

TITLE: Halogens in chondritic meteorites and terrestrial accretion

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INTRODUCTORY PARAGRAPH: Volatile element delivery and retention played a fundamental role in Earth's formation and subsequent chemical differentiation. The heavy halogens (Cl, Br and I) are key tracers of accretionary processes due to their high volatility and incompatibility, but have low abundances in most geological and planetary materials. Noble gas proxy isotopes produced during neutron irradiation provide a high sensitivity tool for the determination of heavy halogen abundance. Here we show that Cl, Br and I abundances in carbonaceous, enstatite, Rumuruti and primitive ordinary chondrites have concentrations ~6, ~9 and between 15-37 times lower, respectively, than previously reported and most commonly accepted estimates¹. This is independent of the chondrites' oxidation state or petrological type. Bromine/Cl and I/Cl in all studied chondrites show a limited range, indistinguishable from bulk silicate Earth (BSE) estimates. Our results demonstrate that BSE depletion of halogens relative to primitive meteorites is now consistent with lithophile elements of similar volatility. The new results for carbonaceous chondrites demonstrate that late accretion, constrained to a maximum of 0.5 ± 0.2 % of Earth's silicate mass²⁻⁵, cannot solely account for present-day terrestrial halogen inventories^{6,7}. It is estimated that 80–90% of heavy halogens are concentrated in Earth's surface reservoirs^{7,8} and have not undergone the extreme early loss observed in

atmosphere-forming elements⁹. Therefore, in addition to late accretion of halogens and mantle degassing, which is <50% efficient over Earth history¹⁰, efficient extraction of halogen-rich fluids⁶ from the solid Earth during the earliest stages of Earth formation is also required. The hydrophilic nature of the halogens supports this requirement, and is consistent with a volatile/water rich late-stage terrestrial accretion^{5,11–14}.

MAIN TEXT: Chondrites provide the reference frame for understanding the processes that controlled the accretion of the Solar System's inner planets. The depletion of highly volatile elements in the Earth relative to the carbonaceous Ivuna (CI)-type chondrites is well documented¹⁵ but, for some elements, the difference predicted from volatility, or decreasing condensation temperature (50% T_C), is insufficient to explain the extent of depletion actually observed. This has been particularly problematic for the heavy halogens Cl, Br and I, which have previously been shown to be depleted on Earth compared to CI chondrite by factors of ~28, 46 and 33 for Cl, Br and I, respectively¹⁶. For example, the degree of chlorine depletion is far higher than that of lithophile elements with similar 50% T_C , leading to models accounting for special halogen behavior during the accretionary process including; early hydrodynamic escape of hydrogen¹⁷, sequestration of halogens into an unidentified reservoir such as the core^{18,19}, impact-driven erosive loss of halogen-rich surface reservoirs on early Earth²⁰, or a higher nebular volatility (lower 50% T_C) of the halogen elements^{16,21}.

Accurate and precise knowledge of the halogen abundances in different chondrite classes is clearly essential for understanding terrestrial volatile evolution. However, progress towards characterizing the halogen abundances of chondrites has been hampered by the lack of precise measurement techniques for the particularly low abundance of Br and I, coupled with the limited amounts of suitable meteorite specimens available for analysis. Approximately an order of magnitude variation in halogen abundances within individual meteorite classes was reported during the 1960s and 1970s, typically analysed using neutron activation analysis and pyrohydrolysis. Using high sensitivity neutron-irradiation noble gas mass spectrometry (NI-NGMS) (**online Methods**), we have determined the halogen abundances and Br/Cl and I/Cl ratios for 24 chondrites (**Table 1, Figures 1 and 2**

and online Methods) covering four different classes; carbonaceous, enstatite, Rumuruti and ordinary chondrites.

Relative to data for other Solar System materials, including lunar, martian and terrestrial compositions, the Br/Cl and I/Cl variances of the carbonaceous, enstatite, Rumuruti and primitive ordinary chondrite classes are remarkably low (**Fig. 1**). Evidence of systematic elemental halogen fractionation during formation of chondrites is negligible. Additionally, secondary aqueous alteration is isochemical for the heavy halogens, as demonstrated by consistency in Type 1 and Type 2 chondrites (**Fig. 1; online Methods**). Bromine/Cl and I/Cl in chondrites are also indistinguishable from BSE values (**Fig. 1, 2**). This relationship implies that mechanisms of delivery to, and retention within Earth occurred without significant fractionation of the halogens. Critically, such an observation is also independent of which chondrites are dominant sources of terrestrial material. Only the thermally metamorphosed ordinary and enstatite chondrites show distinctly different halogen concentrations and ratios. The latter is particularly evident in thermally metamorphosed ordinary and enstatite chondrite I/Cl ratios (**Fig. 1h**), and explained by both their different halogen-mineralogy (e.g., phosphates, sulfides), and more extensive thermal metamorphism than experienced by the most unequilibrated chondrites (**online Methods**).

