

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 abundances¹. 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 nebula² and to calculate the relative proportions of Cl in the mantle and crust³. Here we report that large isotopic differences do not exist, and that carbonaceous chondrites, mantle and crust all have the same ³⁷Cl/³⁵Cl 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 $\delta^{37}\text{Cl}$ 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 bombardment⁴. In addition to Cl abundances alone, an independent constraint is provided by ³⁷Cl/³⁵Cl ratios. Distinct nebular reservoirs, or mixing between different reservoirs, could be identified by variations in the ³⁷Cl/³⁵Cl ratio of different materials. Using mass balance constraints, differences in the $\delta^{37}\text{Cl}$ 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 $\delta^{37}\text{Cl}$ value of 0‰ (ref. 5) and evaporites are generally within 0.5‰ of the ocean value⁶ (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 $\delta^{37}\text{Cl}$ 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 mantle³. The $\delta^{37}\text{Cl}$ 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 activity². 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 chondrites⁸ 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 ³⁶Cl and ²⁶Al anomalies, suggesting that its formation occurred very early in the history of the Solar System⁹.

We analysed twelve MORB glasses to determine the $\delta^{37}\text{Cl}$ 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 kimberlite¹⁰. (3) Djerfisherite (K₆Na(Fe,Cu,Ni)₂₄S₂₆Cl) 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 $\delta^{37}\text{Cl}$ 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 $\delta^{37}\text{Cl}$ 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 $0.0 \pm 0.7\text{‰}$ (1 σ) (all data are reported relative to the Standard Mean Ocean Chloride or SMOC⁵) (Table 1). (The Orgueil chondrite is a >2 σ outlier when

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excluded from the average and standard deviation. Although it is known to have undergone terrestrial alteration¹¹, we cannot see how this would change the $\delta^{37}\text{Cl}$ value, nor why the other CI chondrite, Ivuna, does not show the same ^{37}Cl enrichment. Orgueil is therefore included in the average.) Sodalite $\delta^{37}\text{Cl}$ values average -1.3% ($\pm 0.6\%$, 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 $-0.3 \pm 0.1\%$ (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.

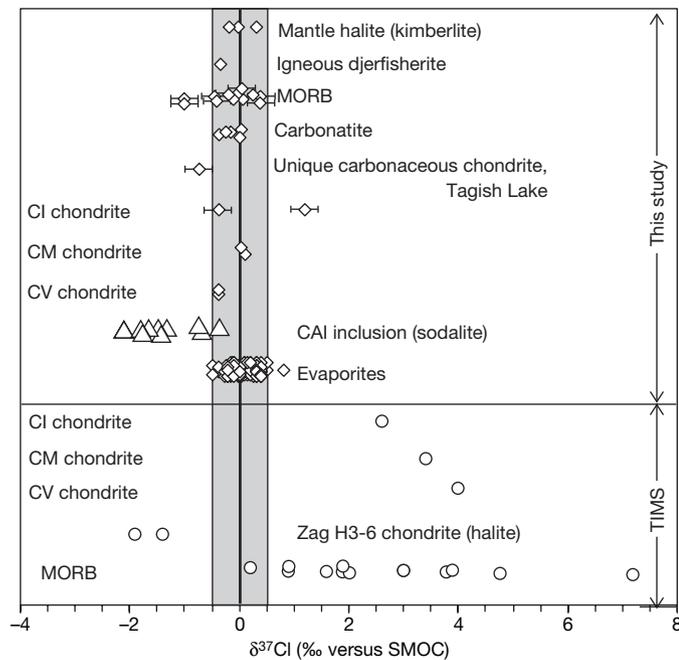


Figure 1 | $\delta^{37}\text{Cl}$ values of selected terrestrial and chondritic samples. Samples were analysed from the crust, mantle and chondritic meteorites by gas source mass spectrometry (shown as diamonds). Crustal evaporites and the ocean have $\delta^{37}\text{Cl}$ values clustering tightly around 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 $53^\circ\text{--}57^\circ\text{S}$, 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 kimberlite¹⁰; fresh carbonatite from Oldonyo Lengai²⁷ and an igneous djerfisherite ($\text{K}_6\text{Na}(\text{Fe,Cu,Ni})_{24}\text{S}_{26}\text{Cl}$) 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 $-0.1 \pm 0.4\%$ (1σ), with some scatter that may represent minor mantle heterogeneity. Bulk carbonaceous chondrite samples have more scatter, but still average $0.0 \pm 0.7\%$, indistinguishable from the terrestrial reservoir. Previous analyses made with solid source mass spectrometry (open circles, bottom of figure) have higher $\delta^{37}\text{Cl}$ 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 spectrometry², and selected evaporites⁶ and carbonatites²⁸ for which only samples with $\delta^{18}\text{O}$ values close to primary were considered. Analytical uncertainty (1σ) is equal to symbol size except where indicated.

