The Provenances of Asteroids, and Their Contributions to the Volatile Inventories of the Terrestrial Planets

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Science **337**, 721 (2012);
DOI: 10.1126/science.1223474

The Provenances of Asteroids, and Their Contributions to the Volatile Inventories of the Terrestrial Planets

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Determining the source(s) of hydrogen, carbon, and nitrogen accreted by Earth is important for understanding the origins of water and life and for constraining dynamical processes that operated during planet formation. Chondritic meteorites are asteroidal fragments that retain records of the first few million years of solar system history. The deuterium/hydrogen (D/H) values of water in carbonaceous chondrites are distinct from those in comets and Saturn's moon Enceladus, implying that they formed in a different region of the solar system, contrary to predictions of recent dynamical models. The D/H values of water in carbonaceous chondrites also argue against an influx of water ice from the outer solar system, which has been invoked to explain the nonsolar oxygen isotopic composition of the inner solar system. The bulk hydrogen and nitrogen isotopic compositions of CI chondrites suggest that they were the principal source of Earth's volatiles.

Two recent dynamical models of the orbital evolution of the outer planets (*1*, *2*), designed to explain the small mass of Mars and the late heavy bombardment, predict that the objects in the asteroid belt have two sources: S-complex asteroids formed in situ, whereas D-type, P-type, and C-complex asteroids formed either between the giant planets or in the trans-Neptunian region. Chondrites, the most primitive meteorites, are fragments of main-belt asteroids and are divided into several classes (ordinary, OC; Rumuruti, RC; enstatite, EC; and carbonaceous, CC) that are subdivided into numerous groups. On the basis of their reflectance spectra and other evidence, the OCs and CCs have been linked to the S- and C-complex asteroids, respectively. It was suggested (*2*) that D- and P-type asteroids are the sources of primitive micrometeorites, rather than meteorites. However, most micrometeorites appear to be related to CI and CM CCs (*3*), and at least one ungrouped CC, Tagish Lake, has been spectroscopically linked to D-type asteroids (*4*). At present, there is no evidence that a major type of primitive asteroid is unrepresented in our meteorite collections (*3*). There is isotopic evidence for a difference in the provenances of the OC-EC-RCs and the CCs (*5*), but there are no reliable indicators of where in the solar nebula they formed.

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The proposed formation locations for the D-type, P-type, and C-complex asteroids are potentially the same as those of comets—Oort cloud comets are thought to have formed in the giant planet region and the trans-Neptunian region, while Jupiter-family comets (JFCs) probably formed in the trans-Neptunian region (*6*). Although chondrites share many similarities with comets (*3*), they do not now contain ice. The CCs, as well as the OCs and RCs, accreted water, presumably as ice, but the record of this is now preserved only in hydrated silicates (*7*, *8*). Perhaps the CC parent bodies were larger than typical comets, so that internal heating caused much of the water to be consumed by alteration of silicates, Fe-metal, and sulfides and what remained sublimed away in the ~4 to 4.5 billion years that they have resided in the inner solar system. Nevertheless, if CCs have a cometary heritage, a record of it should be preserved in the hydrogen isotopes of their hydrated silicates.

In a static solar nebula, radial temperature gradients, combined with equilibrium and kinetic factors, mean that water D/H values should have increased with increasing formation distance from the Sun (*9*, *10*). Given its dynamic evolution, the spatial and temporal variations in ice compositions in the solar nebula are likely to have been more complex. Nevertheless, objects that formed in the same source regions and at similar times should have accreted ice with similar hydrogen isotopic compositions. Therefore, a comparison of water D/H values in comets and and other icy outer solar system bodies with CCs is potentially a direct test of the predictions of the dynamical models.

Hydrogen isotopic compositions are available for the water in some comets and Saturn's icy moon Enceladus. The D/H values of the OH in hydrated silicates in chondrites are likely to have been modified during alteration from the water compositions at the time of accretion. The chondrites also accreted organic matter (*11*), and the hydrogen in it further complicates the determination of the original isotopic compositions of their water (*3*). Here, we report the bulk hydrogen, carbon, and nitrogen elemental and isotopic compositions of 86 samples of chondrites (table S1) and adopt two approaches to use them for estimating or placing limits on the original hydrogen isotopic compositions of their water (*3*).

In the first approach, we analyzed CCs from the CM and CR groups that experienced different degrees of aqueous alteration. If the bulk hydrogen isotopic compositions are simply the products of mixing between hydrated silicates and organic matter, then, in a plot of δD versus C/H, the bulk compositions should form a line with the hydrogen isotope intercept giving the isotopic composition of the water. In Fig. 1, the data for the CMs and CRs do fall on lines, and the implied δD values for their water are -444 ± 23‰ and 96^{+110}_{-65}‰, respectively [$\delta D = 1000 \times (R_{sample}/R_{standard} - 1)$, where $R_{standard}$ is the D/H value of standard mean ocean water]. The subparallel CM and CR trends converge on the region where the most primitive insoluble organic material (IOM) plots (Fig. 1B). This implies that the CMs and CRs shared a common primitive organic component. The IOM in most chondrites is less deuterium-rich than that in the most primitive meteorites (Fig. 1B), suggesting that there has been hydrogen isotope exchange between the water and the organics in essentially closed systems.

The CIs and the most primitive COs, CVs, and OCs are not common enough to use the same approach. The two CIs (Orgueil and Ivuna) and the CO (ALH 77307) analyzed here fall on the CM trend, suggesting that they all probably had similar initial water compositions. Three lithologies from Tagish Lake exhibit different degrees of alteration (*12*). Their bulk compositions show limited variations in δD and C/H and suggest that the water in Tagish Lake had a slightly lower D/H value than in the CMs. The bulk hydrogen isotopic composition of the OC Semarkona (Fig. 1B) has a much higher D/H value than any of the CCs.

Because all chondrites, not just the CMs and CRs, probably accreted a common organic component (*11*), the second approach for estimating the water compositions is by subtraction of the organic component. The hydrogen isotopic compositions of the water in CMs and CRs can be estimated, albeit with larger errors (*3*), by assuming that (i) the bulk carbon is in material with IOM-like C/H ratios and (ii) it has an isotopic composition like that of the most primitive IOM (δD ≈ 3500‰). This approach has been used (*3*) to estimate the ranges of likely water compositions in the CIs, COs, CVs, Tagish Lake, and the OCs (Fig. 2 and table S2). The ranges reflect whether the measured IOM C/H values are used, or a more primitive ratio based on the CR IOM that may better represent the IOM

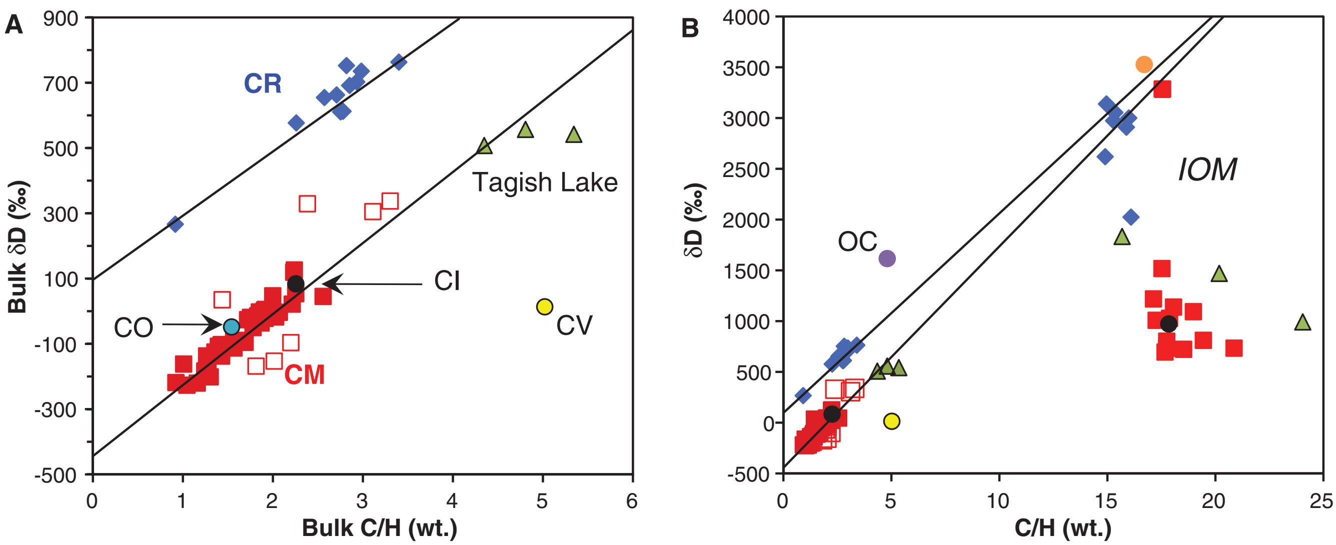
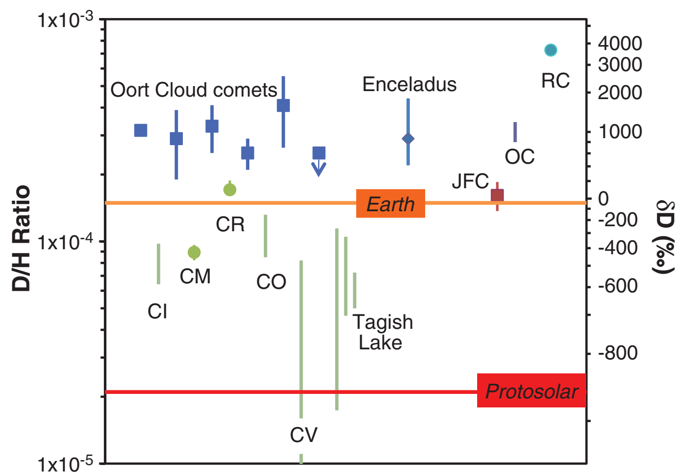