Halogen concentrations in this study (49 analyses of 24 chondrites) are significantly lower and show far less variation than those previously reported (**Table S1 and Extended Data Figure 1**). This is true for all chondrite types (**Fig. 2**). The discrepancy between this study and previous data can likely be attributed to differences in sample preparation techniques (e.g., possible inclusion of surface or terrestrial alteration material²²; **Table S2**). Only the earlier studies using larger samples (≥ 1 g)²³ and the more recent studies on CI chondrites using gas source mass spectrometry²⁴, are most consistent with the data presented here (**Table S1**). It is possible to compare halogen concentration variations in CI-chondrites with elements of similar volatility and geochemical affinity (moderately volatile lithophile elements). For example, the Orgueil CI chondrite has potassium (50% T_C 1006 K¹⁶) concentrations with approximately a factor of two difference (365 – 677 ppm²⁵), while Rb (50% T_C 800 K¹⁶) shows ~1.5 times variation (1.68 – 2.47 ppm²⁵). In contrast, the

variance for CI-chondrite chlorine abundance has been typically reported as ~700 ppm, with Cl abundances ranging from 210–950 ppm (~4.5 times variation). It has been suggested that the greater disparity reflects the effects of terrestrial contamination²⁶, sample variability²⁵ or analytical artifacts²⁷ (**online Methods**). With these caveats in mind, particular care was taken to identify and minimize contamination or bias (**online Methods; Extended Data Figures 2-4**). We obtained significantly lower halogen concentrations with reduced variance of 115 ± 36 (weighted average error) ppm Cl, 189 ± 71 ppb Br, and 57 ± 7 ppb I for CI-chondrite Orgueil (**Table 1 and Table S3**).

All chondrite groups, including the CI chondrites, have consistently lower abundances of Cl, Br and I than previously reported: 32 analyses of 17 unequilibrated carbonaceous, enstatite and Rumuruti chondrites give averages of (weighted average error): 111 ± 38 ppm Cl, 362 ± 39 ppb Br, and 38 ± 3 ppb I. One key observation from our new data is the reduced spread in Cl/Br/I ratios. All historical measurements with high Cl that contain a full Cl/Br/I analysis, show high I/Cl ratios relative to the new data (**Fig. 1**). High I is a strong indicator of terrestrial contamination suggesting that chondritic reference concentrations have been significantly overestimated. Also, the Br/Cl and I/Cl signature of the BSE are chondritic (**Fig. 1**) and BSE and chondrites have identical $\delta^{37}\text{Cl}$ values of -0.1 ± 0.4 and $0.0 \pm 0.7\text{‰}$ ^{24,26}. The similarity of both halogen isotopic and elemental abundance ratios between BSE and chondrites provide key observational constraints in developing any model controlling volatile element delivery to Earth.

Our revised halogen abundances yield higher CI-chondrite normalized abundances of Cl, Br and I, demonstrating that BSE is not significantly depleted in halogens compared with lithophile elements of similar volatility (**Fig. 3**)²⁸. Although Cl is plotted with a 50% T_c associated with sodalite stability¹⁶ (**Fig. 3**), a lower 50% T_c for Cl has been suggested²¹ (**Fig. 3**). A lower condensation temperature for Cl, similar to that of Br and I, would account for the lack of fractionation observed in Cl/Br/I across the different meteorite classes examined here and BSE.

Assuming complete retention of halogens during accretion, from an average chondrite composition (111 ± 38 ppm Cl, 362 ± 39 ppb Br and 38 ± 3 ppb I, as

above), would lead to an overabundance by a factor of 6.5 to 7 for chlorine and bromine, and a factor of 3.5 to 3.8 for iodine in the BSE, thus requiring an efficient volatile-loss mechanism during or after accretion to achieve terrestrial abundances. A similar magnitude of loss for elements with the same range of volatility as the halogens^{29,30} would also be required to preserve approximately chondritic ratios in BSE. Conversely, if we consider total halogen loss during early accretion, Earth would then require ~15% (Cl and Br) to ~26% (I) of the terrestrial mantle's mass addition of chondrites to subsequently replenish the current terrestrial halogen inventory after accretion. This estimate is far greater than late accretion addition of 0.5 ± 0.2 % of Earth's silicate mass required to account for highly siderophile element and moderately volatile chalcophile (S-Se-Te) element compositions of the BSE²⁻⁴. Therefore, the terrestrial halogen budget cannot be accounted for by late accretion alone. More likely, a large proportion of Earth's halogens were delivered and retained during the main stages of accretion and subsequent events (e.g., Moon-forming giant impact), as found for the moderately volatile elements such as Ag⁵. This, however, does not preclude the addition of halogens delivered during late accretion^{2,31}. For example, volatile loss of ~80% during accretion has been suggested for Earth³², which would correspond to 94% Cl, 91% Br and 48% I of the total terrestrial halogen budget. Late accretion addition of $\sim 0.5 \pm 0.2$ % carbonaceous chondrite material³¹ would supplement the halogen budget to ~ 100 % Cl, 97 % Br and 51 % I, of current terrestrial budgets. We do not place significance on the difference between I and Cl-Br, which is accommodated within the uncertainty of the BSE iodine estimate (**online Methods; Table S4 and S5**).

The limited variation in the Br/Cl and I/Cl ratio of chondrites provides a firm reference; irrespective of the detail of the mix of primitive materials with chondrite-like composition or sequence that accreted to form the Earth. This implies that primitive materials forming early in Solar System history should have a limited range in halogen compositions, regardless of their accretionary source. Additionally, the similarity of the Cl/Br/I ratio of BSE to our new average chondrite reference means that the accretionary process delivering and preserving BSE halogens did not significantly fractionate their elemental composition. Mass-dependent processes (e.g., impact erosion, hydrodynamic escape) invoked to argue for halogen-specific loss to account for putative excessive halogen BSE depletion relative to elements of

similar volatility, are unnecessary in light of the new chondrite results. Our results demonstrate that the likely terrestrial building blocks had significantly lower and unfractionated halogen concentrations than previously recognised.

