LETTERS

Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites

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Chlorine in the Earth is highly depleted relative to carbonaceous chondrites and solar abundances[1]. Knowledge of the Cl concentrations and distribution on Earth is essential for understanding the origin of these depletions. Large differences in the stable chlorine isotope ratios of meteoritic, mantle and crustal materials have been used as evidence for distinct reservoirs in the solar nebula[2] and to calculate the relative proportions of Cl in the mantle and crust[3]. Here we report that large isotopic differences do not exist, and that carbonaceous chondrites, mantle and crust all have the same $^{37}Cl/^{35}Cl$ ratios. We have further analysed crustal sediments from the early Archaean era to the Recent epoch and find no systematic isotopic variations with age, demonstrating that the mantle and crust have always had the same $\delta^{37}Cl$ value. The similarity of mantle, crust and carbonaceous chondrites establishes that there were no nebular reservoirs with distinct isotopic compositions, no isotopic fractionation during differentiation of the Earth and no late (post-core formation) Cl-bearing volatile additions to the crustal veneer with a unique isotopic composition.

Quantification of the Cl concentration and distribution on Earth would help to constrain models of planetary formation that are based on depletion due to nebular fractionation processes during formation of the inner planets, or due to early catastrophic degassing followed by expulsion during meteoritic bombardment[4]. In addition to Cl abundances alone, an independent constraint is provided by $^{37}Cl/^{35}Cl$ ratios. Distinct nebular reservoirs, or mixing between different reservoirs, could be identified by variations in the $^{37}Cl/^{35}Cl$ ratio of different materials. Using mass balance constraints, differences in the $\delta^{37}Cl$ value of the mantle, crust and carbonaceous chondrites could also be used to define the proportions of Cl in the crust and mantle reservoir if the chlorine isotope compositions of the different reservoirs were known.

Of all the important Cl-bearing terrestrial reservoirs, the crust is by far the best characterized for Cl isotopes. The oceans and evaporites make up the vast majority of the crustal Cl reservoir; the ocean has a constant $\delta^{37}Cl$ value of 0‰ (ref. 5) and evaporites are generally within 0.5‰ of the ocean value[6] (Fig. 1). Previous estimates of the isotopic composition of the mantle were made from analyses of pristine mid-ocean ridge basalt (MORB) glasses, using the thermal ionization mass spectrometry of CsCl. Values range from 3.0‰ to 7.2‰, and average 4.7‰ (refs 3, 7).

Only a few meteorites have been analysed for chlorine isotope ratios. Three analyses of bulk carbonaceous chondrites are between 2.7‰ and 4.0‰ (refs 3, 7). The positive $\delta^{37}Cl$ values of bulk carbonaceous chondrites are intermediate to those of mantle and crust, and were used to calculate the mantle/crust Cl ratio, with ~60% Cl residing in the degassed mantle[3]. The $\delta^{37}Cl$ values of halite and water-soluble chloride from two ordinary chondrites range from −2.8‰ to −1.4‰ (ref. 2). The negative values for the water-soluble fraction were interpreted either as representing a second reservoir from the early Solar System or reflecting unknown large isotope fractionations linked to low-temperature fluid activity[2]. All meteorite data were measured by thermal ionization mass spectrometry of CsCl.

Details of all samples analysed and methods are given in the Supplementary Information. Five carbonaceous chondrites[8] were analysed for bulk chlorine isotope compositions using gas source mass spectrometry (Table 1). In addition, high-spatial-resolution spot analyses of sodalite grains from calcium aluminium inclusions (CAI) from Allende were made using a large radius ion microprobe. Allende sodalite has been shown to have ^{36}Cl and ^{26}Al anomalies, suggesting that its formation occurred very early in the history of the Solar System[9].

We analysed twelve MORB glasses to determine the $\delta^{37}Cl$ value of depleted MORB (Table 1). All are optically and chemically pristine, and appear to be free of seawater alteration. The samples cover a broad range of MORB types, coming from different ridges, and include low degrees of partial melting with high Cl content to depleted high degree of partial melting with low-Cl-content glasses.