Fig. 1. (**A**) The bulk compositions of the carbonaceous chondrites analyzed here. The lines are fits to the CR and CM data. Open red squares are CMs that were not included in the CM fit. (**B**) An expanded scale to show that the CR and CM lines pass through the compositions of the most primitive chondritic insoluble organic matter (IOM) (*11*, *14*). The bulk composition of the OC Semarkona is also included.

composition at the onset of alteration and metamorphism (*11*).

The six measured Oort cloud comets and Enceladus have water D/H values that are enriched in deuterium by roughly a factor of 2 compared to Earth and more than an order of magnitude relative to the initial solar composition (Fig. 2). The one measured JFC has a water hydrogen isotopic composition that is similar to Earth's (*13*). This suggests that there may not be a monotonic rise in the D/H values of icy bodies with formation distance from the Sun. Nevertheless, the D/H value of this JFC is still enriched in deuterium by almost an order of magnitude compared to the initial solar composition. Consequently, one would still expect that water accreted by asteroids that formed in the asteroid belt (e.g., S-complex asteroids) would have lower D/H values than objects that formed in the giant planet region and beyond (e.g., C-complex asteroids).

Fig. 2. Comparison of the estimated hydrogen isotopic compositions of water in various chondrite groups with those measured in Oort cloud and Jupiter family comets (JFC), and Saturn's icy moon Enceladus. See (*3*) for details and sources.



The OC water hydrogen isotopic composition is similar to that of Oort cloud comets [the RCs are more deuterium enriched (*8*)], whereas the CR water composition is like that of Hartley-2 (Fig. 2). The water compositions of the CIs, CMs, CO, CV, and Tagish Lake are less deuterium-rich than any measured comets, implying formation closer to the Sun. The lower deuterium enrichments in CCs than in OCs and RCs also run counter to the typically assumed order of formation distances for the chondrites (*3*). However, the hydrogen isotopic compositions in Fig. 2 and table S2 should be regarded as upper limits because isotopic fractionation associated with the observed oxidation of Fe by water during alteration and metamorphism is likely to have enriched the residual water in deuterium (*14*).

There has been speculation that some CCs are cometary in origin. On the basis of estimates of their preatmospheric orbits, it has been suggested that Orgueil (CI) is a fragment of a JFC (*15*) and that the CM Maribo is related to comet P2/Encke (*16*). So-called main-belt comets with typical asteroidal orbits have also recently been discovered (*17*). Hence, the suggestion that many outer main-belt asteroids (and therefore CCs) formed in the same regions as conventional comets is attractive, but the subterrestrial D/H values of the water in most CCs do not support this. However, most Oort cloud comets may have formed in the trans-Neptunian region, not the interplanetary region, in which case, the Oort comet-like D/H value of Enceladus provides the only constraint for the possible interplanetary origin (*1*) for the CCs. Enceladus appears to have accreted from material that formed in the solar disk (*18*), rather than in the dense subnebula around Saturn when it was growing rapidly. This suggests that the sources of the CC parent bodies were sunward of Saturn's orbit (3 to 7 astronomical units) as it approached its final mass (*1*), including in the asteroid belt.

All analyzed bodies in the terrestrial planet region (within the orbit of Jupiter), including the Earth and chondrites, have oxygen that is enriched in ^{17}O and ^{18}O, compared to the bulk solar system, represented by the solar wind (*19*). The favored explanation is an early, massive influx of ^{16}O-poor water ice that formed either in the outer solar system or the presolar molecular cloud (*20*, *21*). The bulk and internal oxygen isotopic systematics of OCs and CCs are at least consistent with accretion of ^{16}O-poor ices (*22*, *23*). However, our results are in conflict with the ice influx explanation because outer solar system ice should have D/H values like those of cometary ices and molecular cloud ices are even more deuterium-rich (*24*, *25*).

The range of D/H values in chondritic water could be explained in the context of the ice influx

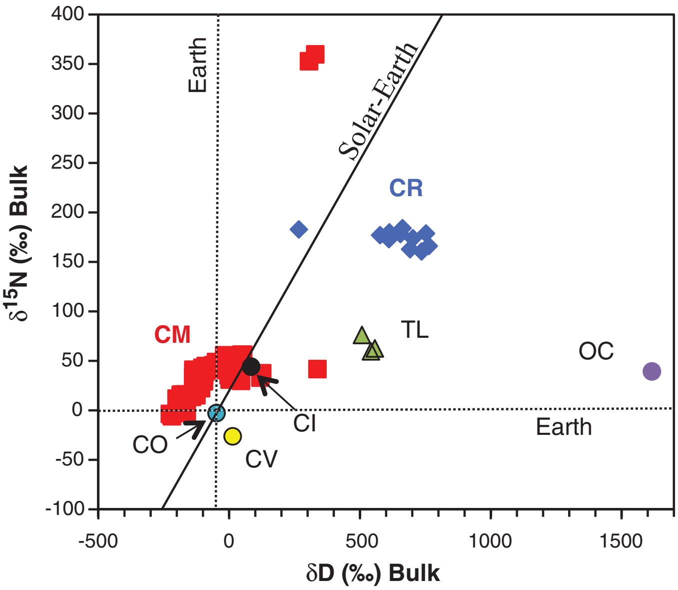


Fig. 3. The bulk hydrogen and nitrogen isotopic compositions of chondrites (TL, Tagish Lake). The line connects the solar and terrestrial isotopic compositions. Bodies similar to chondrites are potential sources of Earth's volatiles. For reasons discussed in the text, CI-like material with ~10% contributions of material with isotopically solar compositions, but a roughly chondritic H/N value, can most simply explain Earth's bulk hydrogen and nitrogen isotopic compositions (*3*).

model if variable amounts of the accreted water had reequilibrated at high temperatures with nebular H_2, thereby acquiring roughly solar hydrogen isotopic compositions. One obvious local heat source is chondrule formation, in which case one might expect an inverse correlation between chondrule abundances in chondrites (OC ≈ RC > CV ≈ CO ≈ CR > CM > Tagish Lake > CI) and their initial water D/H values given in table S2 (RC > OC > CR > CV ≈ CO ≈ CM ≈ Tagish Lake ≈ CI), but this is not the case. Alternatively, the isotopically more solar-like water reequilibrated with nebular H_2 sunward of the snow line and subsequently migrated out to the chondrite-formation regions beyond the snow line—for instance, via the cold-finger effect (*26*). In this scenario, the water in the OCs and RCs would then be essentially pure outer solar system ice. Such an explanation is hard to understand if, as is generally assumed, the OCs and RCs formed closer to the Sun than the CCs and may have formed earlier (*3*). Also, there is no evidence from the internal oxygen isotope systematics of the chondrites that the water in the OCs was much more ^{16}O-depleted than in the CCs (*3*), as this explanation would predict. Thus, at present there is an inconsistency between the ice influx model and our results, unless, perhaps, the major ice influx occurred long before chondrite formation and the ice that chondrites accreted formed more locally (with smaller isotopic anomalies) because transport in the disk had become less efficient.

The possibility that comets may have supplied much of Earth's volatiles has been revived by the discovery that a JFC has water with an Earth-like hydrogen isotopic composition (*13*). However, Earth would not have accreted only cometary ice, but entire comets, including much organic material. From our knowledge of chondrites (*11*, *14*) and interplanetary dust particles (*27*) that may come from comets, this organic material is deuterium-rich. Hence, the bulk hydrogen isotopic composition of a comet is likely to be more deuterium-rich than its water (*3*), in which case even comets like Hartley-2 may not be viable sources of Earth's volatiles.