Unlike other lithophile elements of similar volatility, an estimated ~ 80-90% of the heavy halogens on Earth are sequestered in the surface reservoirs (crust, sediments, oceans)^{7,8}. The mantle degassing efficiency, measured by K-derived ⁴⁰Ar in the atmosphere, at ca. 50%¹⁰, cannot account for this halogen distribution, which must represent an early accretionary process. Notwithstanding late delivery of halogens to the exosphere, the implication is that the Earth's mantle was efficiently depleted in halogens to surface reservoirs relatively early in Earth's history. The terrestrial record of ¹²⁹I and ²⁴⁴Pu-derived xenon isotopes is unequivocal in showing almost complete lack of retention of atmophile volatiles in the first ca. 100 Ma of Earth history^{9,33}. To prevent the halogens from being lost from the Earth system after their transfer to the terrestrial surface reservoirs, the heavy halogens must have been retained at the surface in a non-gaseous state. The hydrophilic nature of the halogens both in hydrous melts⁶ and aqueous solution may provide the unique combination of processes required to account for the modern terrestrial halogen distribution; of wet melting through efficient extraction from the solid Earth and retention within water-rich near-surface phases during the earliest stages of Earth formation¹⁴.

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AUTHOR INFORMATION: Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to PLC (patricia.clay@manchester.ac.uk).

MAIN FIGURE LEGENDS:

FIGURE 1 Bromine/Cl and I/Cl for chondrites and planetary materials. Observed variation for Br/Cl and I/Cl in chondrites is small relative to reference materials: ~5x in carbonaceous chondrites (CC) and ~3-6x in enstatite chondrites (EC). (a, e) Martian meteorites (refs. 41-43); (b, f) Lunar materials, including lunar volcanic glass (LVG, refs. 44-48), (c, g) back arc basin basalts (BABB; refs. 49,50), ocean-island basalts (OIB, ref. 49), diamonds (ref. 8), mid-ocean ridge basalts (MORB, refs. 51–53), serpentinites (refs. 54,55), and seawater (ref 56). Br/Cl and I/Cl chondrite data from this study (d, h). BSE halogen ratio is represented by the light grey band (Table S4). Open symbols are petrologic Type 5/6. RC = Rumuruti chondrites, OC = ordinary chondrites. Error bars represent the square root of the sum of weight factors.

FIGURE 2. Bromine (A) and I (B) (ppb) versus Cl abundance (ppm) in carbonaceous, enstatite, ordinary and Rumuruti chondrites. Previous Cl-chondrite data^{26,57-59} are shown as grey triangles and exclude several lower concentration Cl measurements (290-320 ppm in Ivuna and Orgueil and 510 ppm in Tonk; see Table S1 that do not have corresponding Br or I concentrations. BSE Br/Cl and I/Cl average from various sources (see Table S4 in the Supplement for dataset and references). Dashed line in each panel represent fit to the CC, EC and RC data (indistinguishable from fit to CC data alone in each case). Colour = meteorite group. Shape = petrologic type. Error bars represent the square root of the sum of weight factors.

FIGURE 3 Cl-Chondrite and Mg-normalized bulk silicate Earth abundances as a function of 50% T_c. Open green circles represent previously determined Cl-chondrite Cl, Br and I abundances, green stars are calculated using revised abundances presented here. Dashed lines between the data sets illustrate magnitude of change. Late accretion of a chondritic component of $0.5 \pm 0.2\%$ the BSE mass defined by the highly siderophile elements, Se, Te, S and C estimated abundances is shown in grey [refs. 2,4 and references therein]. The 50% T_c for Cl based on sodalite stability is shown with lower estimates²¹, indicated by the purple

330 arrow. Geochemical affinity (shape), volatility classification (colour) and 50% T_c: ref
331 16.

ONLINE METHODS:

Sample Selection. Twenty-four meteorite samples, falls and finds, were analysed, including six carbonaceous, seven ordinary, seven enstatite, two Rumuruti chondrites, and the Kakangari chondrite. These samples were selected to represent a diverse population of primitive meteorites covering variations in clan and petrologic type, in order to investigate the effects of aqueous and thermal metamorphism on halogen abundances. The selected carbonaceous chondrites were: Orgueil (CI, fall), Murray (CM2, fall), Sutter's Mill (C, fall), Murchison (CM2, fall), Graves Nunataks (GRA) 06100 (CR2, find), Elephant Moraine (EET) 92159 (CR2, find), Efremovka (reduced CV3, fall) and Allende (oxidized CV3, fall). Ordinary chondrites included only falls: Clovis (H3.6), Forrest Vale (H4), Bishunpur (LL3.15), Chelyabinsk (LL5), Barratta (L4), Barwell (L5) and Novato (L6). The selected enstatite chondrites include: Allan Hills (ALH) 77295 (EH3, find), Sahara (SAH) 97096 (EH3, find), Miller Range (MIL) 07139 (EH3, find), MIL 07028 (EH3, find), Indarch (EH4, fall), St. Mark's (EH5, fall) and Daniel's Kuil (EL6, fall). Rumuruti chondrites finds Northwest Africa (NWA) NWA 755 (R3.7) and 753 (R3.9) were also included. Detailed descriptions, including sample masses, modal mineralogy, preparation techniques and allocating institutions are provided in the below and in **Tables S1-S3**.

