Pb) and EM-type reservoirs that are closer to Primitive Mantle (PM) and Continental Crust (CC). d) Nb/U is broadly correlated with H_2O/Ce and e) F/Pr and f) H_2O/Ce is broadly correlated with Cl/K. Note that several HIMU influenced sources including Macquarie Island are relatively enriched in H_2O and halogens.

Table 1. Abundances of halogens and water on Earth

	Mass (kg) $\times 10^{21}$	F ppm	Cl ppm	Br ppb	I ppb	H_2O wt. %
Seawater	1.4 ± 0.07	1.30 ± 0.07	19,300 ± 970	66,000 ± 3,300	58 ± 6	96.5 ± 0.2
Evaporites	0.030 ± 0.005	10 ± 10	550,000 ± 50,000	150,000 ± 100,000	1000 ± 1000	0.2 ± 0.1
Marine sediments	0.5 ± 0.1	1000 ± 300	4000 ± 3000	40,000 ± 20,000	30,000 ± 15,000	20 ± 15
Sedimentary rock	1.5 ± 0.3	550 ± 100	700 ± 400	4,000 ± 3,000	1,500 ± 1,000	3 ± 2
Crustal brines	0.06 ± 0.03	20 ± 15	10,000 ± 5,000	600,000 ± 400,000	15,000 ± 10,000	70 ± 20
Cont. + oc. Crust	26 ± 3	550 ± 100	300 ± 100	600 ± 250	18 ± 9	1.0 ± 0.5
Processed mantle	2800 ± 800	12 ± 2	5 ± 2	13 ± 6	0.3 ± 0.1	0.02 ± 0.01
Primitive mantle	4040	17 ± 6	26 ± 8	76 ± 25	7 ± 4	0.08 ± 0.03

Estimates of halogen and water concentrations in different surface and mantle reservoirs are from various sources (see electronic supplement for details). The processed mantle is assumed to represent 0.7 ± 0.2 of the total mantle. See also Table S2 in electronic supplement.

Table 2. Estimated subduction fluxes of H_2O and Cl

	Mass	H_2O		Cl	
	kg a^{-1} ($\times 10^{13}$)	wt. %	kg a^{-1} ($\times 10^{11}$)	ppm	kg a^{-1} ($\times 10^{9}$)
Volcanic output					
MORB	4.0	0.1-0.4	0.4-1.6	40-80	1.6-3.2
OIB	0.4	0.6-1.2	0.2-0.5	200-400	0.8-1.6
Total output	4.4		0.6-2.1		2.4-4.8
Deep subduction input					
Dehydrated slab (sediments + crust)	~4.4		0.3-0.8		0.2-0.5
Serpentinised lithosphere (1-2%)*	0.07-0.015	13	1-2	2000	1.5-2.9
Total deep input			1.2-2.7		1.6-3.5

*Estimated mantle inputs and outputs based on data from numerous sources including refs. 1,3,47. The H_2O and Cl content of the dehydrated slab is estimated as 5% of the initial values where sediments with 5-10 wt. % H_2O are subducted at a rate of 0.2×10^{13} kg a^{-1}, and altered oceanic crust with 1-3 wt % H_2O is subducted at a rate of 4.4×10^{13} kg a^{-1}. *The amount of serpentinised lithospheric mantle is estimated as 1-2% of the upper 10 km based on the need to balance the deep input and output of H_2O, and generate significant H_2O enrichment in some HIMU reservoirs.*

