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Water Reservoirs in Small Planetary Bodies: Meteorites, Asteroids, and Comets

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Abstract

Asteroids and comets are the remnants of the swarm of planetesimals from which the planets ultimately formed, and they retain records of processes that operated prior to and during planet formation. They are also likely the sources of most of the water and other volatiles accreted by Earth. In this review, we discuss the nature and probable origins of asteroids and comets based on data from remote observations, in situ measurements by spacecraft, and laboratory analyses of meteorites derived from asteroids. The asteroidal parent bodies of meteorites formed ~4 Ma after Solar System formation while there was still a gas disk present. It seems increasingly likely that the parent bodies of meteorites spectroscopically linked with the E-, S-, M- and V-type asteroids formed sunward of Jupiter's orbit, while those associated with C- and, possibly, D-type asteroids formed further out, beyond Jupiter but probably not beyond Saturn's orbit. Comets formed further from the Sun than any of the meteorite parent bodies, and retain much higher abundances of interstellar material. CI and CM group meteorites are probably related to the most common C-type asteroids, and based on isotopic evidence they, rather than comets, are the most likely sources of the H and N accreted by the terrestrial planets. However, comets may have been major sources of the noble gases accreted by Earth and Venus. Possible constraints that these observations can place on models of giant planet formation and migration are explored.

1 Introduction

Despite water's status as the second most abundant molecule in the Solar System, Earth and the rocky planets are highly desiccated worlds. Even if the deep Earth sequesters an order-of-magnitude more water than is in its ocean (e.g., Marty 2012), which is by no means certain, water would still constitute at most 0.2 % of the planet's mass. Nevertheless, this is significantly more than what might be expected based on primary accretion of material from the inner solar nebula (region sunward of Jupiter's orbit). Early-accreted planetesimals from the inner disk would have formed relatively dry because of nebular temperatures that were above the sublimation temperature of water ice. However, even as the temperatures in the region around 1 AU dropped below the ice condensation point later in the evolution of the solar nebula, the local gas is thought to have still remained dry due to the action of proto-

Jupiter preventing the inward drift of earlier-condensed icy particles (Morbidelli et al. 2016). Thus, what water exists in the Earth and rocky planets was probably delivered after the dissipation of the solar nebula gas via later addition of volatile-rich planetesimals that had accreted beyond a “fossilized” snowline (radial distance from the Sun at which H₂O starts to condense at the disk midplane) at around 3 AU (Morbidelli et al. 2016).

The principal reservoirs of such volatile-rich outer Solar System materials are comets and, possibly, the parent asteroids of the carbonaceous chondrite meteorites. It is not known precisely when and at what heliocentric radii each of these classes of primitive Solar System bodies accreted, but it is clear that comets could only have accumulated their volatile inventories in very cold environments (e.g., Bar-Nun and Kleinfeld 1989; Rubin et al. 2015a). Dynamical models of giant planet migration, such as the Grand Tack (Walsh et al. 2011), allow for the formation of asteroids beyond the orbit of Jupiter, well beyond the snowline, and then insertion of some fraction of these water-rich bodies into the present Asteroid Belt during the subsequent outgoing motion of Jupiter. Regardless of the details of their formation, volatile-rich asteroids are known to exist through observations of so-called main-belt comets (Jewitt 2012; Jewitt et al. 2015) and as the parent bodies of carbonaceous chondrites. Many of these meteorites contain ‘water’ at the level of several percent, and in some cases up to 15 % by mass, locked mostly as OH in clay minerals. Thus, considering only mass balance, it is readily apparent that the addition of a few percent of any of these materials to an originally completely dry proto-Earth would be sufficient to account for the abundance of water in this planet. The existence of ample sources is therefore not in question, yet our understanding of the proportion of those sources contributing to the volatile inventory of Earth is far from complete (e.g., Marty et al. 2016; Marty et al. 2017).

This chapter discusses our current understanding of the nature of the asteroidal and cometary reservoirs that may have contributed volatile elements to the Earth and other terrestrial planets. Constraints are derived from the laboratory analysis of meteorites, which are (possibly non-representative) samples of asteroids, and of cometary dust. This cometary dust was either captured from the coma of a comet and returned to the Earth by the Stardust mission (Brownlee et al. 2006) or accreted by the Earth in the form of interplanetary dust particles (IDPs) that were derived from unknown sources. Due to the high-velocity capture of both Stardust particles and IDPs, no laboratory measurements of cometary ices are available, but in situ analyses of molecules in the coma of comet 67P/Churyumov-Gerasimenko have been performed by the Rosetta mission (Le Roy et al. 2015; Rubin et al. 2015a; Rubin et al. 2015b). Here we assess what has been learned about the nature of the volatile inventories of these sources as they relate to those on the Earth and we discuss implications for the accretion of volatiles in the solar nebula, the architecture and dynamics of the Solar System, and processes affecting the distribution of volatiles that may be observed in planetary systems around other stars.

2 Meteorites

2.1 Classification

The classification of meteorites, recently reviewed in detail by Krot et al. (2014), uses both their physical and chemical characteristics. These characteristics reflect both primary

features that were inherited at the time of the accretion of their parent asteroids and secondary features produced by processes that occurred in their parent bodies after accretion. The primary features were set by both ambient conditions (e.g., ice/rock ratios influenced by temperature) at the formation location of a given parent body and by mixing of materials that formed over a wide range of times and radial distances from the Sun. Their secondary features were determined by the extent to which they were heated in their parent bodies and/or interacted with aqueous fluids. The Solar System inherited a number of short-lived radionuclides when it formed, most notably ^{26}Al ($t_{1/2} \approx 720,000$ yrs), whose decay drove the internal heating of the meteorite parent bodies. The extent of parent body processing that a given meteorite experienced primarily reflects the time at which its asteroidal parent body accreted and the depths to which it was buried.