Experimental Methods. Halogen abundances were determined by neutron irradiation noble gas mass spectrometry (NI-NGMS). Details of the noble gas method for halogen analysis have been described in detail in ref. 34. The method utilises the neutron-induced conversion of Cl, Br, and I into the respective noble gas proxy isotopes $^{38}\text{Ar}_{\text{Cl}}$, $^{80,82}\text{Kr}_{\text{Br}}$ and $^{128}\text{Xe}_{\text{I}}$. During irradiation, fast neutrons (>1 MeV) activate the reactions $^{39}\text{K}(n, p)^{39}\text{Ar}$ and $^{40}\text{Ca}(n, \alpha)^{37}\text{Ar}$. Thermal and epithermal neutrons produce noble gas isotopes from halogens through the (n, γ) reaction. These reactions produce noble gases in amounts that are easily measured through conventional noble gas mass spectrometry. NI-NGMS has the benefit of being the most sensitive technique for measurement of heavy halogens in small, bulk samples. After irradiation, halogen abundances can be determined using monitor minerals of known halogen composition, which allows for correction of noble gas production through epithermal neutrons. Depending upon the neutron fluxes, the conversion efficiency during irradiation is typically about $1:10^5$ (i.e., only 1 in every 100,000

parent halogen isotope atoms is converted to a noble gas isotope). However, inclusion of standards with halogen concentrations determined independently by other techniques^{35–37}, irradiated together with the samples, enables the parent halogen abundances to be accurately calculated from neutron-produced noble gas isotopes^{34,38}. The external errors (2σ) are 4% for Cl, 7% for Br and 5% for I, based on the BB1 scapolite monitor.

Sample Preparation and Irradiation. Terrestrial alteration can be problematic for halogen analyses, therefore extreme caution was exercised with sample handling, storage and preparation techniques, to avoid inclusion of surface, weathered, crack or vein material that may be affected by terrestrial alteration. All samples analysed in the current study are given in **Table S2** with sample masses and preparation details. In order to avoid any potential terrestrial contamination issues associated with falls, particularly those from hot and cold desert environments where leaching and/or deposition of halogens on the surface can occur, we took particular care in our sample storage, handling and preparation. Samples were stored in desiccators within Class 1000 clean rooms prior to preparation. Any visible alteration, terrestrial weathering or fusion crust material was generously removed prior to preparation. Sample material was excavated from the interior portion of the sample only. This material was then carefully examined for any indication of terrestrial contamination (see below). Prior to irradiation, samples were either crushed into small chips and sieved, or aliquots extracted from powdered, larger main masses (e.g., 1-2 mg sized aliquots from up to 1.5 g sample) where possible (see below for details and a discussion about sample heterogeneity). Small samples were wrapped in Al-foil and, interspersed with monitor minerals, encapsulated under vacuum in SiO₂-glass tubing before packing in Al canisters for irradiation. Irradiation was done in two batches at the Petten Reactor, Netherlands (MN12f and MN13), continuously over a 24-hour period. A further two samples were irradiated at the Oregon State University (OSU) reactor (MN14a) in a stepped fashion over a 2-month period for a total of ~280 hours. The neutron fluence was monitored in each irradiation with conventional ⁴⁰Ar-³⁹Ar and I-Xe geochronological standards “Hb3Gr” hornblende (1080.4 ± 1.1 Ma ³⁹) and enstatite separated from the Shallowater aubrite ($^{129}\text{I}/^{127}\text{I}_{\text{initial}} = 1.072 \times 10^{-4}$, ⁴⁰). Scapolite minerals (“BB-1” and “SP” ^{34,35}) were used to monitor for epithermal neutron fluence. Thermal and epi-thermal neutron fluxes were estimated as $\sim 6.3 \times$

399 10^{18} n cm⁻² and $\sim 1.4 \times 10^{17}$ n cm⁻² for MN12f, $\sim 6.2 \times 10^{18}$ n cm⁻² and $\sim 1.6 \times 10^{17}$ n
400 cm⁻² for MN13 and $\sim 6.5 \times 10^{18}$ n cm⁻² and $\sim 9.5 \times 10^{17}$ n cm⁻² for MN14a.

401 **Laser-heating and mass spectrometry.** Argon, Kr and Xe were released from
402 irradiated samples using a Nd:YAG infrared laser. Typical sample masses of 0.25 –
403 3.0 mg were either incrementally heated with increasing temperature or in single
404 fusion analyses with a second heating step to ensure complete extraction, on the
405 static vacuum MS1 mass spectrometer at the University of Manchester. Argon
406 isotopes were measured using a Faraday detector (10^{11} or 10^{10} Ohm resistor) while
407 Kr and Xe isotopes were measured using a channeltron electron multiplier. Released
408 gases were purified using hot and room temperature SAES[®] NP10 getters for a
409 combined total of up to 20 minutes prior to analysis. All isotopes we measured in
410 seven cycles over a 50-55 minute period using peak-jumping mode. Identical
411 analytical procedures as for samples were employed for blank and air calibration
412 measurements, though monitors were heated using a resistance furnace.

413 A further two samples (Murchison and Allende) were analysed using a ThermoFisher
414 ARGUS VI, a low volume (680 cm³), Nier-type, static vacuum mass spectrometer
415 designed for multi-collection of Ar isotopes. The ARGUS VI has five Faraday cups
416 and a low mass compact discrete dynode (CDD) ion counting multiplier. Gases were
417 released from meteorite samples using a 55W CETAC Fusions CO₂ laser with a 3
418 mm beam diameter. Samples were fused in a single step of 0.5% to 12% power.
419 After release, gases were purified using an NP10 hot getter and then transferred
420 onto a liquid N₂-cooled charcoal finger for five minutes. The finger was warmed to
421 $\sim 60^{\circ}\text{C}$ to release the gases. A trap current of 230 μA and an acceleration voltage of
422 2.5 kV were used. We report typical sensitivities of: 1.2×10^{-12} cm³ fA⁻¹ Ar, $7.7 \times 10^{-$
423 ¹³ cm³ fA⁻¹ Kr, and 9.5×10^{-13} cm³ fA⁻¹ Xe. After nine measurement cycles, isotope
424 abundances were determined by regression to inlet time.