Methods

Cl, Br and I measurement by the noble gas method at ANU

The heavy halogens (Cl, Br, I) and K were analysed in high purity glass separates of 6-30 mg by measuring irradiation-produced noble gas proxy isotopes ($^{38}Ar_{Cl}$, $^{80}Kr_{Br}$, $^{128}Xe_{I}$ and $^{39}Ar_{K}$)[51]. The samples were included in six different irradiations between 2010 and 2015, conducted in 3 different reactors (McMaster, Canada; USGS Triga; UC Davis, McClellan). The irradiations had durations of 30-80 hrs and the sample canisters were not shielded with Cd. Irradiation parameters and noble gas production ratios ($^{38}Ar/Cl$, $^{39}Ar/K$, $^{80}Kr/Br$ and $^{128}Xe/I$) were monitored using the ^{40}Ar-^{39}Ar flux monitor Hb3gr and 3 scapolite standards[17]. The irradiations had total neutron fluences of $(0.4\text{-}1.3)\times10^{19}$ neutrons cm^{-2} and thermal/fast ratios of 2.6-0.8 (see Table S4 electronic supplement). Following irradiation the samples were returned to the noble gas laboratory, loaded into Sn-foil sample packets and placed in an ultra-high vacuum noble gas extraction system. The noble gases were extracted from the glasses by fusion at 1500 °C in an ultra-high vacuum resistance furnace and analysed for isotopes of Ar, Kr and Xe using an MAP-215-50 noble gas mass spectrometer. Gas handling and data reduction have been described in detail previously[17,51]. The internal precision of elemental concentrations in samples included in a single irradiation is 1-2% (based on the reproducibility of noble gas air standards). However, the reproducibility between irradiations is estimated as ~5% for K, Cl and Br and ~10% for I (2σ) based on analyses of air standards, Hb3Gr and the halogen scapolite standards (Fig S4 electronic supplement).

F measurement by SHRIMP at ANU

Fluorine measurements were undertaken in two analytical sessions using SHRIMP-SI and SHRIMP-II at the Australian National University. Glass chips were mounted in epoxy resin, given a 1 micron polish and 10 nm thick gold coat. The sample mounts were held at a potential of -10kV in an ultra-high vacuum sample chamber and targeted with a primary Cs^+ ion beam focused to a ~30 μm spot on the sample. The ion beam generated with a Kimball Physics Cs gun (IGS-4) was 2 nA and had an energy of 5 kV. Charge compensation was achieved by focussing a 2 kV electron beam generated with a Kimball Physics electron gun onto the sample mount. Secondary ^{19}F and ^{18}O released from the sample were measured by Faraday multi-collection (10^{11} and 10^{12} resistors). The instruments were configured to give resolution of 5000 (1% valley definition). Data was collected over four 20 sec integration periods in static mode (total measurement time 80 sec). The measured ^{19}F signal was calibrated using ^{18}O as the internal standard and a suite of glasses previously measured for F at the Carnegie Institute of Washington[26,52], and three widely available glasses (SRM 610, 612 and BHVO) (Fig S5). The reported measurements for each sample are the average of 3-5 measurements on different glass chips. Internal reproducibility is 1-2% but accuracy is limited to a lower level by the standards available for calibration (Fig S5).

FTIR water measurements at the University of Tasmania

Water measurement were undertaken in 78 MORB and OIB glasses using the Bruker Vertex 70 (FT-IR) + Hyperion 2000 microscope at the University of Tasmania. Spectra and background were collected in transmission mode using 128 scans between 4000 and 1200 cm^{-1}. In most cases the reported analyses represent the average of 3 measurements made on areas of 60×60 μm using a 15x IR objective (NA=0.4). The thickness of the glass (approximately 200 μm) was precisely determined for each measurement area using interference fringes in the spectral region between 2600 and 2400 cm^{-1}. The height of the absorbance peak was measured at 3500 cm^{-1} and 3100 cm^{-1} and converted to a H_2O concentration on the basis of empirically determined calibration factors derived from four glass standards[53].

Major and trace element analyses at the ANU, Utas and UMelb

The concentrations of major elements were measured using the Cameca SX-100 electron microprobe at the ANU and University of Tasmania and the SX-50 at the University of Melbourne. The analytical conditions were broadly similar at each laboratory. At ANU they conbsisted of an accelerating potential of 15 keV, beam current of 20 nA and a 5 µm spot size. Counting times were 1-30 s for the majority of elements. The concentrations of trace elements were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the ANU, University of Tasmania and the University of Melbourne. Each laboratory used a 193 nm Eximer laser and Agilent (7700x, 7500S or 7500cs) mass spectrometer and standardised the analyses using a combination of NIST SRM612, BHVO2G and BCR2G analysed as calibration standards and unknowns. At ANU, the CompexPro 110F ArF excimer laser was run with a frequency of 5 Hz in energy-constant mode, which ensured a stable fluence at the sample surface of 5-6 J/cm^2. A focused spot size of 37 or 105 µm was used for sample and standard analyses (larger spot size for depleted MORB). Ultra-high purity He and Ar were used as the carrier gas. NIST SRM 612 were used as primary calibration standard with CaO used as the internal standard. Counting times were 0.01-0.07 for each element. Analytical conditions were similar at the University of Melbourne and the University of Tasmania. Unknowns were analysed after every 8-10 analyses in each laboratory and gave concentrations close to published values. The reported concentrations represent the averages of 3-5 analyses on different glass chips of each sample.