The most basic division of meteorites is into unmelted (chondrites) and melted ones (non-chondrites). Based on estimates of the initial abundances of the short-lived ^{26}Al and, possibly, ^{60}Fe ($t_{1/2} \approx 2.53 \times 10^6$ yrs) and thermal modeling, meteorite parent bodies would not have experienced widespread melting (and differentiation) if they accreted later than ~ 2 Ma after the beginning of Solar System formation (see Sections 2.3 and 2.4). Hence, the chondrite parent bodies should be younger than those of the non-chondrites. Nevertheless, the chondrites provide the more detailed view of the processes that were operating in the early Solar System and will be described first.

2.1.1 Chondrites—The chondrites are comprised of three dominant components – refractory inclusions and chondrules formed at high temperatures and are embedded in a fine-grained ($<5\text{--}10\ \mu\text{m}$), volatile-rich matrix. Refractory inclusions are a diverse group of objects that are broadly divided into Ca-Al-rich inclusions (CAIs) and amoeboid olivine aggregates (AOAs). They are the oldest dated Solar System solids and formed by condensation from a hot gas and/or by melting and evaporation of pre-existing solids (MacPherson 2014). Chondrules appear to have typically formed 1–4 Ma after refractory inclusions (see below for more details) as molten silicate-metal droplets in brief (hours to days) heating events. Being high temperature products that formed in low pressure environments, both refractory inclusions and chondrules are depleted in volatile elements relative to the bulk solar composition. The majority of the most volatile elements in chondrites were probably accreted in the matrix, along with organic matter and presolar circumstellar grains. The matrix probably also originally contained the ices accreted by most chondrite groups. Because it was so fine grained, the matrix was very susceptible to modification by heating and fluid-rock reaction, thus partially or totally obscuring many of the primary components. Nevertheless, the matrix seems to have originally been dominated by a mixture of crystalline and amorphous silicates.

Almost all chondrites belong to one of five classes that have been further subdivided into a number of groups (Table 1), although a few chondrites remain ungrouped.

Each chondrite group is defined by a relatively narrow range of physical features (e.g., sizes and abundances of chondritic components), major and trace element compositions, and bulk O (and Cr) isotopic compositions. After accretion, the internal heating in the chondrite parent bodies, driven by the decay of ^{26}Al and, possibly, impacts, led to varying degrees of

aqueous alteration and/or thermal metamorphism that have modified some or all of the primary features in chondrites. The extent of this modification is reflected in a chondrite's petrologic type – a chondrite that was minimally affected by either aqueous alteration or thermal metamorphism is assigned a petrologic type of 3.0, while petrologic types 3.01–6 reflect increasing degrees of thermal metamorphism and types 2.9–1 reflect increasing extents of aqueous alteration. A meteorite's petrologic type is normally given after its group (e.g., CM1, L3.0 and R6).

While a few chondrites have been assigned to petrologic type 3.0, they are not completely free of the effects of parent body modification. This is because lithification associated with aqueous alteration and/or thermal metamorphism is necessary to produce rocks from originally unconsolidated 'cosmic sediments' that are strong enough to survive impact-driven excavation from their parent bodies and later passage through the Earth's atmosphere. Unless impact heating was more important than is currently generally accepted, we might not expect meteorites to sample asteroids that accreted more than ~4–4.5 Ma after Solar System formation because they would not have contained enough ^{26}Al to melt the water-ice that is necessary to begin the lithification process. If they exist, these un lithified bodies could be one of the sources of interplanetary dust particles (IDPs), comets being the other.

2.1.2 Non-chondrites—The non-chondrites are divided into (i) primitive achondrites that experienced relatively low degrees of partial melting and melt extraction, and (ii) chemically differentiated meteorites that come from bodies that underwent extensive melting and segregation of metal from silicates. The differentiated meteorites are subdivided on the basis of their Fe-metal contents into achondrites (metal-poor), stony-irons, and irons.

Primitive achondrites —: these meteorites (winonaites, acapulcoites/lodranites and brachinites) occasionally contain relict chondrules (i.e., chondrules that have survived the partial melting of their host rocks). However, they have not been conclusively linked to any known chondrite groups. Nevertheless, they support the widely held belief that most planetesimals originally contained abundant chondrules. Only one primitive achondrite, the ungrouped Tafassasset, has geochemical affinities to the carbonaceous chondrites (Gardner-Vandy et al. 2012).

Achondrites —: These are a diverse class of meteorites, although many are broadly basaltic in composition. The aubrites have geochemical affinities to the highly reduced enstatite (E) chondrites. The howardites, eucrites and diogenites (HEDs) are a suite of basaltic and more slowly cooled rocks that, with perhaps a few exceptions, are thought to come from the asteroid 4 Vesta (e.g., McSween et al. 2011). The angrites are also basaltic in nature, but are from a different parent body than the aubrites and HEDs. Ureilites are complex rocks that appear to have been derived from the mantle of their parent body. They are often quite C-rich and exhibit a range of O isotopic compositions that resemble those of carbonaceous chondrites. However, the isotopic compositions of other elements show that they are not related to carbonaceous chondrites. In fact, to date only one achondrite, the ungrouped basaltic achondrite NWA 011, seems to have formed by melting of a carbonaceous chondrite-like body (Warren 2011).

Stony irons –: Mesosiderites are impact breccias composed of diverse silicate clasts mixed with roughly equal amounts of Fe,Ni-metal and sulfide. Pallasites are composed of Fe,Ni-metal/sulfide that is intergrown with similar proportions of relatively coarse grained olivine and pyroxene crystals. There are three recognized sub-types that probably derive from at least three different parent bodies. Traditionally, it has been assumed that pallasites are core-mantle boundary samples, but they experienced a range of cooling rates that would be more consistent with mixing of core and mantle material after an impact (Yang et al. 2010).