If comets were not the sources of Earth's water, asteroids, including main-belt comets, become the most likely candidates (*28*), along with some nebular gas (*29*). Marty (*29*) has argued that the relative abundances of hydrogen, carbon, and the noble gases in Earth are roughly chondritic. Nitrogen is depleted relative to carbon and hydrogen, perhaps because it is trapped in the core (i.e., the volatiles were not accreted in a late veneer) (*29*). If Earth's volatiles are in roughly chondritic abundances, isotopes might indicate which, if any, of the known chondrites were their major sources. The range of bulk carbon isotopic compositions of chondrites is small (*3*), but the hydrogen and nitrogen isotopes vary greatly (Fig. 3). No single chondrite group is identical in composition to that of the bulk Earth. The primitive CO ALH 77307 has bulk hydrogen and nitrogen isotopic compositions like Earth's, but other isotopic evidence probably rules out COs as the major source of Earth's volatiles (*5*). The CIs plot on the extension of the line connecting solar and bulk Earth. It is possible that a number of chondrite groups contributed to Earth's volatile budget, but perhaps the simplest explanation is that most of the hydrogen and nitrogen (as well other volatiles) was accreted in CI-like material, along with ~10% contributions to both elements from material with a solar isotopic, but elementally fractionated, composition (*3*, *29*).

Note added in proof: Some of the discussion regarding comparison between the meteorites and the Oort cloud comets and Enceladus has been clarified from that in the version published in *Science Express*.

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Acknowledgments: All the data reported in this paper are presented in the supplementary materials. This work was partially funded by NASA Cosmochemistry grant NNX11AG67G (C.M.O'D.A.), the NASA Astrobiology Institute (C.M.O'D.A., R.B., M.L.F., L.R.N.), Carnegie Canada (C.M.O'D.A., C.D.K.H., L.R.N.), the Natural Sciences and Engineering Research Council of Canada (C.D.K.H.), the W.M. Keck Foundation (M.L.F., R.B.), and the UK Cosmochemical Analysis Network (K.T.H.). For supplying the many samples that were necessary for this work, we thank the members of the Meteorite Working Group, C. Satterwhite and K. Righter (NASA, Johnson Space Center), T. McCoy and L. Welzenbach (Smithsonian Museum for Natural History), L. Garvie (Arizona State University), S. Russell, C. Smith, and D. Cassey (Natural History Museum, London).

Supplementary Materials

www.sciencemag.org/cgi/content/full/science.1223474/DC1
Materials and Methods
Supplementary Text
Author Contributions
Figs. S1 to S3
Tables S1 to S5
References (*30–113*)

17 April 2012; accepted 25 June 2012
Published online 12 July 2012;
10.1126/science.1223474

Corrected 10 August 2012; see below

Science AAAS

www.sciencemag.org/cgi/content/full/science.1223474/DC1

Supplementary Materials for

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Published 12 July 2012 on *Science* Express
DOI: 10.1126/science.1223474

This PDF file includes:

Materials and Methods
Supplementary Text
Author contributions
Figs. S1 to S3
Tables S1 to S5
References (*30*–*113*)

Other Supplementary Material for this manuscript includes the following:
(available at www.sciencemag.org/cgi/content/full/science.1223474/DC1)

Table S1 (Excel format)

Correction: The reference list has been updated, and table S1 is now available as an Excel file, in addition to the PDF version.

Supplementary Materials

Materials and Methods

Determining the original hydrogen isotopic composition of the water in chondrites is potentially difficult because of: (i) terrestrial contamination (weathering and adsorbed water), (ii) the often physically intimate association between deuterium-rich organics and hydrated phyllosilicates, (iii) similar release temperatures for volatile organics and water/OH in phyllosilicates, (iv) modification by shock and atmospheric entry heating, (v) sample heterogeneity, (vi) the likelihood for significant evolution of the hydrogen isotopic composition of the fluid resulting from equilibrium/kinetic isotopic fractionation during formation of hydrated silicates, and from isotopic exchange between water and the organics during alteration/metamorphism in the meteorite parent bodies, and (vii) isotopic fractionation associated with oxidation of Fe by water during alteration/metamorphism (*14*).

At first glance, the simplest approach to determining the initial fluid composition would seem to be to analyze individual hydrated mineral grains. However, there is typically a fluid-mineral isotopic fractionation (e.g., *30*) that may be difficult to correct for because the alteration conditions are poorly constrained and the fractionation factors for the minerals that can be measured may not be known. More importantly, as pointed out above, the isotopic composition of the fluid and the secondary minerals that form from it are likely to have evolved with time, particularly if there was little fluid-mineral interaction after formation (Rayleigh process) and the alteration occurred in a closed system. This evolution of the fluid isotopic compositions has apparently been confirmed by the discovery of sometimes very large hydrogen isotopic differences between the compositions of secondary minerals in CRs that formed within a few tens to hundreds of microns from one another (*31*).

If alteration of individual meteorites was essentially closed system, the bulk meteorite compositions will be unchanged even if internally there has been an extensive redistribution of the hydrogen isotopes. Here we use the bulk meteorite compositions to infer the initial hydrogen isotopic compositions of water in chondrites. The sample selection and analytical protocols described below were designed to try to mitigate as many of the potential problems listed at the beginning of this section as possible.

Sample Selection

The meteorites selected (Table S1) were observed falls and Antarctic finds only. These samples are the least likely to have suffered extensive terrestrial weathering that would compromise their bulk hydrogen, carbon and nitrogen elemental abundances and isotopic compositions. Meteorites that are known to have been shock heated were generally avoided, although a few were analyzed to help recognize shocked meteorites amongst those that have not previously been petrologically characterized. X-Ray Diffraction (XRD) studies were performed on a number of the samples in this study to monitor the degree of hydration (*32, 33*). These XRD data show no evidence for shock in samples other than those listed. With the exception of several rare but important meteorites, ~1g of sample was acquired to ensure representative sampling. The samples were made up of interior chips (well away from the fusion crust and sawn surfaces) to minimize the effects of potential terrestrial contamination and possible modification by atmospheric entry heating.

For the CM and CR carbonaceous chondrites (CCs), the samples were selected to cover the known range of petrologic types. For the ungrouped Tagish Lake meteorite, samples from three lithologies with different degrees of parent body aqueous alteration were analyzed (*12*). For the CO and CV CCs and the ordinary chondrites (OCs), only the most primitive samples were selected for this study: CO – ALH 77307, CV – Kaba, and OC – Semarkona (LL3.0). All three of these meteorites have petrologic evidence of aqueous alteration (*34-37*). The possibility that Antarctic weathering could have modified the bulk hydrogen abundance and isotopic composition of ALH 77307 must be considered as Brearley (*34*) was unable to determine if the alteration was parent body or terrestrial (Antarctic). The more thermally metamorphosed members of the CO, CV and OCs contain much less hydrogen, carbon and nitrogen due to dehydration and destruction of their organic material and, as a result, their compositions are much more sensitive to terrestrial contamination. The effects of metamorphism and contamination make it very difficult to extrapolate back to their primordial water compositions. No enstatite chondrites were analyzed because their indigenous hydrogen contents are very low and their reduced mineralogies make them very susceptible to terrestrial weathering.

Sample Preparation

The surfaces of the bulk meteorite chips were first examined optically for evidence of weathering, and contamination. Only two cases required the removal of any extraneous material with a steel drill. Most bulk meteorite samples were subsequently crushed by hand in air, first with a steel crusher and then in an agate pestle and mortar to a grain size of <150 µm. For the CRs, with their abundant coarse-grained metal, the coarse metal (presumably along with other magnetic material) was removed with a hand magnet to try to minimize (i) the influence of associated rust and (ii) the possibility of introducing heterogeneity in the elemental abundances by the random inclusion of large metal grains in the small aliquots used for the analyses. A few CM samples that were originally from the study of (*33*) were crushed under acetone.

For the elemental/isotopic analyses, aliquots of the meteorite powders were weighed into foil capsules (silver for hydrogen, tin for carbon and nitrogen) and were stored in desiccators for days to weeks at room temperature to minimize adsorbed water contents. The samples were weighed prior to being placed in the desiccators and again several days later. Weight losses ranged from unmeasurable (<0.1 µg) to 3-4 wt.%, and generally correlated with the petrologic type of the meteorite, i.e., the higher the abundance of phyllosilicates, the greater the weight loss. A few preliminary samples were also stored in a dry N_2 flushed oven at 50°C, but no systematic differences were observed between these samples and those stored in the desiccators. Room temperature storage in desiccators was deemed the most benign means of removing adsorbed water without potentially losing indigenous labile water and organics. However, it is likely that this process does not remove all of the terrestrial water associated with weathering products, probably producing increased scatter in the data. Nevertheless, there is no obvious correlation in Antarctic CMs, for instance, between weathering grade and either hydrogen abundance or isotopic composition (see below).

Typical sample sizes ranged from 2-10 mg for hydrogen to 8-30 mg for carbon and nitrogen, depending on their anticipated volatile contents. Prior to analysis, the samples were quickly transferred from the desiccators to a zero-blank autosampler, and flushed with zero-grade, dry helium for at least two hours before being analyzed to minimize adsorbed water.