425

426 **Data Reduction.** All isotopes were corrected for extraction line blanks, which
427 typically contributed <1% of ³⁸Ar and <<1% for ⁸⁰Kr and ¹²⁸Xe. All Ar measurements
428 were corrected for mass discrimination, the radioactive decay of ³⁷Ar_{Ca} and ³⁹Ar_K
429 between irradiation and analysis time, and for neutron-produced interference
430 reactions. Corrections for air, trapped or cosmogenic contributions based on ³⁶Ar

were executed on a sample-by-sample basis. Krypton and Xe isotopes were corrected for neutron-induced fission of ^{235}U using ^{134}Xe . Where necessary, a small trapped correction (a mixture of air, solar wind and Q gas), was applied to Xe isotopes based on ^{130}Xe . Krypton and Xe were corrected for epithermal neutron production using the scapolite monitor minerals BB1 and BB2/SP and the Shallowater aubrite.

Halogens in chondrites: previous studies and the CI reference value. Halogen determinations of chondritic materials were predominantly carried-out in the 1960's and 1970's, mainly by neutron activation analysis, and yielded variable concentrations and I/Cl ratios an order of magnitude above known terrestrial reservoirs. These measurements were generally on relatively large samples masses (e.g., hundreds of mg). Notably low or high determinations were sometimes excluded from these studies, particularly for Br and I, on the basis of suspected poor analyses, or suspected halogen addition from contamination or loss during weathering. Compilations, which produce commonly quoted 'reference values' for halogens in CI chondrites (**Table S1**) are updated and extended when new data become available. However, these bulk values are based on primary data from comparatively few studies and variations within each data-set exceed analytical errors on the individual determinations. There is a relatively large data set for chlorine in CI chondrites based on two samples, Orgueil and Ivuna. For example, in one compilation study¹⁶ chlorine abundance is estimated from nine analyses of Orgueil and two analyses of Ivuna (CI sample Tonk, 510 ppm Cl⁶¹ is excluded entirely). The resulting weighted mean and weighted mean error, calculated from the comprehensive data compilation by Lodders, 704 \pm 10 ppm chlorine in CI chondrites, suggests a good level of certainty. However, this value excludes the lowest values of 210 and 290 ppm Cl in Orgueil^{27,62} and 240 and 320 ppm Cl in Ivuna²⁷, and the uppermost high determination of 849 ppm Cl in Orgueil⁵⁸. More recent studies using gas source mass spectrometry have measured chlorine in Ivuna (290 ppm)²⁴ and Orgueil (580, 603 and 630 ppm)²⁶ (**see Extended Data Figure 1**). If all published values are included, then the total spread in published chlorine concentrations in CI chondrites is between 210–950 ppm, a variation of a factor of 4.5. Bromine is calculated from three samples (with the addition of CI chondrite Alais) showing a factor of two difference between the highest (4.82 ppm, Ivuna) and the lowest (2.35 ppm, Alais⁶³), with one analysis of Tonk

excluded (9 ppm Br⁶¹). This discrepancy is not well reflected in the final reported value of 3.43 ± 0.75 ppm bromine¹¹. The case for iodine is similar, where the mean of 0.48 ± 0.16 ppm is based on six analyses from Orgueil, excluding four analyses from Ivuna (1.12 ± 0.51 ppm). Quoted bromine and iodine abundances are sometimes calculated indirectly, due to the observed variability between the samples of Orgueil, Ivuna and Alais, relying instead on Br/In, Br/Cd and I/In and I/Cd ratios in CO, CV, and enstatite chondrites to calculate the bromine and iodine from Cl values of In and Cd⁶³.

Variations are typically attributed to: terrestrial contamination during residence at the Earth's surface²⁷; hydrothermal transport processes on the meteorite parent body³⁴; or analytical artefacts²². The problem is clear – there are only nine Cl or 'Cl-like chondrites' and of these samples, only two (Orgueil and Ivuna) have multiple analyses, due to either low sample mass or the lack of availability of the other samples. As such, our understanding of the benchmark Solar System halogen abundances is derived from 11 analyses for chlorine, 30 analyses for bromine and six analyses for iodine, across two samples, with numerous outliers excluded from the resultant averages. Thus, the concentration variations are likely much greater than reported, particularly for trace elements such as the halogens – the literature would suggest at least a factor of four for chlorine, six for bromine and eight for iodine. There is minimal bulk data for the ordinary chondrites, with the majority being for H and L chondrites. These samples show highly variable halogen concentrations and ratios. This variation is likely heterogeneity controlled by the modal proportions of halogen-rich phases, such as Cl-bearing phosphates and by the effects of thermal metamorphism (see main text **Figure 1d+h**). This is partly the reason why there was a focus on Type 4-6 ordinary chondrites in this study, in order to evaluate the effect of thermal metamorphism. This variation is also seen in the enstatite chondrites, where data from early studies were often discarded as 'anomalous' due to their high concentrations. High concentrations in the enstatite chondrites may indeed be real, due to the unique environment (nebular gas with a composition of C/O $\gg 1$; see discussion by Rubin and Choi⁶⁴) in which they formed and should not necessarily be discarded, but instead may provide insights into halogen behavior under a special set of conditions which may be relevant to early Earth environments.