Irons –: Iron meteorites are divided into 14 chemical groups, although ~15% of irons remain ungrouped (for review, see Goldstein et al. 2009). The chemical groups fall into one of two categories, magmatic and non-magmatic. The intragroup chemical variations in the magmatic irons are consistent with crystal-liquid metal fractionation during solidification of planetesimal cores. The non-magmatic irons often contain silicate clasts and the chemical variations of their metal are more difficult to understand in terms of crystal-liquid fractionation in a slowly cooling core (e.g., Worsham et al. 2016). These irons are most likely the products of impact melting. Many of the ungrouped irons are also probably impact melts.

2.2 Compositions – elemental and isotopic

While large-scale radial thermal gradients in the disk probably produced some of the gross differences in parent body compositions (e.g., rock/ice ratios), the chondrites show that more transient processes (e.g., chondrule formation) were also important, and that radial transport brought together materials with different thermal histories. The thermal processing of dust in the disk has left its imprint on the major and trace element compositions of almost every inner Solar System object that we have samples of. The most obvious feature in these compositional variations is the strong correlation for many elements between abundance and volatility (Figs. 1 and 2). By convention, the estimates of the volatilities of the elements are based on thermodynamic equilibrium calculations of their 50 % condensation temperatures from a gas of solar composition at a total pressure of 10^{-4} bars (e.g., Lodders 2003). It should always be borne in mind that the absolute and relative condensation temperatures are only as good as the assumptions and thermodynamic data in the models, and will change under different conditions (e.g., total pressure or composition). The CI chondrites occupy a special place in meteoritics as they have compositions that are essentially identical, within error, to the condensable component of the solar photospheric composition (e.g., Lodders 2003; Asplund et al. 2009). Since all Solar System materials presumably ultimately evolved from the solar composition, meteorite elemental compositions are often normalized to (divided by) the CI abundances. In addition to a volatility control on abundance, there is also evidence in meteorites for the fractionation of elements in the nebula according to their chemical affinities (lithophile – rock-loving, siderophile – Fe-metal-loving, and chalcophile – sulfide-loving). Physical processes that separated solid/melt from gas (e.g., condensation, evaporation) and silicates from metal (e.g., gravitational settling, aerodynamic sorting) seem the most likely causes for these variations.

Figure 1 plots the CI normalized elemental composition of the CV chondrites as a function of 50% condensation temperature. It is apparent that for elements with condensation

temperatures below ~1400 K there is a fairly smooth decrease in abundance, irrespective of their chemical affinities, that then levels off for elements with condensation temperatures below ~800 K. There is some scatter that at least in part must reflect uncertainties in the abundances and the condensation temperatures, as well as the influences of processes other than equilibrium condensation (e.g., transport and mixing). The fairly smooth decrease in abundance with condensation temperature is something of a puzzle, as is the leveling off below condensation temperatures of ~800 K. The thermodynamic models predict that the degree of condensation of an element should be a steep function of temperature. To produce the continuous fractionations in chondrites (e.g., Fig. 1) seems to require a combination of condensation and gas-solid fractionation, although the environment in which this took place is still a mystery (Ciesla 2008).

The CV abundance pattern is not unique. The CK, CO and CR abundance patterns are quite similar to those of the CVs. The CM and ordinary (OC) chondrites exhibit, respectively, less and more volatile element fractionation than the CV, but the overall shapes are similar (Fig. 2). The abundances of elements with condensation temperatures below ~800 K roughly correlate with the relative abundance of matrix. This can be seen more clearly in Figure 3a where Zn abundances are plotted vs. the approximate matrix abundances of the different chondrite groups. Not all of the most volatile elements behave in such a systematic way. Cadmium abundances, for instance, are highly variable even within chondrite groups, probably because this element has been redistributed by parent body processes and shock heating (Wombacher et al. 2008).

The simplest interpretation of the fact that the Zn data in Figure 3a fall very close to the line that passes through CI chondrite (essentially 100 % matrix) is that the matrices of all chondrites are dominated by material that is similar in composition to CI chondrites and that the volatile element fractionations are carried by the chondrules and refractory inclusions (Alexander et al. 2001; Alexander 2005; Zanda et al. 2009; Zanda et al. 2012). The enstatite chondrites do not fall on the Zn trend, probably because they formed under highly reducing conditions and as a result the chemical affinities and condensation temperatures for many elements would have been very different to those of the other chondrite groups. It should be pointed out that the dominance of CI-like material in matrix is not universally accepted (e.g., Bland et al. 2005; Hezel and Palme 2010; Palme et al. 2015). Nevertheless, the abundances of circumstellar nanodiamonds (carriers of supernovae derived Xe-HL) (Huss and Lewis 1995) and SiC (Davidson et al. 2014) and bulk C (Fig. 3b) also seem to be in roughly CI-like proportions in chondrite matrices. The bulk of the C (and N) in the most primitive carbonaceous and OC chondrites is in a complex solvent/acid-insoluble, macromolecular organic matter that is generally referred to as IOM (e.g., Alexander et al. 2017a). The organic matter and the presolar circumstellar grains are not Solar System condensates and would not have survived chondrule or refractory inclusion formation, so clearly they are tracers of the presence of very primitive materials in chondrites. Enstatite (E) chondrites do contain circumstellar grains (Huss and Lewis 1995) and C that may once have been organic (Alexander et al. 1998; Alexander et al. 2007). However, all the E chondrites studied to date have been heavily metamorphosed, making the direct comparison with the more primitive carbonaceous and OC chondrites difficult.

The Earth shows a similar pattern of volatile element fractionations to the chondrites, at least for lithophile elements that would not have been affected by core formation (Fig. 2), although Earth is more enriched in refractory elements and more depleted in volatile elements than any chondrite. The addition of 2–4 wt.% of CI- or CM-like material can explain the abundances of many of the most volatile elements in the Earth (Alexander et al. 2012; Marty 2012). There are at least two possible explanations for how CI/CM-like material could be added to the Earth. (1) The conventional explanation is that most of the Earth's planetesimal building blocks were volatile-free but included a small fraction of CI/CM-like planetesimals that were scattered into the terrestrial planet region from the outer asteroid belt (Raymond et al. 2009) or beyond (Walsh et al. 2011; Raymond and Izidoro 2017). (2) Alternatively, like the chondrites, most of the building blocks included some CI-like matrix. Which of these explanations is more likely has important implications for the mechanism of volatile delivery to the terrestrial planets and the dynamical evolution of the inner Solar System (see Section 5).