Elemental and Isotopic Analysis

Elemental and isotopic analyses were made with: 1) a Thermo Scientific DeltaV^{plus} mass spectrometer connected to a Carlo Erba (NA 2500) elemental analyzer (CE/EA) via a Conflo III interface for carbon and nitrogen analyses, and 2) a Thermo Finnigan Delta^{plus}XL mass spectrometer connected to a Thermo Finnigan Thermal Conversion elemental analyzer (TC/EA) via a Conflo III interface for hydrogen analyses. The Conflo III interface facilitates the introduction of the N_2 and CO_2 reference gases for the nitrogen and carbon isotope analyses, while a dual inlet system facilitates introduction of the D/H reference gas for the hydrogen isotope analyses. International standards were used to calibrate and correct the data; internal working gas standards were analyzed at regular intervals to monitor the accuracy of the measured isotopic ratios and elemental compositions throughout the run. An H_3^+ correction was determined and applied to the hydrogen measurements.

For hydrogen analyses, two samples of each meteorite were analyzed sequentially to check for both sample heterogeneity and small memory effects that are known to occur with deuterium enriched samples. Blanks were run between different meteorites, again to reduce any memory effects. Except for the CRs, there was little evidence for significant heterogeneity or memory effects. For example, the hydrogen abundances of the CMs varied by 1-4 % of their absolute values and δD by 0.2-4.5 ‰ (the δ notation stands for the deviation of a sample ratio from a standard ratio in parts per thousand, $\delta=(R_{smp}/R_{std}-1)*1000$ and in this case R=D/H). For the CRs, the hydrogen abundance is unaffected by the memory effect, but in some cases the second analysis of a pair was significantly (>30 ‰) more deuterium-rich than the first. In these cases, only the second hydrogen isotope analysis was used. There is no memory effect for carbon and nitrogen analyses, and the larger sample sizes ensured more representative sampling of the powders. Generally, only one sample of each meteorite was analyzed for carbon and nitrogen. Repeat analyses of some samples indicate that carbon and nitrogen abundances typically vary by 1-5 %, $\delta^{13}C$ values varied by 0.1-0.7 ‰, and $\delta^{15}N$ values varied by 0.1-1 ‰.

Results

The results for the meteorites used in this study are given in Table S1. The analytical protocols outlined above were designed to minimize artifacts due to adsorbed atmospheric water and to produce a self-consistent dataset. Previous studies (*38-41*) using different sample sizes, sample preparation and analytical techniques have reported a wide range of compositions even for the same meteorites. For instance, reported hydrogen abundances for the CIs Orgueil and Ivuna varied from 0.66-1.75 wt.% and δD values varied from -30 ‰ to 230 ‰. In this study, two samples of Orgueil (obtained from different institutions) and one sample of Ivuna had average hydrogen abundances of 1.55±0.02 wt.% and average δD values of 78.0±6.7 ‰.

For most CMs, there is an inverse correlation between hydrogen abundance and isotopic composition (Fig. S1). Some meteorites scatter to lower hydrogen abundances, including several for which petrologic evidence of heating ("Heated" symbols), possibly by shock, has been reported (*42-45*). Those that lie between the heated samples and the main trend are indicated by the "Heated?" symbols. In this paper (see Fig. 1), we only consider those CMs that clearly belong to the unheated category.

Figure S1 includes both falls and Antarctic finds. The fact that both falls and finds exhibit the same range of elemental and isotopic compositions suggests that weathering has not significantly modified the bulk compositions of the finds. The Antarctic finds have been classified according to their apparent extent of terrestrial weathering. The unheated CMs are plotted according to their weathering classification (A-C) in Fig. S2. As can be seen, there is no correlation between composition and weathering grade. One might expect that the influence of weathering would be more severe in more Fe-metalrich meteorites, such as the CRs and COs. For the CRs, we also found little difference between falls and finds, or between finds of different weathering grade (Fig. S2), although the sample suite is much smaller. These results give us a measure of confidence in the results for the primitive CO ALH 77307, but the influence of weathering remains a concern.

Estimation of Water Hydrogen Isotopic Compositions

The linear trends in Fig. 1 are the result of mixing between water/OH in phyllosilicates and hydrogen in organics. The hydrogen isotopic composition of the water, indicated by the δD intercept (Fig. 1), was determined by linear least squares fits to the CM and CR data using ISOPLOT (*46*). Excluded from the fit to the CMs (open symbols in Fig. 1) were samples with unusual compositions, along with Bells and Essebi (the most deuterium-rich samples) whose CM affinity has been questioned by some. Three of the CMs with open symbols that fall to the right of the main trend (high C/H values) were crushed under acetone and may be contaminated. Most samples do not have realistic errors for their C/H values due to the lack of multiple carbon measurements, and the as yet undetermined small and presumably variable carbonate contribution to the bulk carbon (*47*). Even the hydrogen isotopic compositions, which in general do have multiple analyses, may be subject to uncertainties associated with weathering, and adsorbed water that are difficult to quantify. As a result, in the fits all samples were given the same weights. For the C/H values the 1σ uncertainties were assumed to be 5 %. For the δD values, the uncertainty was assumed to be 5 ‰ for the CMs and for the CRs 15 ‰.

There are only sufficient numbers of CMs and CRs to estimate the water isotopic compositions as we did in Fig. 1. Since the CM and CR trends in Figure 1 suggest that they share a common organic end member, it is possible to estimate the water compositions by subtraction of this end member, if its abundance is known. The organic end member has a composition like that of the most primitive insoluble organic material (IOM), often stated to make up 70-99 % of the organic carbon in chondrites. However, this is not necessarily the case, as first noticed by Smith and Kaplan (*48*). Previous measurements of IOM abundances (*11*, *14*) account for roughly half of the bulk carbon in the chondrites measured here. Most of the remaining carbon appears to be insoluble in typical solvents, is not in inorganic carbon (e.g., carbonate or graphite), and is released by treatment with ≥1N HCl. This acid soluble material must have a composition that is very similar to the IOM, otherwise the CM and CR lines seen in Figure 1 would not pass through the region of primitive IOM compositions. It seems likely that the acid soluble material is bonded to the IOM by acid hydrolysable functional groups, but it cannot be ruled out that some is trapped in phyllosilicates (*49*, *50*).

The hydrogen isotopic compositions of the water in CMs and CRs, like those inferred from Figure 1, can be estimated, albeit with larger errors, by assuming that the bulk carbon is in material with IOM-like C/H values, and primitive IOM δD values (≈3500 ‰). This will result in significantly larger organic corrections than in past estimates of water compositions (*14*, *51*). As proof of concept, we first applied this approach to the CRs and CMs. The CRs appear to have the most primitive IOM (*11*, *14*, *52*, *53*). Assuming an end member organic composition of δD=3500 ‰ and a mean C/H weight value of 0.061, the calculated δD value of 91±47 ‰ is comparable to the water composition inferred from Fig. 1 (δD=96+110/-65 ‰). This C/H value is only slightly lower than the average of the CR IOM (0.065±0.002) measured by (*11*, *14*). Using the same approach, the water composition for CMs was estimated assuming either the average C/H (0.055) for CM IOM measured by (*11*, *14*), or the ratio of 0.061 determined for the CRs. These two ratios gave water compositions of δD=-441±59 ‰ and -485±63 ‰, respectively, which compare favorably with the least squares fit results (Fig. 1, Table S2) of δD=-445±23 ‰.

This approach of subtracting the organic hydrogen to estimate water compositions was then applied to the CIs, the three Tagish Lake lithologies, the CV Kaba, the CO ALH 77307 and the OC Semarkona (Fig. 2, Table S2). In all cases, the likely ranges of water compositions were estimated using either the measured C/H values of the IOM in each meteorite or the CR ratio of 0.061, the latter probably being closer to the composition of the organics prior to the onset of aqueous alteration and/or thermal metamorphism. Apart from assuming a common organic precursor composition, this approach also assumes closed system behavior after the onset of isotopic exchange between the organics and water. A change in the fractions of hydrogen in water or organics during or after the isotopic exchange will result in over or under estimates of the δD values of the water depending on which hydrogen reservoir is preferentially lost. The IOM C/H values in most meteorites are less than in the CRs, which appear to contain the most primitive IOM. The lower C/H values are probably the result of metamorphism/alteration, as clearly demonstrated for the Tagish Lake samples (*12*). The use of the CR C/H value attempts to compensate for the loss of any hydrogen from the organics. However, if the lost organic hydrogen did not isotopically exchange with the water before leaving the system, this will result in an over correction to the water composition (it will be too depleted in D). Similarly, if there was water loss after water-organic exchange is complete, this will also lead to an over correction of the water composition. In the different Tagish Lake lithologies, the IOM systematically decreases in C/H and δD with increasing degree of alteration, suggesting that there was isotopic exchange and modification of the IOM during alteration (*12*). For the most altered of the Tagish Lake lithologies studied here (11i), the water composition estimated using the CR C/H value is very D-poor. While the carbon content of this lithology is similar to the others, its bulk hydrogen content is lower, suggesting that it has indeed lost some water since the water-organic exchange ended. Use of the 5b lithology (contains the most primitive IOM) water content, produces a minimum estimate for the water hydrogen isotopic composition for lithology 11i that is more comparable to that of lithologies 5b and 11h. The very D-poor lower limit for the CV water D/H value also probably reflects some sort of open system behavior.