Our Phanerozoic crustal halite data average $0.0 \pm 0.3\%$, 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 $-0.7 \pm 1.0\%$. 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 solution¹². More importantly, however, is that there is no correlation with age, as is seen also with the Proterozoic halite samples.

The $\delta^{37}\text{Cl}$ 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 $\delta^{37}\text{Cl}$ 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 reservoirs¹³. That this is not the case further supports our contention that the crust and mantle have indistinguishable $\delta^{37}\text{Cl}$ values. The identical mantle and crustal $\delta^{37}\text{Cl}$ values suggest a common single Cl reservoir in the Earth, and

Table 1 | $\delta^{37}\text{Cl}$ values of mantle and carbonaceous chondrite samples

Material	Sample ID	$\delta^{37}\text{Cl}$ (‰ versus SMOC)	Cl content (p.p.m.)
Carbonaceous chondrites			
CM chondrite	Murchison (<i>di</i>)	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 (<i>di</i>)	-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 (<i>di</i>)	0.06	1,400
Pacific–Antarctic rise crest, $53\text{--}57^\circ\text{S}$	D64-2	0.37	66
Pacific–Antarctic rise crest, $53\text{--}57^\circ\text{S}$	D62-1A	-0.46	203
Pacific–Antarctic rise crest, $53\text{--}57^\circ\text{S}$	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 (<i>di</i>)	0.04	n.d.
Carbonatite, Tanzanian rift valley	OL-D3 (<i>di</i>)	-0.15	n.d.
Carbonatite, Tanzanian rift valley	OL-D2 (<i>di</i>)	0.00	n.d.
Halite from kimberlite, Siberia	UV-2-03 (<i>di</i>)	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.

Table 2 | $\delta^{37}\text{Cl}$ values of halite and fluid inclusion samples of various ages

Sample	Location	Age (Myr ago)	Cl content (p.p.m.)	$\delta^{37}\text{Cl}$ (‰)	
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.)	$\delta^{37}\text{Cl}$ (‰)
Chert samples from the Precambrian Paleobiology Research Group sample suite²⁶					
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
Gamohaam 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 degassing¹⁴ of Cl was not accompanied by isotopic fractionation.

The similar $\delta^{37}\text{Cl}$ 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 ejection⁴. 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 core¹⁵, 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 $\delta^{37}\text{Cl}$ 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 $\delta^{37}\text{Cl}$ 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 nature¹⁴, 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 $\delta^{37}\text{Cl}$ 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.

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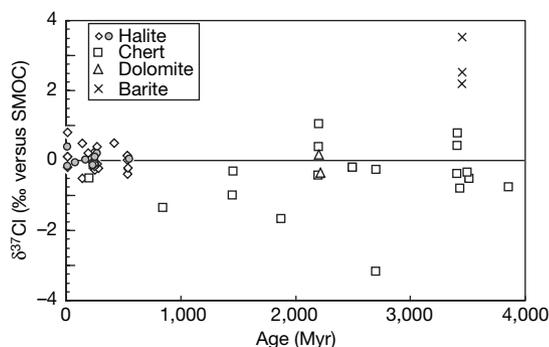


Figure 2 | Measured $\delta^{37}\text{Cl}$ values of crustal sediments plotted as a function of age. Phanerozoic halite data plotted as diamonds (from this study and ref. 6) and as circles (mean $\delta^{37}\text{Cl}$ values of halite-facies salt from ref. 29). Older sediments include chert, barite and dolomite. There is no correlation with age for either the halite or the chert data, although the latter have an average $\delta^{37}\text{Cl}$ 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 $\pm 0.12\%$ (1σ) for halite and $\pm 0.3\%$ (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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