There is increasing stable isotopic evidence that the carbonaceous chondrites are distinct from all other inner Solar System materials for which we have samples of. For many years, bulk O isotopes were the only isotope system used for the classification of meteorites (e.g., Clayton 1993). It is now apparent that variable excesses in ^{54}Cr and ^{50}Ti abundances can also be used to distinguish between the different meteorite groups (Trinquier et al. 2007; Trinquier et al. 2009; Qin et al. 2010; Warren 2011). The sizes of certain isotopic anomalies in other elements also hold promise, such as ^{62}Ni , ^{92}Mo and ^{100}Ru (Regelous et al. 2008; Burkhardt et al. 2011). Except for O, these isotopic anomalies are thought to ultimately be nucleosynthetic in origin. However, it remains unclear whether the anomalies reflect spatial/temporal heterogeneities in the material accreted by the Solar System or an 'unmixing' of an originally homogeneous mixture of presolar materials by unidentified physical and/or chemical processes operating in the disk. Heating of dust composed of materials with different thermal stabilities coupled with gas-solid fractionation is one possible mechanism for 'unmixing' in the disk (e.g., Trinquier et al. 2009; Burkhardt et al. 2012), although there appears to be no simple correlation with the volatility trends seen in the chondrites. The isotopic differences between carbonaceous chondrites and all other materials is certainly consistent with the suggestion of the Grand Tack model that the carbonaceous chondrites formed in the outer Solar System, beyond the orbit of Jupiter (Walsh et al. 2011). Indeed, it is possible that the isotopic differences reflect the isolation of the inner and outer Solar Systems by the growth of Jupiter to a size of about 20 Earth masses by ~1 Ma after CAIs (Kruijer et al. 2017a). However, this still leaves unexplained the cause(s) of the differences in the inner and outer Solar System compositions.

2.3 Timing of differentiation, metamorphism and aqueous alteration

While the timing of various parent body processes are important in their own right, they are also a means for indirectly estimating the times of accretion of the various meteorite parent bodies (next section). Constraints on the timing of accretion of meteorite parent bodies would allow inferences regarding variations in the composition of dust in the regions of the disk where the parent asteroids of meteorites formed, including the snowline. In addition, since parent body processes have profoundly modified the H (and C and N) budgets of most

planetesimals, understanding the timing of these processes with respect to planet formation timescales is essential.

In recent years there have been tremendous advances in our understanding of the timing of chemical differentiation and core formation in planetesimals. This has been largely based on the short-lived ^{182}Hf - ^{182}W system ($t_{1/2}=8.9\times 10^6$ yrs). For instance, core formation in the IIAB, IIIAB, IVA, IVB, and IID iron meteorite parent bodies occurred at 0.7 ± 0.3 , 1.2 ± 0.3 , 1.4 ± 0.5 , 2.9 ± 0.5 , and 3.1 ± 0.8 Ma after CAIs, respectively (Kruijer et al. 2014). Kleine et al. (2012) were also able to determine that core formation in the angrite parent body occurred 2 Ma after CAIs. Estimates for the timing of differentiation of the HED parent body, 4 Vesta, range from 2.2 ± 1.1 Ma (Trinquier et al. 2008) based on the short-lived ^{53}Mn - ^{53}Cr system ($t_{1/2}=3.7\times 10^6$ yrs), to ~ 1 Ma using the ^{182}Hf - ^{182}W system (Touboul et al. 2015), and to $\leq 0.6^{+0.5}_{-0.4}$ Ma (Schiller et al. 2011) using the short-lived ^{26}Al - ^{26}Mg system. Taken together, these results demonstrate that planetesimal accretion and planetary-scale melting and chemical differentiation occurred rapidly, within a few million years (or less) of the formation of the first Solar System solids.

Large, fully differentiated asteroids or their collisional remnants are not likely to be volatile-rich and are generally not considered as important sources of water to the inner Solar System. Instead, it is the smaller, later formed planetesimals, the parent bodies of the chondritic meteorites, that are the best candidates for being the sources of water and other volatiles. The abundances of water in such bodies, and in the meteorites derived therefrom, would be largely dictated by the peak temperatures experienced during early geologic processing on a given parent asteroid. On the one hand, if temperatures never exceeded the melting temperature of ice, there would have been no lithification and samples of these parent bodies are unlikely to be delivered to Earth as meteorites. On the other hand, if peak temperatures exceeded the low-pressure stability limits of common phyllosilicates, most of the water is likely to have been lost to space. There is no single age for such metamorphism since the cycle of heating and cooling will have taken place over a protracted length of time. However, since ^{26}Al with a half-life of ~ 0.72 Ma was the main internal heat source, peak metamorphic temperatures ought to have been achieved within 5–10 Ma of Solar System formation (e.g., Miyamoto et al. 1981; Kleine et al. 2008).

Some idea of when aqueous alteration occurred in the affected chondrites comes from the dating of two products of fluid-rock interaction, fayalitic olivine (Fe_2SiO_4) and carbonates (e.g., CaCO_3), that incorporated short-lived ^{53}Mn . Fayalitic olivine in the OC chondrites formed at $2.4^{+1.8}_{-1.3}$ Ma after CAIs, while in CV and CO chondrites it formed at $4.2^{+0.8}_{-0.7}$ Ma and $5.1^{+0.5}_{-0.4}$ Ma after CAIs, respectively (Doyle et al. 2015). The carbonates in CI, CM and CR chondrites and the ungrouped C2 Tagish Lake also formed within this 4–5 Ma interval (Fujiya et al. 2012; Fujiya et al. 2013; Jilly-Rehak et al. 2017; Steele et al. 2017). Of course, these ages are only the formation ages of these particular minerals. We have few constraints on the total length of time liquid water was present in these chondrites.