Supporting Information

Comet-Chondrite Connections

There are many reasons to think that there is a genetic link between chondrites and comets, or at least between many of their components. Chondritic porous (CP-) interplanetary dust particles (IDPs) are generally thought to be the most primitive Solar

System objects available to us for study, and it has been argued that the most primitive IDPs are from comets (*54*). The most primitive chondritic IOM has similar D- and ^{15}N-rich bulk compositions and isotopic hotspots to organics in IDPs (*11*, *14*, *53*). It seems likely that all other chondrites accreted similar material, but it has been modified to varying degrees by parent body processes (*11*). There is a striking resemblance between the bulk elemental compositions of comet Halley CHON particles, $C_{100}H_{80}N_4O_{20}S_2$ (*55*), and the meteoritic IOM with the most anomalous isotopic compositions, e.g., EET92042 (CR2) - $C_{100}H_{75}N_4O_{17}S_3$, GRO95577 (CR1) – $C_{100}H_{79}N_3O_{11}S_1$, and Bells (CM2) - $C_{100}H_{69}N_3O_{21}S_5$) (*11*). Samples of comet 81P/Wild 2 returned by the Stardust mission contain organic particles with higher nitrogen and oxygen contents, as well as generally more modest D and ^{15}N enrichments, compared to IOM in IDPs and primitive meteorites (*56-58*), but issues of modification (possibly even synthesis) during capture and contamination have yet to be fully explored.

There is also evidence that the ices accreted by chondrites contained some of the same volatiles as cometary ices (e.g., CO, CO_2, HCN and NH_3). Strecker synthesis, reaction in aqueous solution of ketones and aldehydes with HCN and NH_3, is the most commonly invoked mechanism for the formation of the α-amino acids and hydroxy acids found in the most primitive chondrites (*59*). The HCN and NH_3 would presumably have been in the ices that were the sources for the water in which the reactions took place and that were responsible for the aqueous alteration in chondrites. Aqueously altered chondrites also generally contain carbonate minerals. The source of the CO_2 needed to form these carbonates is unknown, but the CO_2/H_2O values for chondrites are of the order of those in comets. Some CO_2 could also have been generated in chondrites by conversion of CO in the ices to CO_2 via Fischer-Tropsch-type (FTT) synthesis. If CO was present in the ices, the condensation temperature of CO would imply that chondritic ices formed at very low temperatures.

Finally, there are many similarities in the silicate mineralogies, compositions and microstructures between pristine chondritic matrix material, CP-IDPs and comet 81P/Wild 2 material (*35*, *60-63*). Like chondrites, comet 81P/Wild 2 also appears to contain chondrules and calcium-aluminum-rich inclusions (*64*, *65*).

Bulk Hydrogen Isotopic Composition of Comet Hartley 2

If we use the bulk composition (43 wt% water, 26 wt% organics) of comet Halley estimated by (*66*) as representative of Hartley 2, and assume that the composition of the organics is like Halley CHON particles (and chondritic IOM, see above), roughly 20% of the hydrogen would be in the organics. If, as in primitive chondritic IOM, the D/H value of the organics is about 4.5 times terrestrial, the bulk D/H of Hartley 2 would be about 1.7 times its roughly terrestrial water composition. In this case, the source region of Hartley 2 would not be a good candidate for the source of terrestrial hydrogen.

Oxygen Isotopic Compositions of Altering Fluids

One of the most ubiquitous products of aqueous alteration in chondrites is magnetite, which inherited its oxygen from the altering fluids. Contrary to what one might expect if the large variations in the hydrogen isotopes of the water reflect changes in the source regions, the secondary magnetites in OCs (*67*), RCs (*68*) and CCs (*69-73*) exhibit a rather modest range of $\Delta^{17}O$ values (OC ~5 ‰, RC ~3.5‰, CV ~-1‰, CO ~-2‰, CI ~1.7‰, and CM ~1.3‰). The highest $\Delta^{17}O$ values are found in the OCs and RCs, which have the most deuterium enriched water. However, overall there is no simple correlation between the oxygen isotopes of the magnetite and the estimated initial hydrogen isotopic compositions of the water (Table S2).

The $\Delta^{17}O$ values of the magnetites are small compared to the values that may have been present in presolar and outer Solar System ices (*20*, *21*, *74*), and to the most ^{16}O-poor Solar System material found in meteorites ($\Delta^{17}O \approx 89$‰: *75*). If the oxygen isotopic composition of this material is more representative of the water originally accreted by chondrites, the water in most chondrites must have experienced considerable oxygen isotope exchange with silicates prior to magnetite formation. Because of this potential exchange, at present the oxygen isotopes of secondary minerals cannot be used to constrain possible variations in the initial isotopic compositions and source regions of chondritic water.

Formation Times and Locations of Chondrites

There is growing evidence that asteroids that melted and differentiated formed earlier than the parent bodies of chondrites (*76*, *77*). The internal heating of asteroids was almost certainly primarily caused by the decay of the short-lived radionuclide ^{26}Al ($t_{1/2}\approx0.7$ Myr). The extent of internal heating will have depended on the time of formation of an asteroid, as well as its size (*78-80*). In the solar nebula, dust densities will have decreased and dynamical times increased with radial distance from the Sun. As a result, it is likely that in general asteroids in the inner main-belt would have formed earlier and been more internally heated than those in the outer main-belt (*79*). This is consistent with the radial distribution of asteroidal types. The order of maximum heating experienced by the various chondrites is EC≥OC≈RC>CO≈CV>CI≥CR≥CM (*7*, *81-84*). The sizes of the parent asteroids are unknown and none of the meteorites in a group may have come from the centers of their parent bodies. Nevertheless, if our picture of what processes controlled the internal heating of asteroids is correct, the above ordering of maximal chondrite heating can be used to provide very crude estimates of their relative formation ages and formation distances from the Sun.

Formation location relative to the so-called snowline is also important. Since most chondrites show some evidence for water activity in them, presumably they accreted beyond the snowline. Given the highly reduced nature of ECs and the general absence of evidence for water activity in them, it is typically assumed that they accreted sunward of the snowline. However, EC and aubrite clasts in the Kaidun breccia have been aqueously altered (*85-87*). It is still not clear where this alteration occurred, but if it was on the EC parent bodies this will require a major change in the thinking about the formation location of the EC parent bodies with respect to the snowline.

Are There Primitive Asteroid Types not Represented in our Meteorite Collections?

To achieve Earth-crossing orbits, meteorite-sized (or larger) objects must encounter one of four major resonances (*88*) - the ν_6 secular resonance (2.0 AU) and the 3:1, 5:2 and 2:1 mean motion resonances with Jupiter (2.5, 2.8 and 3.2 AU, respectively). The relative efficiencies of these resonances for delivering meteoroids to Earth are estimated to be 1:0.2:0.025:0.003, respectively. Thus, the immediate parent bodies of meteorites are likely to be heavily biased towards asteroids in the inner asteroid belt, but processes like the Yarkovsky effect can cause the orbits of small bodies to drift inwards or outwards over large distances.

There is an overall gradient of spectral classes in the asteroid belt (*89*, *90*), with C-complex objects dominating the outer belt and the S-complex objects dominating the inner belt. However, there is considerable radial mixing of asteroidal classes, and it is likely that the meteorite collection has sampled many of them. Nevertheless, it is possible that there are asteroid types that are not represented in our meteorite collections, either because of their orbital locations or because their physical properties mean that they do not usually survive atmospheric entry.

For small particles, Poynting-Robertson drag becomes increasingly important, enabling them to drift into Earth-crossing orbit from throughout the asteroid belt. Small (order millimeter-sized or less) particles should, therefore, provide a more representative sampling of objects in the asteroid belt than meteorites.

Polymict microbreccias, such as Kaidun, are useful as the collections of small clasts that they contain provide unique views of the fluxes of chondritic fragments that were present in the asteroid belt in the past (*91*). Not withstanding their potential modification during the formation and subsequent evolution of the breccias, as well as the difficulty of definitively classifying small fragments, most primitive clasts are related to known chondrite groups. Most CC clasts are related to CI, CM and CR chondrites (*85*, *86*, *91*, *92*), although some apparently unique C1 and C2 clasts are present. The exceptions seem to be the clasts in the CH/CB association (*93*). In many ways, the clasts in these meteorites petrologically resemble CI, CM and CR chondrites, but they also differ in important ways. Most notably, they contain large ^{15}N enrichments, but no isotope anomalies in hydrogen or carbon (*94*, *95*).