Modal mineralogy. Halogens are present in varying amounts in silicate, phosphate and sulfide carrier phases. Important carrier phases may include sodalite, djerfisherite, lawrencite, etc. An understanding of the likely distribution of some of these carrier phases in different chondrite classes can aid in interpretation of halogen concentration data. A general modal abundance of components including matrix, chondrules, metal, calcium-aluminum rich inclusions (CAI) and amoeboid olivine aggregates (AOA), is given below in **Table S6**⁷² and a more specific modal mineralogy of clans from previous studies ^{73–78} also listed. Likely halogen carriers for each clan are italicised.

Testing for surficial terrestrial contamination. Halogens show enrichment in surface environments including both hot and cold deserts. At the surface, minor contributions from anthropogenic⁷⁹ and natural biological organohalogen compounds⁸⁰ are known, as well as halogens derived from marine aerosols⁸¹. The presence of these reactive halogen sources necessitates a consideration of what, if any, effect these have on halogen abundance measurements in meteorites. This is notable in polar ice regions, particularly the Antarctic (where many meteorites are collected annually), with biological production of organoiodine (e.g., methyl iodide) enhanced at sea ice margins and where there is potential for deposition of halogen-bearing sea-salt; indeed instances of iodine contamination in cracks on exterior surfaces of Antarctic meteorites have been documented⁸². Extreme care was taken during sample preparation (see above) to ensure selection of interior material to avoid terrestrial contamination issues. Despite this, we assessed potential contamination by examining different sample populations for terrestrial weathering, aerosol deposition, and other contaminants through the following processes: (1) hot and cold desert meteorites were compared to non-Antarctic and non-desert meteorites (**Extended Data Figure 2**); (2) meteorite ‘falls’ and meteorite ‘finds’ were compared (**Extended Data Figure 3**); (3) halogen results were plotted with known terrestrial contaminants for identification of contributions (**Extended Data Figure 4**); (4) modal mineralogy was compared to halogen chemistry to determine the likelihood that halogens came from an indigenous source, rather than terrestrial atmospheric contamination (see **Tables S6**); and (5) noble gas isotope ratios (e.g., ⁴⁰Ar/³⁶Ar) and other accessible neutron-induced elements (e.g., K, Ca, Ba) were used to support identification of terrestrial contamination.

One sample (MIL 07139) consistently suffered from contamination issues in the low-temperature steps, identified and characterised by high potassium (monitored by concomitant $^{39}\text{Ar}_K$ release) concentrations (possibly deposition of a K_2SO_4 salt) of up to 2.85 wt.% compared to a more typical potassium concentration of ~800 ppm in EH chondrites⁶⁷. Paired sample MIL 07028 from the same Miller Range icefield seems unaffected. Additionally, EH3 SAH 97096 from the Sahara Desert is affected by either a contaminant with a high-bromine component or more likely, leaching of chlorine (**Extended Data Figure 4**). The lowest-temperature step data was removed and the resultant halogen totals are therefore a minimum value, though the relative consistency of results between three different sample aliquots suggests that it is an indigenous component (26 ± 2 , 30 ± 2 and 33 ± 2 ppm Cl).

Halogen condensation and secondary alteration in chondrites. The pronounced difference in mineralogy (**Table S6**) and the heterogeneous nature of matrix, chondrules and inclusions amongst the C, E and R chondrites sits in stark contrast to the narrow range of observed concentrations and Br/Cl and I/Cl values in these meteorite groups. This provides a unique view on how the halogens condensed out of the solar nebula and their response to, and redistribution during, secondary processing (aqueous alteration and thermal metamorphism). Assuming equilibrium condensation from a gas of solar composition, primary halogen condensation host phases are predicted to be sodalite (50% $T_C = 948$ K) for chlorine and CaBr_2 and CaI_2 in apatite (544 and 533 K 50% T_C respectively¹⁶) for bromine and iodine. (We note, however, that there is significant uncertainty in the 50% T_C determinations for the halogens and lower estimations do exist²¹.) There is significant uncertainty in these predicted phases with Type 1 and 2 chondrites losing their primary minerals through aqueous alteration. Secondary phases which are the result of aqueous or thermal processing such as serpentine $[(\text{Mg}, \text{Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4]$, are however, capable of accommodating halogen ions substituting for OH^- (up to 0.5 wt.% chlorine)⁸⁴ due to the large vacancies in the lattice structure. Hydrated, brecciated and matrix-rich, the CM chondrites also contain abundant phyllosilicates. CV chondrite halogen budgets are likely dominated by the less abundant but chlorine-rich, sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$; ~7 wt.% chlorine and up to 7 % modal abundance).

Pervasive aqueous alteration of Type 1 and Type 2 chondrites has replaced all primary silicates with hydrous secondary minerals. Lack of evidence for systematic fractionation of Br/Cl and I/Cl ratios (main text **Fig. 1**) suggests that the halogens were quantitatively redistributed during the aqueous alteration of CI (type 1) and CM (type 2) material isochemically. This is probably due to the limited fluid flow and short length scales for water transport (10–100s μm) during alteration, as suggested by Bland et al.⁸⁰, in their study documenting low permeability (10^{-19} to 10^{-17} m^2) in chondritic materials (though we note this is not universally observed, e.g., for Au redistribution⁸⁵). Our data indicates that bulk halogen abundances have not been affected by aqueous alteration, and therefore type 1 and 2 altered chondrite samples (along with pristine type 3 chondrites) are likely to be representative of the nebula environment in which they formed.