2.4 Timing of accretion

At present, the accretion ages of chondrites cannot be measured directly, but there are indirect methods for estimating the time of accretion. This subject has recently been reviewed by DeMeo et al. (2015) and is only briefly summarized and updated here and in Table 2.

One way to estimate the accretion ages of the chondrite parent bodies is to assume that they are the same as the ages of their youngest chondrules. Chondrules ages can be dated using both short-lived chronometers, such as the ^{26}Al - ^{26}Mg system (e.g., Ushikubo et al. 2013), and the long-lived Pb-Pb system (e.g., Connelly et al. 2012). However, parent body processes can disturb these chronometers producing younger apparent ages that do not date chondrule formation. So, it is essential to study only the most primitive chondrites and to select only those chondrules that can be shown to have undergone no secondary modification. As noted earlier, chronology based on the ^{26}Al - ^{26}Mg system depends on the assumption of an initially uniform $^{26}\text{Al}/^{27}\text{Al}$ ratio throughout the solar nebula which is still the subject of debate. Given that the number of chondrules with fairly precisely measured ages for any chondrite group also tends to be small and the possibility that particularly young chondrules are disturbed, DeMeo et al. (2015) used averages of measured chondrules to constrain accretion ages. The most careful ^{26}Al - ^{26}Mg study of chondrule ages to date has been for the ungrouped carbonaceous chondrite Acfer 094 in which 9 of 10 chondrule ages are within error of a mean of $2.3^{+0.5}_{-0.3}$ Ma after CAIs (Ushikubo et al. 2013). As can be seen from Table 2, the mean ages for the OC, CO and CV chondrite chondrules are similar to Acfer 094. On the other hand, Schrader et al. (2016) have estimated an average age for 95% of CR chondrite chondrules of $3.7^{+0.3}_{-0.2}$ Ma after CAIs. This compares favorably with a corrected bulk CR chondrule Pb-Pb age of $3.7^{+0.9}_{-0.9}$ Ma after CAIs (Schrader et al. 2016). However, there are some CR chondrules without detectable ^{26}Mg excesses that may be significantly younger than these mean chondrule ages, prompting Schrader et al. (2016) to suggest a limit on the CR accretion age of $> 4.0^{+0.5}_{-0.3}$ Ma after CAIs.

The timing of accretion of chondrites can also be constrained from their thermal histories since accretion time will determine the abundance of the dominant heat source, the short-lived ^{26}Al , at the time of accretion. For instance, several modeling studies of the H ordinary chondrite parent body suggest that it formed ~ 2 Ma after CAIs (Table 2), which is consistent with estimates of the mean OC chondrule ages (Table 2). Modeling of the formation conditions and ages of secondary minerals during aqueous alteration suggests accretion ages after CAIs for the OC parent bodies of ~ 1.8 Ma, for the COs and CVs of ~ 2.5 Ma, and 3–4 Ma for the CI, CM, CR and Tagish Lake chondrites (Table 2). Based on the properties of their insoluble organic matter (IOM) that are indicative of peak temperatures during alteration, the CIs and CMs may have accreted slightly earlier than Tagish Lake and the CRs (Alexander et al. 2014b). To estimate accretion ages, Sugiura and Fujiya (2014) took the maximum peak temperatures experienced by any member of a chondrite group to be the peak central temperature achieved in their parent body. Despite the many assumptions in their approach, the estimates by Sugiura and Fujiya (2014) are broadly consistent with the other constraints (Table 2). The fact that no known chondrites have accretion ages much

younger than ~4 Ma after CAIs is consistent with our earlier statement that there would not have been enough short-lived radioactivity in bodies that accreted later than this for them to become lithified. It is true that the CB chondrites (and possibly the related CHs) formed 4.6 ± 0.5 Ma after CAIs (Krot et al. 2005; Yamashita et al. 2010), but they seem to be the product of an impact. A gaseous disk protects material near the midplane from the solar wind. The lack of solar wind implanted noble gases in the CRs suggests that the gas disk dissipated later than ~4 Ma after Solar System formation.

Further complicating the estimates of chondrite accretion ages has been the suggestion that the CV chondrites, at least, formed in the presence of a magnetic field that was generated by a core dynamo (Weiss and Elkins-Tanton 2013). If correct, this means that the CVs are the unheated crusts of differentiated bodies and that they must have accreted significantly earlier than estimated by Sugiura and Fujiya (2014). This may be more consistent with their ~2 Ma chondrule ages (Table 2). However, no achondrites or iron meteorites have yet been found that can be linked to the CV group. The search for evidence in other chondrite groups for formation in the presence of magnetic fields (both disk- and asteroid-generated) is ongoing.

Thermal modeling of differentiated bodies is even more problematic than for chondrites because, for instance, the initial bulk composition is not known and how the melts segregate within the bodies can have a profound effect on internal heating (e.g., Moskovitz and Gaidos 2011; Neumann et al. 2014). Nevertheless, models of varying degrees of sophistication have been used to estimate their accretion times, and range from ~0.1–0.3 Ma after CAIs for some iron meteorites, to <1 Ma after CAIs for 4 Vesta, and 1.5 Ma and ~1.6 Ma after CAIs for the angrite and ureilite parent bodies, respectively.

2.5 Water in chondrites

The initial abundances and isotopic compositions of water in chondrites can help constrain the ambient conditions when they accreted as well as the origin of the water.

Parent body processes will have modified the initial water abundances of chondrites. Thermal metamorphism, for instance, will have largely dehydrated the interiors of the earlier-formed chondrites (E, OC, R, CK, CV, CO). In the aqueously altered chondrites, much of the water will have been consumed in the formation of phyllosilicates (clay minerals, etc.) and is now stored as OH in the mineral structures. However, the H in water will also have been lost through oxidation reactions mostly involving Fe, such as $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$. For chondrites that accreted with high metal/water ratios, a large fraction of the water may have been lost in this way (Sutton et al. 2017).