Three mantle-derived samples in a continental setting were analysed. (1) Fresh carbonatite lavas from Oldoinyo Lengai, Tanzanian rift valley, collected during an active eruption in 2005. Rare gas and carbon and oxygen isotope ratios are consistent with a mantle source and lack of surficial alteration. (2) Massive halite nodules found in the surficially unaltered Siberian Udachnaya-East kimberlite[10]. (3) Djerfisherite ($K_6Na(Fe,Cu,Ni)_{24}S_{26}Cl$) from pegmatites from the Khibina massif, Kola peninsula, Russia. The Khibina massif is an enormous intrusive complex, presumably of mantle origin of Caledonian age (500–360 Myr ago).

Sediments covering a wide range of ages were analysed to determine whether secular variations in the $\delta^{37}Cl$ value of the crust exist. Twelve chert samples from the Archaean and Proterozoic eras and one from the Jurassic period were analysed. Other Precambrian bulk samples include an iron formation, modified evaporite (barite) and dolomite. Data from these samples and Phanerozoic halites (including the oldest-known salt deposit) are given in Table 2, and plotted in Fig. 2. An experiment was undertaken in order better to understand fractionation mechanisms that might be relevant to chlorine partitioning between phases in the nebular reservoir and, in particular, sodalite as a primitive Cl-bearing phase in chondrites. Nepheline and excess NaCl were reacted in a sealed platinum capsule at 825 °C for 48 h to form sodalite. The sodalite and excess salt in the reaction capsule were analysed for their $\delta^{37}Cl$ values using isotope ratio mass spectrometry (Supplementary Table SI-2) to determine the equilibrium fractionation between these two phases.

The average of all carbonaceous chondrites is 0.0 ± 0.7‰ (1σ) (all data are reported relative to the Standard Mean Ocean Chloride or SMOC[5]) (Table 1). (The Orgueil chondrite is a $>2\sigma$ outlier when

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excluded from the average and standard deviation. Although it is known to have undergone terrestrial alteration[11], we cannot see how this would change the δ^{37}Cl value, nor why the other CI chondrite, Ivuna, does not show the same ^{37}Cl enrichment. Orgueil is therefore included in the average.) Sodalite δ^{37}Cl values average −1.3‰ (±0.6‰, 1σ), statistically lighter than bulk meteorite data. The low values, compared to bulk chondrites, may represent a second nebular Cl reservoir, but can also be explained, and are indeed expected, in terms of equilibrium fractionation. The $1{,}000\ln\alpha_{\text{sodalite}-\text{NaCl}}$ value (where $\alpha_{a-b} = (\delta_a + 1{,}000)/(\delta_b + 1{,}000)$) from our experiment (see Supplementary Information) is -0.3 ± 0.1‰ (1σ) at 825 °C, a fractionation that should increase with decreasing temperature. Fractionations of −1‰ at lower temperature are reasonable, and there is no need to call on multiple nebular reservoirs, although the data do not preclude it.