Isotopic analysis at PSO-Brest

The Pb, Sr and Nd isotope compositions of Foundation and St Helena samples were acquired using the Pôle de Spectrométrie Océan facilities (PSO-Brest). In order to eliminate potential seawater alteration, chips of the glasses totalling 100mg were rigorously cleaned by leaching with 4 ml of 6N HCl at 85°C for 20 to 40 min, and the leached glasses were then rinsed three times with de-ionized water. Leached glass chips were digested with a HF-HBr 3:1 (Romil-UpA™ - [Pb < 1 ppt]) mixture for 48 h and then evaporated to dryness. The residue was re-dissolved in HBr and aliquots of Pb, Sr and Nd were purified from the resulting solution by chemical chromatography following a procedure adapted from Manhes et al., (1984)[54].

First, the dissolved sample was loaded into anionic AG1X8 200–400 mesh columns and eluted to produce a Pb solution and waste fractions that were retained for Sr and REE extraction (below). The Pb fraction was purified a second time on the same column and the resulting high purity Pb solution was evaporated, redissolved in HNO_3 2% and spiked with Tl prior to analysis. Pb isotopes were measured on a Thermo Fischer Neptune MC-ICP-MS (PSO/Ifremer, Plouzané, France). NIST 981 standard was used for internal control (mean values (n = 36) $^{206}Pb/^{204}Pb = 16.931 \pm 0.006$ (2σ); $^{207}Pb/^{204}Pb = 15.488 \pm 0.005$ (2σ); $^{208}Pb/^{204}Pb = 36.692 \pm 0.014$ (2σ); recommended values $^{206}Pb/^{204}Pb = 16.937 \pm 0.006$; $^{207}Pb/^{204}Pb = 15.491 \pm 0.008$; $^{208}Pb/^{204}Pb = 36.721 \pm 0.016$). Blanks were less than 100 pg of Pb.

The waste fractions eluted from the Pb protocol were evaporated to dryness then re-dissolved twice in HNO_3 14N and dried again. The residue was finally dissolved in HCl 2.5N and loaded for Sr and REE separation on cationic AG50X8 columns. Later Nd was separated from the REE fraction using LnSpec Eichrom resin. Sr and Nd isotopes were determined on a Thermo Electron™ Triton T1 (PSO/IUEM, Plouzané, France) using procedures adapted from White and Patchett [1984][55] and Richard et al. [1976][56]. Sr isotopes were determined on a single W filament coated with Ta activator[57]. NBS 987 was used for internal control (mean value (n = 31) $^{87}Sr/^{86}Sr = 0.710262 \pm 0.000016$ (2σ)/recommended value $^{87}Sr/^{86}Sr = 0.710248$). $^{87}Sr/^{86}Sr$ ratios were corrected online for mass fractionation using $^{86}Sr/^{88}Sr$ of 0.1194 (ref. [58]). Blanks were less than 600 pg of Sr. Nd isotopes determinations were run on a Re double filament. La Jolla standard was used for internal control (mean value (n = 16) $^{143}Nd/^{144}Nd =$

0.511845 ± 0.000017 (2σ); recommended value ^{143}Nd/^{144}Nd = 0.511850). ^{143}Nd/^{144}Nd ratios were corrected online for mass fractionation using ^{146}Nd/^{144}Nd = 0.7219. Blanks were less than 400 pg of Nd.

Data availability

The authors declare that all data supporting the findings of this study are available within the article and its supplementary information files.

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Additional references for the methods

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