It is very unlikely that the chondrites in our collections retain much, if any, indigenous water. If any chondrite parent bodies did retain some unreacted water it would have refrozen as they cooled, but it would have subsequently sublimed away when the meteorites were small objects in space. However, many of the more primitive chondrites do contain OH in phyllosilicates, phosphates and hydroxides that are the products of aqueous alteration. Some phyllosilicates can have water in their structures, but this water is easily lost in vacuum or exchanged once in the terrestrial environment. The chondrites also contain H associated with organic matter that when delivered to a growing planet could be oxidized to produce water.

Hence, in terms of their potential as sources of 'water' to growing terrestrial planets, it is the bulk H contents of chondrites that are important and are listed in Table 3. Also given in Table 3 are the bulk C and N contents, and the bulk H and N isotopic compositions as they can also be used to constrain the contributions that the different chondrite groups may have made to the volatile inventories of the terrestrial planets.

The H contents in chondrites can be highly variable even between meteorites belonging to the same group. This is due to the variable degrees of alteration and/or thermal metamorphism they experienced. For the CI, CM and CR chondrites and Tagish Lake the averages of the samples that have been analyzed are given in Table 3, with the uncertainties reflecting the intra group variations. It is not clear why the extent of alteration and H content is particularly variable amongst the CM and CR chondrites. It is possible that the abundance of ice at the time of accretion was heterogeneous at the scales sampled by the meteorites, but it seems more likely that there was some redistribution of water within the parent bodies once the ice melted.

For the CV, CO, and OC chondrites that experienced variable degrees of thermal metamorphism and dehydration, the values in Table 3 are for the most primitive known members of the groups. There are no known very primitive (i.e., type 3.0) E, K, CK, or R chondrites. The H, C, and N contents of the more metamorphosed chondrites fall to near zero by petrologic types 3.6–3.7 and above. Thermal models suggest that the lowest petrologic types will have been confined to relatively thin layers near the surfaces of the metamorphosed chondrite parent bodies (e.g., Miyamoto et al. 1981; Harrison and Grimm 2010; Henke et al. 2012). Hence the H, C, and N abundances in Table 3 should be considered as upper limits for the final bulk compositions of the chondrite parent bodies, although it is possible that at least early on these bodies had ice-rich, near-surface layers as a result of re-freezing of water expelled from their interiors.

As we have seen, the peak of metamorphism and aqueous alteration would have been over within the first 5–10 Ma of the Solar System. The Earth did not reach its final mass until ~60 Ma after CAIs (Touboul et al. 2007; Barboni et al. 2017). However, there is geochemical evidence that Mars had reached ~50 % of its present mass in $\leq 1.8_{-1.0}^{+0.9}$ Ma after CAIs (Dauphas and Pourmand 2011; Tang and Dauphas 2014). Hence, it is possible that the planetary embryos from which the Earth and rocky planets formed accreted some or all of their volatiles very early when many chondrite-like planetesimals were more volatile-rich than they are now.

The H contents of the most primitive members of the CV, CO and OC chondrites provide lower limits on the initial contents of their parent bodies at the time of accretion (i.e., pre-metamorphism/alteration) because of the potential loss of H (as H₂O, H₂, etc.) to space. An alternative estimation of their initial H contents can be made if the earlier argument is correct that the matrices of chondrites were largely CI-like. Figure 4 plots the H contents vs. matrix contents of the various chondrites listed in Table 3.

The H contents of CVs, Tagish Lake and OCs are significantly below what would be predicted if their matrices initially had CI-like H concentrations. This probably reflects a

combination of H loss associated with oxidation of Fe by water (Alexander et al. 2010; Alexander et al. 2012; Sutton et al. 2017) and thermal dehydration. The CO and CR chondrites fall very close to the CI mixing line, but this may partially be coincidence as the COs are represented by the Antarctic meteorite DOM 08006 that has seen some terrestrial weathering and the CR value is quite uncertain (Table 3). Alteration in the CI chondrites has essentially gone to completion. Since it is very unlikely that the CI chondrites coincidentally accreted just enough water to achieve this, they probably accreted significantly more water than they currently contain in their clay minerals. This may explain why the generally less altered CM chondrites fall well above the CI mixing line – unlike for the CIs, in the CMs excess water after alteration of the matrix could then react with chondrules. If correct, the average CM value would suggest that the initial H contents of CI chondrites (and chondrite matrices) could have been at least 50 % higher than observed today. Note, however, that even this elevated water content is significantly less than the roughly equal masses of water and silicates predicted for a system of solar composition (e.g., Lodders 2003). The fate of water that was not incorporated into clay minerals or consumed by oxidizing Fe is uncertain. It could have simply refrozen in pore spaces – ice-bearing asteroids are present in the asteroid belt (see below). Alternatively, it may have been lost to space while the interiors of the chondrite parent bodies were still warm.

The isotopic composition of water can also be revealing about its origins. It has long been suspected that water was responsible for producing the intragroup and, to some extent, intergroup mass independent O isotopic variations seen in chondrites (e.g., Clayton and Mayeda 1999; Young et al. 1999). Typically, O isotope compositions are given in the geochemical delta notation, for instance where $\delta^{17}\text{O} (\text{‰}) = 1000 \cdot (R_{\text{sample}}/R_{\text{standard}} - 1)$ and $R = {}^{17}\text{O}/{}^{16}\text{O}$, with the scale normalized to Standard Mean Ocean Water or SMOW. Most physical and chemical processes fractionate O isotopes in a mass dependent fashion, such that in a plot of $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ samples will lie on a line with a slope of ~ 0.52 . Unlike almost all terrestrial materials, most extraterrestrial materials exhibit some mass independent fractionation (i.e., they do not fall on the terrestrial mass fractionation line or TFL). This mass independent fractionation is usually expressed as ${}^{17}\text{O} (\text{‰}) = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$, i.e., the distance from the TFL for a given value of $\delta^{18}\text{O}$. By definition, anything lying on the TFL has a ${}^{17}\text{O} = 0\text{‰}$. Most available Solar System materials (Earth, Moon, Mars, bulk meteorites, chondrules, matrix, and interplanetary dust) have ${}^{17}\text{O}$ values that fall fairly close to the TFL ($\pm 5 \text{‰}$), but remarkably the Sun has a ${}^{17}\text{O} = -28.4 \pm 1.8\text{‰}$ (McKeegan et al. 2011). The only known objects with O isotopic compositions that are close to solar are refractory inclusions and a few rare chondrules (Kobayashi et al. 2003).