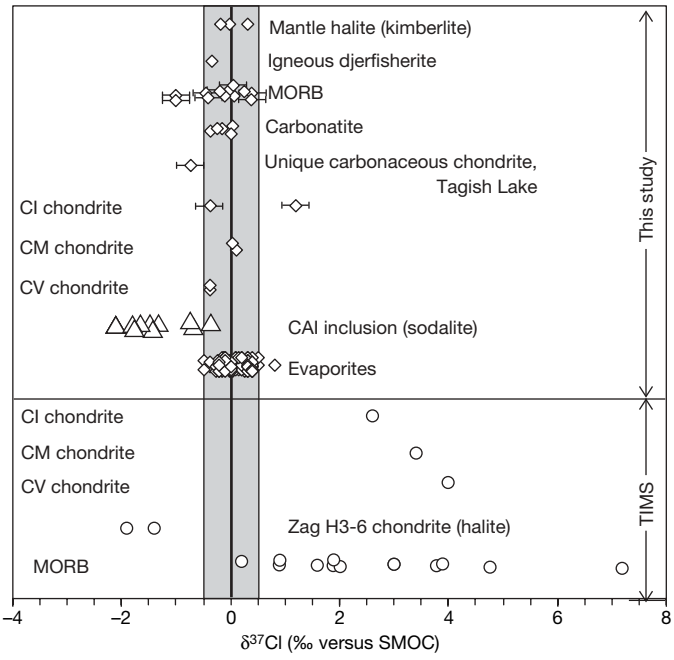


Figure 1 | δ^{37}Cl values of selected terrestrial and chondritic samples. Samples were analysed from the crust, mantle and chondritic meteorites by gas source mass spectrometry (shown as diamonds). Crustal evaporites and the ocean have δ^{37}Cl values clustering tightly around 0‰ versus SMOC. Mantle samples include MORB (samples from the 9° N and 12° N regions of the East Pacific Rise, the Pacific–Antarctic rise crest 53°–57° S, Iceland and Macquarie Island, an above-sea level exposure of the Macquarie Ridge, representing the Miocene spreading of the Australia–Pacific plate boundary), and sub-continental mantle (halite nodules in dimondiferous kimberlite[10]; fresh carbonatite from Oldonyo Lengai[27] and an igneous djerfisherite ($K_6Na(Fe,Cu,Ni)_{24}S_{26}Cl$) from the Kola peninsula, Russia). Although the MORB samples may have suffered some seawater contamination, the low Cl/K and Cl/Nb ratios and the lack of correlation between Cl content and these ratios argues against significant seawater infiltration. The average for all mantle samples is -0.1 ± 0.4‰ (1σ), with some scatter that may represent minor mantle heterogeneity. Bulk carbonaceous chondrite samples have more scatter, but still average 0.0 ± 0.7‰, indistinguishable from the terrestrial reservoir. Previous analyses made with solid source mass spectrometry (open circles, bottom of figure) have higher δ^{37}Cl values and are more variable. These data probably suffered from analytical artefacts and are not considered reliable (see Supplementary Information). The sodalite inclusions in a CAI from Allende was measured using a Cameca 1270 ion microprobe (triangles). The isotopically light sodalite may represent a second light nebular reservoir or may be explained in terms of equilibrium fractionation at low temperatures. All data are from this study, except for carbonaceous chondrites[3,7] and H3-6 chondrite, both analysed with thermal ionization mass spectrometry[2], and selected evaporites[6] and carbonatites[28] for which only samples with δ^{18}O values close to primary were considered. Analytical uncertainty (1σ) is equal to symbol size except where indicated.

Our Phanerozoic crustal halite data average 0.0 ± 0.3‰, and show no correlation with age (Fig. 2). Bulk chert data (presumably from saline fluid inclusions) covering an age range of 3,500 to 150 Myr ago, average -0.7 ± 1.0‰. The data have a lower average isotopic composition than for the halite, which may in part be explained by a small positive equilibrium fractionation between halite and aqueous solution[12]. More importantly, however, is that there is no correlation with age, as is seen also with the Proterozoic halite samples.

The δ^{37}Cl values of bulk carbonaceous chondrites, depleted oceanic mantle, subcontinental mantle and the crust are statistically indistinguishable (Table 1, Fig. 1). If the mantle and crust had different δ^{37}Cl values, then simple box modelling shows that there would be a measurable secular variation in the crust, given the enormous Cl flux between the two reservoirs[13]. That this is not the case further supports our contention that the crust and mantle have indistinguishable δ^{37}Cl values. The identical mantle and crustal δ^{37}Cl values suggest a common single Cl reservoir in the Earth, and