Micrometeorites are also potential sources of material from bodies not sampled by the meteorite collections. Indeed, recent dynamical modeling has been used to argue that most micrometeorites are from Jupiter-family comets (*96*). As with the clasts in breccias, most micrometeorites resemble the matrices of CI and CM chondrites (*97*). Engrand et al. (*98*) measured the water hydrogen isotopic compositions of a number of fine-grained (least heated during atmospheric entry) Antarctic micrometeorites and found that they all had D/H values that fell within ~20-25 % of the terrestrial ratio. This range is similar to those seen in bulk CM and CI chondrites, but not in CRs. The compositions are more deuterium-rich than the initial water compositions inferred for CM and CI chondrites here, but isotopic exchange between IOM and water during alteration means that the present hydrogen isotopic composition of water will be more deuterium-rich than at the start of alteration. Perhaps more importantly, it is still unclear to what extent the hydrogen isotopic compositions of the micrometeorites have been modified by atmospheric entry heating and/or terrestrial contamination.

Sources of the Earth's Volatile and non-Volatile Components

Figure 3 suggests that the terrestrial hydrogen and nitrogen isotopic compositions could be explained by the mixing of CI-like and solar isotopic composition materials. CIs are the most volatile-rich chondrites. Other chondrite groups would have to contribute proportionally higher mass fractions to the Earth to reproduce its volatile content, making it difficult to reconcile other isotopic systems even if the volatile element isotopic compositions could be explained. Mixing calculations using the solar, CI and terrestrial hydrogen and nitrogen isotopic compositions (Tables S2, S3 and S4) indicate that the hydrogen and nitrogen from solar contributions would be ~13% and ~10%, respectively. This is consistent with the previous estimates of (*29*). There is a two orders of magnitude difference in the solar ($1.3x10^4$) and CI ($1.2x10^2$) H/N values (Table S5). Thus, the similar contributions of isotopically solar material to the Earth's hydrogen and nitrogen would require a significant elemental fractionation in the solar and/or CI material. As pointed out by (*29*), the concentrations of many of the volatiles in the bulk Earth are ~2% of those in bulk CI (Table S5). In bulk Earth, nitrogen is depleted relative to most other volatiles and CI (H/N= 2.5×10^3), but this could be because nitrogen has been sequestered into the core. Unless the roughly chondritic relative abundances of the volatiles in Table S5 are a coincidence, it seems likely that it is the isotopically solar material that was elementally fractionated - depleted in hydrogen relative to nitrogen by roughly a factor of ~100 (more if the nitrogen depletion relative to CI is primary and not due to nitrogen in the core). If correct, this will place significant constraints on how the solar material was accreted.

The CIs are much more volatile-rich than Earth, so most (~98%) of the accreted material would have to have been in volatile-poor bodies that were presumably degassed as a result of melting and differentiation prior to accretion. EC-like planetesimals are attractive candidates for the dominant building blocks of the Earth because their oxygen isotopes lie on the terrestrial mass fractionation line (TFL). Unlike other volatile-rich chondrites, CIs have oxygen isotopic compositions that also fall very close to the TFL. The ECs contain significant carbon, nitrogen and noble gases, but most of these volatiles could have been lost if there was melting and differentiation of the planetesimals prior to accretion by the Earth. There is additional support for a CI-EC mixing model in the stable isotopes of chromium, titanium and nickel (*5*). Molybdenum and osmium isotopic compositions are not consistent with a CI-EC mix (*99*, *100*), but they may be dominated by late veneer material. The major objection to a CI-EC mixing model is the poor fit to the estimated major and trace element composition of the bulk Earth (*101*).

Author Contributions: C.M.O'D.A. was responsible for selection and preparation of most samples, as well as analysis of the elemental and isotopic data. RB and MLF carried out all elemental and isotopic measurements. KTH selected and prepared a subset of the CM and CI samples. CDKH and LRN were responsible for the selection and preparation of the Tagish Lake samples. All authors participated in the preparation of this manuscript.

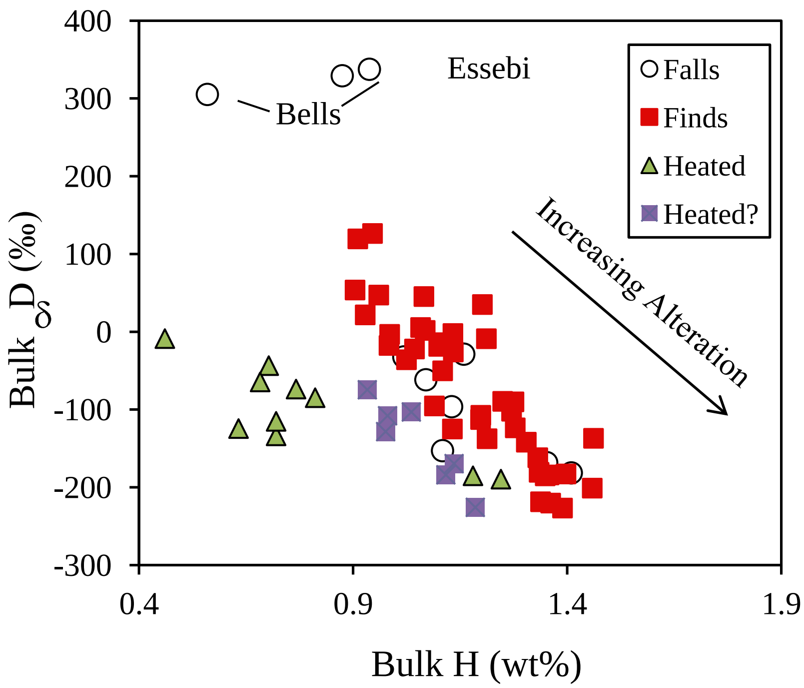

Fig. S1. The bulk hydrogen abundances and isotopic compositions of CMs. The correlated behavior of hydrogen abundances and isotopes also correlates with petrologic indicators of the extent of aqueous alteration. Falls and Antarctic finds exhibit the same behavior, suggesting that Antarctic weathering has not significantly affected the bulk hydrogen systematics. A number of meteorites fall to the left of the main trend. Petrologic examination of some of these indicate that they have been heated. Two heated meteorites lie just to the left of the main trend, and as a result other similarly positioned meteorites have been classified as possibly heated. Only those belonging to the main trend are used in this paper.

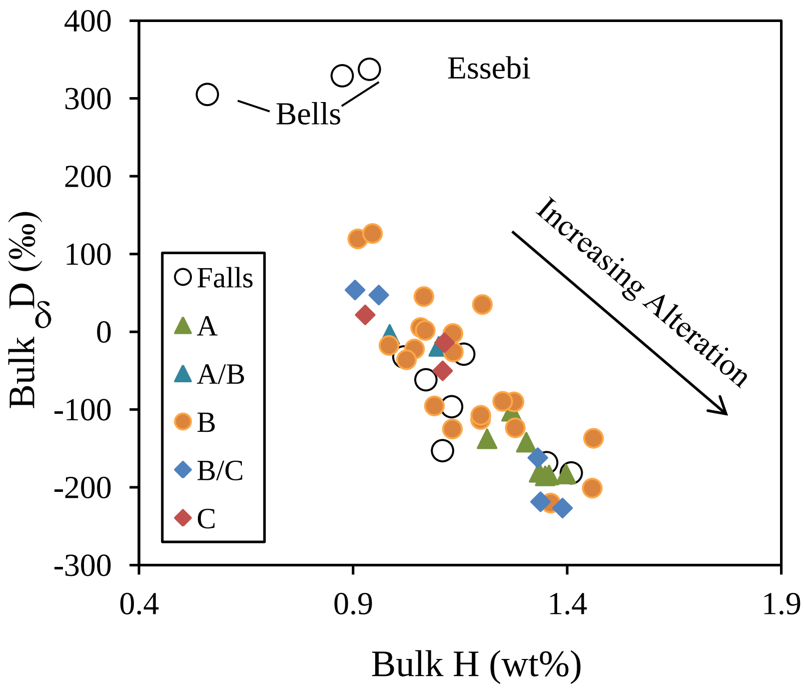

Fig. S2. The bulk hydrogen abundances and isotopic compositions of the unheated CMs (Fig. S1). The Antarctic finds are plotted separately according to their weathering grades (A – least weathered, C - most weathered). As pointed out in Fig. S1, falls and Antarctic finds exhibit the same behavior. Also, amongst the Antarctic finds there is no systematic variation with weathering grade. Both these observations suggest that Antarctic weathering has not significantly affected the bulk hydrogen systematics.