It has been suggested that an influx of water produced by UV dissociation of CO either in the protosolar molecular cloud (Yurimoto and Kuramoto 2004) or in the disk (Lyons and Young 2005) was responsible for the near-terrestrial O isotopic compositions of almost all inner Solar System solids. The models predict that the water should have large mass independent O isotope anomalies, although the exact values depend on the model parameters. The most extreme ${}^{16}\text{O}$ depletions observed in any Solar System material is ${}^{17}\text{O} \approx 86 \text{‰}$ in a rare mineral association (magnetite-sulfide) found only in the ungrouped meteorite Acfer 094 (Sakamoto et al. 2007). It is often assumed to reflect the isotopic

composition of the water responsible for modifying the composition of dust in the inner Solar System.

The O isotopic compositions of the fluids responsible for the alteration in the chondrites can be estimated from the O isotopic compositions of secondary minerals such as magnetite (Fe_3O_4), fayalite (Fe_2SiO_4) and calcite (CaCO_3). It is likely that prior to forming these secondary minerals the fluid interacted with primary, anhydrous silicates that tend to be more ^{16}O -rich. Nevertheless, the most ^{16}O -poor secondary mineral compositions from a chondrite group (Table 4) can be used to place lower limits on the compositions of the altering fluids. As can be seen from Table 4, the compositions of the fluids that produced the secondary minerals in the chondrites do not seem to have been particularly anomalous. Nor is there any obvious evolution in isotopic composition with the inferred accretion ages of the chondrite parent bodies, despite the fact that material and the snowline would have been migrating sunwards during this time (e.g., Oka et al. 2011). The O (and H) isotopic composition of water is likely to have evolved with time and radial location along with the thermal structure of the disk (e.g., Yang et al. 2013).

Hydrogen isotopes can also be informative about the origins of the water in meteorites. The potential extremes for the water H isotopic composition, relative to SMOW ($\text{D}/\text{H}=1.5576\times 10^{-4}$), range from $\delta\text{D}=-865\text{‰}$ ($\text{D}/\text{H}=2.1\times 10^{-5}$) for water that equilibrated with solar H_2 at high temperatures to $\delta\text{D}\approx 5400\text{‰}$ ($\text{D}/\text{H}=1\times 10^{-3}$) for interstellar water inherited from the protosolar molecular cloud (e.g., Liu et al. 2011; Coutens et al. 2012; Coutens et al. 2013). Unlike molecular clouds, disks are probably unable to make D-rich water even in their cooler regions (Cleeves et al. 2014; Cleeves et al. 2016). The bulk Earth δD value is estimated to be about -43‰ (Lécuyer et al. 1998).

Estimating the initial water isotopic compositions in chondrites is made difficult by the intimate association of phyllosilicates and D-rich organic matter in meteorite matrices, as well as the possibility of isotopic exchange between water and organics during aqueous alteration. Alexander et al. (2012) estimated the initial water compositions (Table 4) by assuming that all chondrites accreted the same D-rich organic matter and subtracting this from the bulk H compositions. There are three major features of the estimated H isotopic compositions. The waters in CIs, CMs and Tagish Lake seem to have had H isotopic compositions that fall between the solar and terrestrial values, the CR chondrite water were slightly heavier than terrestrial, whereas the waters in OC and R chondrites were very D-rich.

If taken at face value, the compositions of the OC and R chondrites imply that they accreted proportionally more interstellar water than any carbonaceous chondrites (Deloule et al. 1998; Piani et al. 2015), although the matrices of the OC chondrites at least are no richer in circumstellar grains or organics than the carbonaceous chondrites. An alternative explanation is that when H_2 was lost as a result of Fe oxidation, the H_2 was very D-poor and left behind increasingly D-rich water (Alexander et al. 2010; Alexander et al. 2012; Sutton et al. 2017). On Earth, H_2 generated by Fe oxidation during low temperature serpentinization can have very isotopically light (δD as low as -700 to -800‰) compositions (e.g., Coveney et al. 1987; Fritz et al. 1992; Proskurowski et al. 2006). As discussed above, the OC and R

chondrites probably had amongst the lowest water/rock ratios of the chondrites, and so the isotopic effect of H₂ loss would have been largest in them. Given this scenario, the initial δD value of water in OC chondrites might have been similar to those estimated for the CIs and CMs (Sutton et al. 2017). This fractionation process should have also affected the carbonaceous chondrites. It should have had a relatively modest effect on the CIs, CMs and Tagish Lake because of their relatively high water/rock ratios, but may explain the higher δD value of the CR chondrites than other carbonaceous chondrites (Sutton et al. 2017). At present, there is little evidence for isotopic fractionation of H associated with Fe oxidation in the CV and CO chondrites, which is a puzzle.

The fact that both the ¹⁶O depletions and D-enrichments in chondritic water are much less than predicted for interstellar water, and in the case of O less than predicted for water produced by UV dissociation of CO near the disk surface, suggests that most of the water in chondrites had been reprocessed in the disk prior to accretion by the chondrites (Alexander et al. 2017c).