Table 1 | δ^{37}Cl values of mantle and carbonaceous chondrite samples

Material	Sample ID	δ^{37}Cl (‰ versus SMOC)	Cl content (p.p.m.)
Carbonaceous chondrites			
CM chondrite	Murchison (*di*)	0.46, 0.15	n.d.
CI chondrite	Ivuna	−0.35	290
CI chondrite	Orgueil	1.21	603
C2 ungrouped chondrite	Tagish Lake	−0.71	n.d.
CV chondrite	Allende (*di*)	−0.39, −0.37	n.d.
Average bulk meteorite	Average 1σ	0.0 (0.7)	
Sodalite in Allende	CAI 4-2	−2.09	
Sodalite in Allende	CAI 4-3	−1.62	
Sodalite in Allende	CAI 4-4	−0.72	
Sodalite in Allende	CAI 4-5	−1.44	
Sodalite in Allende	CAI 4-7	−0.65	
Sodalite in Allende	CAI 4-8	−1.76	
Sodalite in Allende	CAI 4-9	−1.72	
Sodalite in Allende	CAI 2-1	−1.40	
Sodalite in Allende	CAI 2-2	−0.39	
Sodalite in Allende	CAI 2-3	−1.33	
Average sodalite in allende	Average 1σ	−1.3 (0.6)	
MORB glass			
9° N on-axis, East Pacific Rise	ALV 2358-4	−0.40	59
9° N off-axis, East Pacific Rise	ALV 2746-12	−0.24	78
9° N off-axis, East Pacific Rise	ALV 2772-1	0.27	63
9° N off-axis, East Pacific Rise	ALV 2772-2	0.05	59
10° N, East Pacific Rise	CHEPR	−0.09	86
12° N on-axis, East Pacific Rise	CH7-1	−1.04	327
12° N on-axis, East Pacific Rise	CH116-2	−1.03	214
Iceland, North Atlantic	DICE 13	0.36	160
Macquarie Ridge	47963 (*di*)	0.06	1,400
Pacific-Antarctic rise crest, 53–57° S	D64-2	0.37	66
Pacific-Antarctic rise crest, 53–57° S	D62-1A	−0.46	203
Pacific-Antarctic rise crest, 53–57° S	D17-1A	−0.16	67
Average MORB glass value	Average 1σ	−0.2 (0.5)	
Subcontinental mantle materials			
Djerfisherite, Kola Peninsula		−0.35	12,200
Carbonatite, Tanzanian rift valley	OL-D1 (*di*)	0.04	n.d.
Carbonatite, Tanzanian rift valley	OL-D3 (*di*)	−0.15	n.d.
Carbonatite, Tanzanian rift valley	OL-D2 (*di*)	0.00	n.d.
Halite from kimberlite, Siberia	UV-2-03 (*di*)	0.30, −0.03, −0.18	
Average subcontinental mantle value	Average 1σ	−0.03 (0.25)	

Multiple values denote repeats. See ref. 8 for a detailed discussion of chondrite classification. The Tagish Lake chondrite has an extremely high volatile content and is classified following ref. 16. Except for sodalite in Allende, samples were analysed in dual inlet (*di*) mode; all others were measured in continuous flow (see Supplementary Information). Sodalite was measured using the Cameca 1270 ion microprobe at CNRS, Nancy, France using conditions similar to ref. 17. A natural sodalite was used as a standard (calibrated using gas source mass spectrometry). The standard deviation of the sodalite standard analysed in the same session was 0.19‰ (1σ), suggesting that the scatter in Allende is not an analytical artefact (see Supplementary Information). Cl contents from the ALV and CH MORB samples from E. Hauri (Petrological Database, PETDB; http://www.petdb.org/) determined using ion microprobe.

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Table 2 | δ^{37}Cl values of halite and fluid inclusion samples of various ages

Sample	Location	Age (Myr ago)	Cl content (p.p.m.)	δ^{37}Cl (‰)
Halite				
Wieliczka salt mine	Poland[18]	13		0.09
WIPP (Waste Isolation Pilot Plant)	New Mexico, USA[19]	250		−0.02, −0.15
Ghafeer-5	Oman[20]	543		−0.24, −0.37
Minha-1	Oman[20]	544		0.14, 0.03
Bulk sediment samples				
Chert, Onverwacht Group	South Africa[21]	3,400	23.	0.77, 0.42
North Pole barite	West Australia[22]	~3,450	n.d.	2.20, 2.52
Kona dolomite	Michigan[23]	~2,200	n.d.	0.16, −0.39
Holy Cross Mountains chert	Poland[24]	~155	14	−0.51
Isua iron formation	Greenland[25]	3,850	15	−0.78