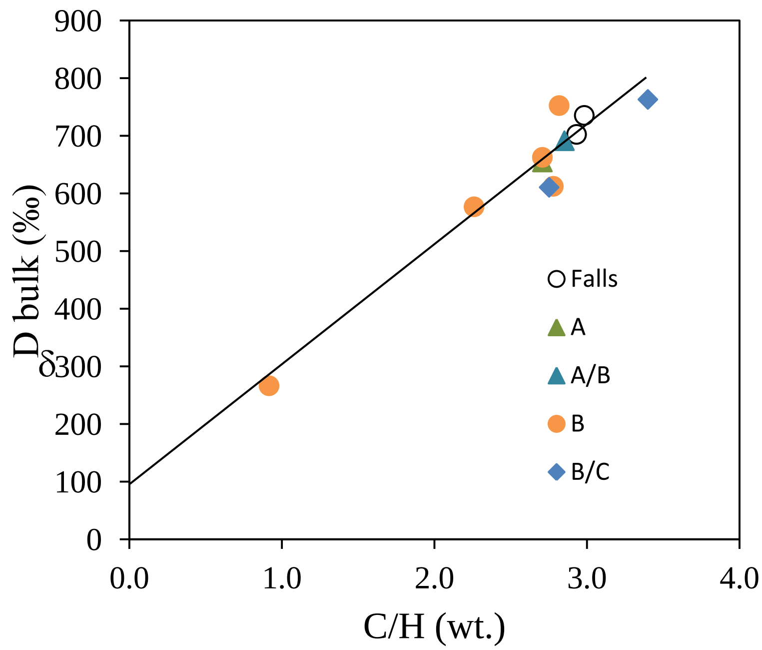

Fig. S3. The bulk hydrogen abundances and isotopic compositions of the analyzed CRs. The Antarctic finds are plotted separately according to their weathering grades (A – least weathered, C - most weathered). As with the CMs (Fig. S2), falls and Antarctic finds show no systematic differences, and amongst the Antarctic finds there is no systematic variation with weathering grade. Both these observations suggest that Antarctic weathering has not significantly affected the bulk hydrogen systematics.

Table S1. The bulk hydrogen, carbon and nitrogen elemental and isotopic compositions of chondrites analyzed in this study. Also included are the classifications of each meteorite, and for the Antarctic finds their weathering grades and the pairing groups that they belong to.

	Classif.	Weath.	Pairing group	H (wt.%)	δD (‰)	C (wt.%)	δ^{13}C (‰)	N (wt.%)	δ^{15}N (‰)
CM									
ALH 81002*	CM2	Ae	ALH 81002	1.304±0.009	-142.0±1.8	1.66	-9.4	0.069	13.6
ALH 83100*	CM1/2	Be	ALH 83100	1.458±0.009	-201.1±0.5	1.90	-2.7	0.070	11.9
ALH 84029	CM2	Ae	ALH 83100	1.357±0.009	-184.1±2.5	1.71	2.4	0.061	15.5
ALH 84034	CM2	A	ALH 83100	1.397±0.002	-182.9±2.9	1.74	2.2	0.061	16.1
ALH 84042	CM2	A	ALH 83100	1.349±0.011	-185.3±0.5	1.68	0.8	0.060	15.3
ALH 84044	CM2	Ae	ALH 83100	1.334±0.008	-180.7±1.9	1.71	2.3	0.061	15.3
ALH 85013	CM2	A	ALH 85005	1.213±0.003	-137.6±0.5	1.73±0.05	-0.7±0.2	0.087±0.003	32.6±0.3
Banten	CM2			1.018±0.010	-32.4±0.8	2.02	-6.2	0.091	44.8
Bells C$	CM2			0.559±0.010	305.2±1.7	1.74	-19.9	0.064	352.8
Bells W$	CM2			0.874±0.038	329.2±0.0	2.08	-8.9	0.087	359.7
Cold Bokk.*	CM2			1.352±0.004	-168.3±0.3	2.45	-10.9	0.067	16.0
DNG 06004	CM2	A/B		0.985±0.013	-3.4±1.1	2.04	1.8	0.112	49.9
DOM 08003	CM2	B		1.461±0.006	-137.0±11.1	1.85	-0.5	0.095	41.1
DOM 08013	CM2	B/C		0.960±0.010	47.2±2.4	1.92	-2.4	0.116	56.3
EET 96006	CM2	Be	EET 96005	1.276±0.001	-90.1±0.6	1.99	-1.8	0.124	39.2
EET 96016	CM2	Be	EET 96005	1.249±0.007	-89.5±0.1	2.09	-1.4	0.121	44.8
Essebi*				0.938±0.005	337.5±0.0	3.10	-0.6	0.137	41.7
GRA 98074	CM2	Ce	GRA 98005	1.113±0.028	-14.1±4.3	2.04	0.7	0.116	49.4
GRO 95566	CM2	A/Be		1.100±0.016	-18.8±1.1	1.93	0.5	0.110	55.7
LAP 02239	CM2	B	LAP 02239	1.025±0.021	-36.0±0.7	1.91	3.7	0.101	45.6
LAP 02333	CM2	B	LAP 02239	1.133±0.005	-2.2±4.6	2.10	1.0	0.141	35.4
LAP 02336	CM2	B	LAP 02336	1.058±0.005	5.5±2.3	2.02	-1.2	0.144	33.7
LAP 03718	CM2	Be	LAP 03718	1.068±0.011	1.7±3.6	2.03	-0.6	0.154	31.1
LAP 03785	CM2	B	LAP 03718	1.279±0.008	-123.6±0.8	1.81	-0.6	0.096	36.6
LEW 85311	CM2	Be	LEW 85306	0.911±0.040	119.4±2.9	2.03	-3.1	0.156	33.1
LEW 85312	CM2	B	LEW 85306	0.945±0.019	126.3±4.1	2.12	-0.8	0.171	37.5
LEW 87016	CM2	B		1.134±0.010	-26.0±2.0	1.95	-1.8	0.124	48.1
LEW 87022	CM2	B	LEW 87001	1.198±0.014	-112.9±2.4	1.88	1.6	0.093	29.9
LEW 87148	CM2	Ae		1.270±0.032	-102.2±4.5	1.81	-1.9	0.099	43.0
LEW 88001	CM2	Ce	LEW 88001	1.109±0.008	-50.2±0.0	1.97	0.9	0.101	48.8
LEW 90500	CM2	B		1.090±0.005	-95.4±2.9	1.84±0.04	-1.6±0.0	0.094±0.004	35.6±0.2
LON 94102	CM2	Ce	LON 94101	0.928±0.013	21.7±0.7	2.06±0.05	-1.8±0.0	0.123±0.003	38.0±0.1
MAC 88101	CM2	Be		1.202±0.001	35.0±5.1	1.73±0.01	1.2±0.1	0.097±0.004	51.6±1.0
MAC 88176	CM2	Be		1.198±0.016	-107.4±2.7	1.67	-3.0	0.093	22.4
MCY 05230	CM2	B	MCY 05229	0.984±0.007	-17.6±3.7	2.00	1.5	0.110	47.3
MET 00432	CM2	B		1.065±0.020	45.3±0.2	2.72±0.02	3.0±0.5	0.118±0.004	29.8±1.0
MET 01070*	CM1	Be	MET 01070	1.361±0.000	-220.3±0.0	1.58	-9.0	0.087	-4.8
Mighei*	CM2			1.130±0.003	-96.3±0.2	2.48	-10.1	0.087	29.3
Murchison	CM2			1.070±0.002	-61.7±3.1	2.08	-2.9	0.105	45.6
Murray*	CM2			1.158±0.019	-28.8±3.2	2.33	-7.4	0.106	45.0
Nagoya	CM2			1.409±0.072	-181.5±1.0	1.89±0.11	-8.3±0.7	0.068±0.004	15.5±0.9
Nogoya*	CM2			1.109±0.006	-152.9±0.7	2.23	-13.0	0.069	15.6
QUE 97990*	CM2	Be		1.043±0.014	-22.2±1.0	2.00	-4.2	0.109	40.9
QUE 99355	CM2	B	QUE 99342	1.132±0.001	-125.0±2.3	1.53±0.01	-8.4±0.1	0.077±0.000	15.3±0.3
SCO 06014	CM2	B/C	SCO 06012	1.331±0.009	-162.0±2.0	1.34	-5.5	0.063	-2.8
SCO 06043*	CM1	B/Ce		1.389±0.004	-226.7±0.0	1.45	-11.3	0.071	-3.6
SCO 06043	CM1	B/Ce		1.338±0.025	-218.6±4.0	1.23	-8.0	0.063	-6.0
TIL 91722	CM2	B/Ce		0.904±0.014	53.7±0.7	2.04	0.7	0.121	56.3
Y 791198*	CM2			1.211±0.000	-8.9±1.0	2.43	-2.4	0.133	47.4
Heated (?)									
DOM 03183	CM2	B		1.036±0.001	-103.2±2.0	1.60	-5.5	0.077	19.4
GRA 98005	CM2	Ce	GRA 98005	0.976±0.094	-128.4±0.1	1.32	-11.2	0.049	3.1