Thermally metamorphosed ordinary chondrites, however, are distinct from these clans. Major halogen-bearing species in the OCs include silicates (feldspars, chlorine-rich glass in chondrule mesostasis) but more importantly, the halogen-rich phosphate-group mineral, apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$], which is likely the dominant halogen carrier phase. Thermal metamorphism has affected abundances and halogen ratios (particularly I/Cl) in both the OCs and some ECs (main text **Fig. 1**). Petrologic types 4 to type 6 experienced varying degrees of parent body thermal metamorphism, with increasing severity from type 4 (weakly metamorphosed) to type 6 (heavily metamorphosed). In both ECs and OCs, the lowest halogen concentrations tend to occur in type 5–6, with progressively increasing concentrations in type 4 and in the least metamorphosed type 3. The lower halogen abundances in type 5 (e.g., Daniel's Kuil EL6 and St. Marks EH5) and type 6 (e.g., Novato L6) indicate severe halogen loss with progressive parent body metamorphism. The mechanism by which secondary apatite forms during thermal metamorphism (or metasomatic processes) on the OC parent bodie(s)⁸⁶ may be an important factor in controlling the preserved halogen ratios.

In ECs, the extent of depletion in chlorine and bromine is not mirrored by iodine. In these samples sulphides may dominate as halogen hosts (~12 modal % in EH chondrites), including troilite (FeS) which has been suggested to host comparable amounts of iodine as silicates⁸⁷ (~ 1 ppm), without chlorine. The lithophile element bearing sulphide djerfisherite [$(\text{K}, \text{Na})_6(\text{Cu}, \text{Ni}, \text{Fe})_{25}\text{S}_{26}\text{Cl}$; ~1.3 wt. % chlorine⁸⁸], is

able to host significant chlorine. Djerfisherite in primitive ALHA 77295 (EH3) has yielded I–Xe ages of 4564.2 ± 1.1 and 4564.7 ± 2.5 Ma⁸⁹, comparable to the age of chondrule formation in EH3 Qingzhen and Kota Kota⁹⁰ and therefore has been suggested to be a nebular condensate⁹¹ as well as an important halogen-bearing phase. In some ECs, however, sulphides may decompose readily at even low temperatures⁹² (**Extended Data Figure S5**), where progressive halogen loss in the manner of Cl>Br>I may be expected. Halogens in type 5–6 chondrites have been affected by thermal processes and are therefore, unsurprisingly, not representative of their primary abundances acquired during condensation from the solar nebula.

Estimates of Bulk Silicate Earth (BSE) halogens. Bulk silicate Earth (BSE), or ‘primitive mantle’ (PM), is that portion of silicate crust and mantle differentiated from the metallic core, in the approximate proportions of ~68 and 32% by mass, respectively. This large reservoir is difficult to be accurately characterised for trace elements such as the halogens, but determining this global geochemical budget is essential for comparisons within the solar system and to other terrestrial planets. Early studies focused on the development of the ‘pyrolite’ model, developed by Ringwood⁹³ by mixing amounts of basalt (as melt) and peridotite (as residue) with many other derivations of this model developed since (e.g., 30,94) based on terrestrial upper mantle samples (see **Table S4**). Mass balance calculations can also be used to estimate primitive mantle composition by using reservoir size and estimated reservoir concentration⁸ (see **Table S5**). Alternatively, primitive mantle estimates can be constrained using meteorite data and the assumption of chondritic refractory lithophile elements in BSE (e.g., 95–97). Most of these different formulations result in similar chemical compositions for BSE (**Table S4**), for both compatible and moderately incompatible major and minor element compositions. For example, estimated BSE halogen concentrations range from 8–44 ppm chlorine, 0.045–0.4 ppm bromine and 0.007–0.04 ppm iodine (see **Table S4** for references). Up to one order of magnitude variation is not unexpected given the trace nature of the halogens and the lack of data available, particularly for bromine and iodine. Estimates for the heavy halogens in BSE are uncertain due to the low abundances of bromine and iodine, but also their difference in geochemical behavior (e.g., hydrophilic to biophilic). BSE halogen reference values are based on cosmochemical and petrological approaches and both make use of chondrite data, in

this study those based heavily on meteorite data⁹⁵ were avoided due to potential circularity in calculations.

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837 **DATA AVAILABILITY:** All data generated during this study are included in this
838 published article and its supplementary information files.

EXTENDED DATA FIGURE LEGENDS:

EXTENDED DATA FIGURE 1. Histograms of chlorine (A), bromine (B) and iodine (C), showing the distribution of halogens in CI-chondrites, as reported in Table S1. Data for Orgueil from this study are shown in each panel by the black line, with uncertainty shown in grey (for iodine, this is within the thickness of the line).

EXTENDED DATA FIGURE 2. Total halogen concentrations in hot desert, cold desert and non-desert meteorites analysed in this study.

EXTENDED DATA FIGURE 3. Comparison of chlorine in meteorite finds and falls. Chlorine is expected to be higher in the finds compared to falls, where contamination has occurred, due to high relative Cl in the terrestrial environment. However, no significant difference is observed between falls and finds, illustrating that the samples are not strongly contaminated, and some of the highest concentrations are present in the falls. This is considered to reflect variations in the amounts of halogen carrier phases present, rather than resulting from terrestrial input.