Geologic/tectonic unit	Sample location	Sample number	Age (Myr ago)	Cl content (p.p.m.)	δ^{37}Cl (‰)
Chert samples from the Precambrian Paleobiology Research Group sample suite[26]					
Bitter Springs Formation/Amadeus basin	Northern Territory, Australia	1,315	850	627	−1.35
Siyeh Formation/Belt basin	Montana, USA	1,026	1,450	15	−1.01, −0.30
Gunflint iron formation	South Ontario, Canada	1,284	1,878	67	−1.68
Towers Formation/Pilbara block	West Australia	1,437	2,200	25	1.04
Fig Tree group/ Barberton greenschist belt	Transvaal, South Africa	2,569	2,200	28	−0.41, 0.37
Gamohaan Formation/Kaapvaal craton	Transvaal, South Africa	2,515	2,500	21	−0.21
Maddina basalt/Hamersley basin	West Australia	2,033	2,700	25	−3.16
Tumbiana Formation/Hamersley basin	West Australia	2,095	2,700	15	−0.24
Hooggenoeg Formation/Barberton greenstone belt	Transvaal, South Africa	1,386	3,450	68	−0.83
Apex basalt/Pilbara block	West Australia	1,998	3,500	34	−0.57, −0.36

Halites measured in dual inlet, all others measured in continuous flow.

that early mantle degassing[14] of Cl was not accompanied by isotopic fractionation.

The similar δ^{37}Cl values of terrestrial reservoirs and carbonaceous chondrites requires that there should be little to no fractionation associated with volatile loss during the early stages of planetary accretion or with volatile loss due to later impact heating and ejection[4]. Further, no Cl isotope fractionation occurred between the crust and mantle. The question of the core is unresolved, but if a significant fraction of Earth's chlorine resides in the core[15], then fractionation between the core and the bulk silicate Earth must also be nearly zero for the bulk Earth and carbonaceous chondrites to have the same δ^{37}Cl value. The discrepancy between the present data set and previously published data are explained by analytical artefacts of the latter. The thermal ionization mass spectrometry analyses of CsCl resulted in artificially high δ^{37}Cl values (see Supplementary Methods).

The similarity of all major Cl reservoirs measured in this study supports the idea of isotopic homogeneity at all stages of planetary formation. Equally important, the new data eliminate some unreasonable constraints on nebular heterogeneity and mantle–crust fractionation that were required by the previous data. Whether catastrophic or continual in nature[14], Cl transfer from the mantle to crust occurred without measurable isotopic fractionation. Chondritic averages are identical to those in the bulk Earth, but the range of δ^{37}Cl values of chondritic reservoirs is well outside analytical uncertainty. The spread can be explained solely by low-temperature isotopic fractionation, although further work is warranted to identify possible variations in nebular material.

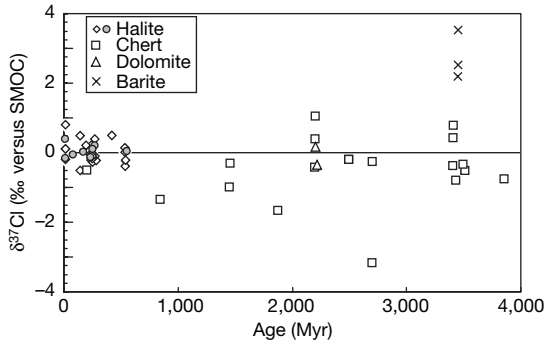


Figure 2 | Measured δ^{37}Cl values of crustal sediments plotted as a function of age. Phanerozoic halite data plotted as diamonds (from this study and ref. 6) and as circles (mean δ^{37}Cl values of halite-facies salt from ref. 29). Older sediments include chert, barite and dolomite. There is no correlation with age for either the halite or the chert data, although the latter have an average δ^{37}Cl value that is 0.7‰ less than the halite. The high, heterogeneous values for the barite may be related to diagenesis and exchange with a non-marine reservoir. Analytical uncertainties (1σ) are ±0.12‰ (1σ) for halite and ±0.3‰ (1σ) for all others.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Methods

The chlorine isotope composition of all of the samples, except sodalite in Allende, was determined using gas source isotope ratio mass spectrometry (IRMS) at the University of New Mexico. Samples were crushed and leached, and Cl^- was extracted using pyrohydrolysis[30]. Silver chloride was then precipitated from the solutions, converted to CH_3Cl by reaction with CH_3I at 80°C, purified in a custom made ¼" diameter, 20 cm long glass gas chromatographic column packed with HayeSep® Q 80/100 resin, and analyzed on a gas source mass spectrometer[31]. Samples with high Cl concentrations were analyzed in dual inlet; all other samples were analyzed in continuous flow. The continuous flow method is similar to that described previously[32] except that CH_3Cl gas is purified in the gas chromatography column and passes through a simple open split into the mass spectrometer instead of being frozen in a cold trap and analyzed using dual inlet mass spectrometry. Samples are reported relative to Standard Mean Ocean Chloride (SMOC) using seawater (sampled at Carmel, California, USA and Elba, Italy) as a standard with a defined value of 0.0‰. Uncertainties are ±0.10‰ and ±0.26‰ (1σ) for dual inlet and continuous flow, respectively. There is no long-term drift (Table SI-1). Cl contents of solutions were determined using a Dionex DX-100 Ion Chromatograph, which has a minimum detection limit of 0.22 ppm for Cl^-.