LAP 02277	CM1	A		1.185±0.009	-225.8±3.8	1.32	-6.1	0.076	-16.2
MAC 88100	CM2	Be		0.980±0.010	-108.0±5.7	1.56	-6.0	0.075	21.6
MET 01075	CM2	B	MET 01071	1.117±0.007	-183.9±1.4	1.59	-0.1	0.080	1.3
MET 01072	CM2	B	MET 01071	1.136±0.003	-169.5±4.8	1.72	1.3	0.060	11.9
PCA 91084	CM2	Be	PCA 91084	0.933±0.009	-74.6±4.2	1.58	-5.5	0.113	21.8
Heated									
ALH 84033	CM2	Ae	ALH 81002	0.703±0.018	-43.5±5.0	1.70	-5.0	0.096	37.9
EET 83355	CM2	A/B	EET 83226	0.460±0.001	-8.8±0.2	0.92	-4.8	0.068	10.7
EET 87522	CM2	Be		0.767±0.001	-73.7±0.6	1.52	-7.0	0.126	11.6
EET 96029	CM2	A/B	EET 96005	0.811±0.012	-84.8±1.6	1.51	-6.0	0.101	20.3
MIL 07675	CM2	Be	MIL 07497	0.720±0.009	-115.2±2.2	1.23	-10.0	0.079	19.8
MIL 05152	CM2	B		0.683±0.025	-64.5±1.2	1.72	0.3	0.088	30.0
MIL 07700	CM2	A		0.632±0.016	-124.5±0.7	1.12	-11.3	0.039	3.9
PCA 91008	CM2	B		0.720±0.007	-133.8±1.0	0.68	-11.6	0.043	8.8
QUE 93005*	CM2	A/Be	QUE 93005	1.180±0.008	-185.2±1.9	2.00	1.4	0.053	-3.3
QUE 93005	CM2	A/Be	QUE 93005	1.245±0.003	-189.5±0.3	1.80	1.3	0.057	-2.5
CR									
Al Rais	CR2			0.893±0.008	735.5±7.2	2.66	-11.4	0.103	160.6
EET 92042	CR2	B	EET 87711	0.418±0.012	752.5±14.9	1.18	-4.9	0.091	178.7
EET 96286	CR2	B/C		0.375±0.023	610.7±33.9	1.03	-1.9	0.074	173.0
GRA 95229	CR2	A		0.423±0.017	654.6	1.09	0.0	0.078	178.2
GRO 95577	CR1	B		1.288±0.025	266.4±4.5	1.18	-9.2	0.061	182.8
LAP 02342	CR2	A/B		0.395±0.024	691.5±12.8	1.13	-1.9	0.088	162.8
LAP 04720	CR2	B/C		0.380±0.015	763.1±9.1	1.29±0.04	-1.2±0.2	0.100±0.004	166.1±1.0
MET 00426	CR2	B		0.361±0.008	612.4	1.00	-3.3	0.068	179.8
PCA 91082	CR2	Be		0.579±0.015	576.9	1.31	-2.2	0.101	177.1
QUE 99177	CR2	Be		0.466±0.025	662.7	1.26	-7.3	0.088	184.1
Renazzo	CR2			0.452±0.008	702.5±12.4	1.33	-7.1	0.053	173.9
CI									
Orgueil BM	CI1			1.561±0.015	83.9±2.5	3.52	-14.7	0.149	44.1
Orgueil SI	CI1			1.564±0.019	70.7±1.1	3.92	-11.0	0.208	35.9
Ivuna	CI1			1.524±0.094	79.5±0.3	3.50	-4.3	0.207	44.9
Tagish Lake									
TL 11i	C2			0.738±0.009	542.0±8.7	3.95	14.0	0.174	59.7
TL 11h	C2			0.872±0.004	556.6±6.2	4.13	9.4	0.190	62.6
TL 5b	C2			0.945±0.003	507.6±4.0	4.11	10.1	0.241	76.2
CV									
Kaba	CV3			0.225±0.002	13.5±7.8	1.13	-17.1	0.130	-23.7
CO									
ALH 77307	CO3	Ae		0.546±0.010	-48.2±4.4	0.84	-7.1	0.025	-2.7
OC									
Semarkona	LL3.0			0.123±0.000	1,615.9±18.9	0.59	-22.6	0.012	39.3

*These samples were crushed under acetone.

$The Bells C sample was from a stone that was recovered shortly after the fall, while the Bells W sample was from a stone that was recovered after a hurricane. Their similar hydrogen isotopic compositions suggest that these different histories had little effect on their hydrogen contents.

Table S2. A summary of the estimated hydrogen isotopic compositions and abundances in water/OH in the chondrites analyzed, along with the ranges for the bulk meteorites.

	Water D/H ($x10^{-4}$)	Water H (wt.%)	Bulk D/H ($x10^{-4}$)	Bulk H (wt.%)
CI[a]	0.643-0.976	1.33-1.34	1.68±0.01	1.55±0.02
CM	0.865±0.036	0.46-1.36	1.20-2.08	0.56-1.46
CR	$1.71^{+0.17}_{-0.10}$	0.30-1.22	1.97-2.75	0.38-1.29
CO[b]	0.849-1.32	0.49-0.52	1.48	0.55
CV[b]	≤0.820	0.17-0.20	1.58	0.23
Tagish Lake - 11i	0.164-1.14	0.50-0.57	2.40	0.74
Tagish Lake - 11h	0.499-1.07	0.62-0.67	2.43	0.87
Tagish Lake - 5b	0.500-0.723	0.68-0.69	2.35	0.94
OC[b]	2.80-3.44	0.09-0.10	4.08	0.12
RC[c]	7.26±0.13			

[a] The range is based on two samples of Orgueil and one of Ivuna.

[b] These values are for the most primitive members of their groups.

[c] From (*8*).

Table S3. The D/H values for the bulk Earth, the protosolar nebula and in water in the various objects used in Figs. 1-3. By convention, VSMOW (Vienna standard mean ocean water) is the usual reference ratio for calculating δD values. All errors are 1σ.

	D/H	Reference
VSMOW	1.558×10^{-4}	
Bulk Earth	$1.49 \pm 0.03 \times 10^{-4}$	(*102*)
Protosolar	$0.21 \pm 0.05 \times 10^{-4}$	(*103*)
Oort Cloud Comets		
1P/Halley	$3.16 \pm 0.11 \times 10^{-4}$	(*104*)
Hyakutake	$2.9 \pm 1.0 \times 10^{-4}$	(*105*)
Hale-Bopp	$3.3 \pm 0.8 \times 10^{-4}$	(*106*)
C/2002 T7 (LINEAR)	$2.5 \pm 0.4 \times 10^{-4}$	(*107*)
8P Tuttle	$4.09 \pm 1.45 \times 10^{-4}$	(*108*)
153P/Ikeya-Zhang	$<2.5 \times 10^{-4}$	(*109*)
Jupiter family Comet		
103P/Hartley 2	$1.61 \pm 0.24 \times 10^{-4}$	(*13*)
Saturn icy moon		
Enceladus	$2.9^{+1.5}_{-0.7} \times 10^{-4}$	(*18*)
Molecular Clouds	0.001-0.08	(*24*, *25*)

Table S4. The $^{15}N/^{14}N$ values in air (bulk Earth), CI and the protosolar nebula used in Fig. 3. By convention, air is the usual reference ratio for calculating $\delta^{15}N$ values. All errors are 1σ.

	$^{15}N/^{14}N$ ratio	Reference
Air ≈ Bulk Earth	3.6765×10^{-3}	(*110*)
CI	$3.83 \pm 0.02 \times 10^{-3}$	This work
Protosolar	$2.27 \pm 0.03 \times 10^{-3}$	(*111*)

Table S5. The abundances of selected volatiles in the solar composition, bulk CI chondrites and the bulk Earth.

	Solar[a] (mol/g)	CI[b] (mol/g)	Bulk Earth[c] (mol/g)	Bulk Earth/CI (%)
H	7.11×10^{-1}	1.55×10^{-2}	3.00×10^{-4}	1.93
^{12}C	2.05×10^{-4}	3.04×10^{-3}	4.37×10^{-5}	1.44
^{14}N	5.68×10^{-5}	1.34×10^{-4}	1.20×10^{-7}	0.09
^{22}Ne	4.29×10^{-6}	1.81×10^{-12}	2.66×10^{-14}	1.47
^{36}Ar	2.54×10^{-6}	3.26×10^{-11}	1.01×10^{-12}	3.10
^{84}Kr	9.18×10^{-10}	3.57×10^{-13}	2.10×10^{-14}	5.89

[a] Abundances taken from the proto-solar composition of (*112*).

[b] Hydrogen, carbon and nitrogen abundances from this work. Noble gases are the averages for the bulk CI analyses of (*113*).

[c] Abundances from (*29*). 1σ uncertainties are ~50%.

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