EXTENDED DATA FIGURE 4. Halogen ratios plotted with some known terrestrial contaminants, marine aerosol, ice, and atmospheric particles from McMurdo and the South Pole. The dashed lines encompass the region of contamination. Samples are generally below these values, apart from SAH 97096 (EH3), which is affected by a contaminant with a high Br concentration. The composition of the contaminants is given in ref. 83.

EXTENDED DATA FIGURE 5. Sulphide breakdown reaction⁹² due to thermal metamorphism in enstatite chondrite SAH 97096 (EH3). Djerfisherite $[(K, Na)_6(Cu, Ni, Fe)_{25}S_{26}Cl]$ breaks down into porous troilite, with loss of Na, K, Cl, etc. Original djerfisherite is shown in the red boxes, while the reaction product is the large mass in the centre of the image. If djerfisherite is a host to bromine and iodine as well as chlorine, halogen loss may be synchronous with alteration, which could be an explanation for the consistent loss of all halogens in ECs with increasing petrologic type.

868 **Table 1** Weighted average halogen abundance (reported as ppm chlorine and ppb
869 bromine and iodine) and ratio data as determined by NI-NGMS. Uncertainty is the
870 square root of the sum of the weight factors.

Sample	Clan	Type	N	Cl (ppm)	Br (ppb)	I (ppb)	Br/Cl x 10 ⁻³ (wt.)	I/Cl x 10 ⁻³ (wt.)
<i>Carbonaceous Chondrites</i>								
Orgueil	CI	1	2	115 ± 36	189 ± 71	57 ± 7	1.6 ± 0.1	0.5 ± 0.1
Murchison	CM	2	1	231 ± 9	971 ± 56	65 ± 3	4.2 ± 0.1	0.28 ± 0.01
Sutter's Mill	C?		2	218 ± 12	725 ± 50	48 ± 4	3.3 ± 0.1	0.22 ± 0.01
Murray	CM	2	2	151 ± 9	123 ± 11	14 ± 2	0.8 ± 0.1	0.09 ± 0.01
EET 92159	CR	2	2	77 ± 6	173 ± 22	28 ± 5	2.3 ± 0.1	0.37 ± 0.01
GRA 06100	CR	2	2	60 ± 4	98 ± 8	27 ± 2	1.6 ± 0.1	0.46 ± 0.01
Allende	CV _{ox}	3	1	85 ± 3	397 ± 23	35 ± 1	4.7 ± 0.2	0.41 ± 0.02
Efremovka	CV _{red}	3	2	18 ± 2	50 ± 5	6 ± 1	2.8 ± 0.1	0.31 ± 0.08
<i>Enstatite Chondrites</i>								
MIL 07028	EH	3	3	143 ± 7	548 ± 79	41 ± 13	3.8 ± 0.1	0.29 ± 0.01
MIL07139*	EH	3	3	29 ± 2	59 ± 6	4.4 ± 0.4	nd	nd
SAH 97096*	EH	3	1	13 ± 1	583 ± 54	64 ± 6	nd	nd
ALH 77295	EH	3	1	324 ± 22	982 ± 90	51 ± 5	3.0 ± 0.1	0.16 ± 0.01
Indarch	EH	4	3	84 ± 6	327 ± 34	62 ± 6	3.9 ± 0.1	0.74 ± 0.01
St. Mark's	EH	5	1	51 ± 3	141 ± 15	11 ± 1	2.8 ± 0.2	0.22 ± 0.03
Daniel's Kuil	EL	6	2	14 ± 1	20 ± 2	1.6 ± 0.2	1.43 ± 0.5	0.12 ± 0.14
<i>Ordinary Chondrites</i>								
Clovis	H	3.6	3	11 ± 3	5 ± 2	1.5 ± 0.1	0.4 ± 0.2	0.14 ± 0.3
Forest Vale	H	4	2	76 ± 15	185 ± 66	22 ± 2	2.5 ± 0.1	0.28 ± 0.01
Barratta	L	4	2	102 ± 8	312 ± 31	28 ± 4	3.1 ± 0.1	0.27 ± 0.01
Barwell	L	5	1	278 ± 19	424 ± 81	71 ± 7	1.5 ± 0.1	0.26 ± 0.01
Novato ¹	L	6	1	5 ± 0	4 ± 2	0.3 ± 0.1	0.8 ± 0.3	0.13 ± 0.04
Novato ²	L	6	1	14 ± 1	nd	1.7 ± 0.3	nd	0.05 ± 0.01
Bishunpur	LL	3.15	2	400 ± 42	120 ± 17	9 ± 2	0.3 ± 0.1	0.13 ± 0.04
Chelyabinsk	LL	5	3l	16 ± 1	25 ± 9	nd	1.5 ± 0.1	nd
<i>Rumuruti Chondrites</i>								
NWA 755	R	3.7	2	53 ± 3	225 ± 15	29 ± 3	4.3 ± 0.1	0.55 ± 0.01
NWA 753	R	3.9	2	230 ± 12	535 ± 26	108 ± 11	2.3 ± 0.1	0.47 ± 0.01
<i>Other</i>								
Kakangari	K	3	2	45 ± 4	13 ± 1	3.0 ± 0.4	0.29 ± 0.01	0.07 ± 0.06
Reported values represent the totals from NI-NGMS laser single fusion or multi-step-heating experiments								
*minimum concentration values, ratios not reported; see online Methods								
1: Novato 'dark' lithology								
2: Novato 'light' lithology								
N: number of aliquots analysed								
nd =not determinable								

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