Accuracy of chlorine isotope analyses from silicates was determined by synthesizing a MORB glass with a known isotopic composition. A ^{37}Cl-enriched solution was made by boiling a 1 M HCl solution and collecting the condensate[33]. The condensate was then neutralized with an NaOH solution and dried, precipitating a ^{37}Cl-

enriched solution. A split of this salt was mixed in with a synthetic MORB glass (courtesy of Bruce Watson, RPI) to make a 660 ppm Cl powder. The powder was heated to 1300°C at 10 kbar in a sealed $Au_{80}Pd_{20}$ capsule in the high pressure laboratory at the University of New Mexico (courtesy of David Draper). Finally, the glass was analyzed for δ^{37}Cl value and compared to the value of the NaCl starting material. The δ^{37}Cl value of the synthetic glass was found to be 2.65‰ and the NaCl was 2.41‰, indistinguishable within analytical error.

Sodalite from Allende was analyzed using a Cameca 1270 ion microprobe (CNRS, CRPG, Vandoeuvre-les-Nancy, France) at a mass resolution of 2500 using Cs^+ bombardment and analyzing $^{35}Cl^-$ and $^{37}Cl^-$ secondary ions in multi-collection mode with two Faraday cups[34]. For typical primary beam intensities of ≈ 3nA, the count rate on ^{37}Cl was from $\approx 1 \times 10^7$ to $\approx 4 \times 10^7$ counts/sec depending on whether the Cs beam was sputtering sodalite only. A natural sodalite standard from Mont St-Hilaire syenite[35], Quebec with a δ^{37}Cl value of 0.11‰ analyzed conventionally, was used to determine instrumental mass fractionation, which was found to be reproducible (n = 8) within ±0.19‰ (1σ) (Table SI-1).

The fractionation between sodalite and NaCl was determined by reacting nepheline with a large excess of NaCl in a Pt capsule at 825°C. All nepheline reacted to form sodalite. The sodalite and excess salt in the reaction capsule were analyzed for their δ^{37}Cl values using IRMS. Combined uncertainty for $1000ln\alpha_{\text{sod-NaCl}}$ is given by $1\sigma_{a+b} = \sqrt{(1\sigma_a)^2 + (1\sigma_b)^2}$ and is 0.14‰.

The present data are in marked contrast to earlier published estimates, where fresh

MORB glasses averaged 4.7‰ and CI chondrites ranged from 2.7 to 4.0‰[30,36]. These earlier analyses were measured using thermal ionization mass spectrometry of CsCl. The likely explanation for the discrepancy is related to analytical artifacts associated with the TIMS technique. The presence of F^- and SO_4^{2-} suppresses ionization, and although efforts are made to remove F^- from the sample, Cs_2F^+ is observed in the mass spectrum[30]. A recent abstract reporting MORB $\delta^{37}Cl$ values obtained with gas source dual inlet isotope ratio mass spectrometry range from -1.6 to -0.6‰[37]. These values are close to our own, but slightly more negative. The reason for the discrepancy is not known, but may be related to having analyzed different samples.

Sample Description

Samples ALV-*xx* were collected at 9°N on the fast-spreading East Pacific Rise by Mike Perfit using the Alvin submersible. All have Cl contents below 80 ppm and low Cl/Nb ratios between 17 and 23, indicating minimal interaction with seawater (analyzed by E. Hauri, pers. comm.). Cl contents were determined using ion microprobe and no veins or 'hot spots' were detected. Samples CH-*x* were collected by John Bender at 12°N using dredging techniques. The spreading rate is slightly slower at 12°N (10.4 cm/yr vs 12.0 cm/yr at 8-10°N). Chlorine contents are higher (CH7-1 = 327 ppm; CH116-2 = 214 ppm) and Cl/Nb ratios (CH7-1 = 31; CH116-2 = 27). See[38] and the Petrological Database (http://www.petdb.org/) for details.

CHEPR 93D is from 9°58.7′N and 104°18.3′W on the East Pacific Rise, depth of 2610mbs. Major element data for similar samples are given in the Petrological Database

of the Ocean Floor. The very low Cl content (this study) argues against seawater alteration. See Batiza and Niu[39] for information on the region.

Samples D17-1A, D62-1A and D64-2 are all chemically defined N-MORB glasses from the Pacific-Antarctic risecrest[40]. $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios for D62-1A and D64-2 are 0.702441 & 0.513111 and 0.702415 & 0.513090, respectively.

DICE-13 is subglacial basaltic glass from the Reykjanes Peninsula, Iceland, with a $^{3}He/^{4}He$ ratio of 17.1 (Ra) and $\delta^{18}O = 4.36‰$, slightly less than unaltered values of 4.6‰[41].

Sample 47963 come from an above-sea level exposure of the Macquarie Ridge, representing the Miocene spreading of the Australia-Pacific plate boundary. All geochemical indicators suggest a primitive, unaltered glass[42]. Chlorine concentrations of all glasses vary regularly with respect to La/Sm ratio and the Cl/K and Cl/Nb ratios are 0.1 and 15[42], respectively, indicative of minimum alteration by seawater.

Sample UV-2-03 is from a 400-500 m deep excavation of an extremely fresh kimberlite of the Udachnaya-Vostochnaya pipes, Yakutia[43]. The groundmass is predominantly olivine–carbonate–chloride in composition and shows almost no evidence of replacement. There is no serpentine and low water content (<0.5 wt %). Halite, sylvite, aphthitalite $K_3Na(SO_4)_2$, shortite ($Na_2Ca_2(CO_3)_2$ are water soluble minerals that are present in the fresh exposure. The chlorides, alkali sulfates are found also in the Oldoinyo Lengai natrocarbonatite volcano in Tanzania (samples OL-D*x*), and are thought to be primary mantle minerals.

Table SI-1. Analyses of reference materials. In every mass spectrometry run, two to three standard CH_3Cl gases were prepared from seawater (collected at Carmel, CA and Elba, Italy). The raw $\delta^{37}Cl$ values relative to our reference CH_3Cl gas are given below. There is no drift with time. For a given series of analyses (a single non-stop session on the mass spectrometer), seawater and samples were corrected by adding a constant value such that the standard seawater value was 0.0 (the value of seawater on the SMOC scale). Standardization covers period of 5/1/06 to 10/17/06 for dual inlet analyses and 6/12/06 to 11/3/06 for continuous flow. All sodalite analyses were made in a single session, S.D. (1σ) are given for each sample from raw counts.

Dual inlet CH_3Cl	Cont. flow CH_3Cl	Ion probe (sodalite)	
$\delta^{37}Cl$ raw	$\delta^{37}Cl$ raw	$\delta^{37}Cl$ raw	S.D. of analysis
-3.78	-3.95	5.30	0.04
-3.83	-3.68	5.29	0.04
-3.68	-3.89	5.28	0.03
-3.67	-4.00	5.49	0.03
-3.63	-3.63	5.60	0.04
-3.77	-4.30	5.01	0.04
-3.83	-3.56	5.24	0.04
-3.76	-4.08	5.06	0.03
-3.83	-4.04	5.33	0.03
-3.90	-4.43	5.03	0.04
-3.77	-3.94		
-3.79	-3.66		
-3.77			
-3.73			
-3.63			
-3.76			
-3.81			
-3.64			
-3.77			
-3.95			
-4.01			
Average/Standard Deviation (1σ)			
-3.78 (0.10)	–3.93 (0.26)	5.26 (0.19)	

Table SI-2. $\delta^{37}Cl$ values of sodalite (repeated analysis) and NaCl $\delta^{37}Cl$ results from 800°C experiment.

Sample	$\delta^{37}Cl$
Sodalite A1	-0.07
Sodalite A2	-0.02
NaCl (run product)	+0.28

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