2.6 Water in achondrites

While most of the work on water in meteorites has focused on the chondrites, HEDs and angrites are known to contain trace amounts of water in minor phases such as phosphate (Sarafian et al. 2014; Barrett et al. 2016; Sarafian et al. 2017a; Sarafian et al. 2017b). They may also contain water, albeit at even lower abundances, in nominally anhydrous minerals like olivine and pyroxene. The other achondrite groups have yet to be studied in detail. Nevertheless, the implication of these observations is that even differentiated bodies should be considered as potential sources of some of the water in the terrestrial planets, although at present there are no accurate estimates for the bulk water contents of even the HED and angrite parent bodies.

The H isotopic compositions of the HEDs and angrites are broadly consistent with those of bulk carbonaceous chondrites (Sarafian et al. 2014; Barrett et al. 2016; Sarafian et al. 2017a; Sarafian et al. 2017b). It has been argued that this water was acquired by late accretion of carbonaceous chondrite material while Vesta and the angrite parent body were still at least partially molten (Sarafian et al. 2014; Sarafian et al. 2017a; Sarafian et al. 2017b). A few HEDs and angrites have crystallization ages that are <4 Ma after CAIs, presenting a bit of a conundrum since this is roughly contemporaneous with the formation times of the CI, CM and Tagish Lake parent bodies and before formation of the CRs or the Grand Tack. In which case, what was the source of the water-rich, carbonaceous-chondrite-like bodies that collided with Vesta and the angrite parent bodies? Raymond and Izidoro (2017) have presented one potential solution by arguing that outer Solar System objects would have been continuously scattered into the inner Solar System as the giant planets grew. On the other hand, it has not been definitively demonstrated that differentiated bodies would lose all the water that they may have accreted when they formed. Matrix material with several characteristics that resemble CI chondrites was present in the inner Solar System when the OC and R chondrites formed ~2 Ma after CAIs (Section 2.2), despite the evidence that Jupiter may have more-or-less sealed off the inner Solar System 1 Ma earlier (Kruijer et al. 2017a). If chondrite matrix material and the snowline were present in the inner Solar System earlier than 2 Ma after

CAIs, bodies that differentiated could have accreted some water. However they acquired their water, it is possible that differentiated bodies were contributors to the volatile budgets of the terrestrial planets, but to assess this possibility quantitatively requires knowledge of the volatile inventories of differentiated bodies, which remains unknown.

3 Asteroids

3.1 Classification

The Asteroid Belt is often divided into annular regions based on the locations of major resonances. Accordingly, the asteroids can be grouped dynamically based on the semi-major axes of their orbits into: (1) the Hungaria 1.8–2 AU; (2) inner belt bodies 2.1–2.5 AU; (3) the middle belt bodies 2.5–2.8 AU; (4) outer belt bodies 2.8–3.3 AU; (5) Cybeles 3.3–3.6 AU; (6) Hildas 3.9–4 AU; and (7) Jupiter Trojans (5–5.4 AU).

Historically, three spectroscopic classification schemes have been proposed for asteroids (for an overview see DeMeo et al. 2015). All three classification schemes are based on features in the reflectance spectra of asteroids at visible and, when possible, near infrared wavelengths, as well as their albedos, if measured. The asteroid spectra have been divided into three main groups or complexes (S-complex, C-complex and X-complex) that have been subdivided into a number of types. It is important to note that membership in a given complex does not necessarily imply a genetic relationship between bodies. There are also a number of asteroid types that do not belong to any of these complexes.

When asteroids are separated into these broad groups, it is apparent that for the larger (>50 km diameter) asteroids there is a systematic variation in their relative abundances with heliocentric distance (Gradie and Tedesco 1982; DeMeo and Carry 2013, 2014) with the inner belt being dominated by S-complex asteroids and Vesta, the middle and outer belts by C-complex asteroids, the Cybeles and Hildas by P-types, and the Jupiter Trojans by D-types. Whereas P-types are members of the X-complex, the D-types do not belong to any of the complexes, although both P- and D-types are thought to be amongst the most primitive (least heated and most organic-rich) asteroids.

While particular groups may dominate in one region, it is important to bear in mind that asteroids of that group are not confined to that region. For example, although S-complex asteroids dominate in the inner belt, if one excludes Vesta, more than half the mass of S-complex bodies is found in the middle belt and a further ~15% in the outer belt. Similarly, E-type asteroids (members of the X-complex) are often associated with the Hungaria (interior to 2 AU), but most of the mass of E-types is to be found in the inner and middle belts. Finally, the D-types dominate the Jupiter Trojans but can also be found in the inner belt (DeMeo et al. 2014).

3.2 The asteroid-meteorite connection and the distribution of water-bearing bodies

Establishing links between meteorite groups and asteroid types can help illuminate the age distribution of asteroids, the abundances of potential sources of water for the terrestrial planets, and constrain how the Asteroid Belt was populated. The subject of asteroid-meteorite links was reviewed in detail by Burbine et al. (2002), and here we highlight more

recent developments. The E-asteroids have been linked to the aubrites (or enstatite achondrites) (Zellner et al. 1977; Gaffey et al. 1992; Binzel et al. 2004). The OCs have long been thought to be associated with S-complex and ungrouped Q asteroids, although R chondrites, primitive and basaltic achondrites, and pallasites have also been linked to S-complex asteroids. Specifically, the LL chondrites have been associated with the Flora family (~2.2 AU) (Vernazza et al. 2008; Dunn et al. 2013), the L chondrites to the Gefion family (~2.8 AU) (Nesvorný et al. 2009), and the H chondrites to Hebe (~2.4 AU) (Gaffey and Gilbert 1998), although there are many potential sources of the H chondrites between the Kirkwood gaps at the 3:1 (2.5 AU) and 5:2 (2.82 AU) resonances with Jupiter (Vernazza et al. 2014).

The vast majority of the HED meteorites are thought to derive from Vesta (~2.4 AU) and the V-type asteroid members of the Vesta family (McCord et al. 1970; McSween et al. 2011). However, a small number of eucrites are isotopically distinct from the other HEDs and may come from five other differentiated bodies (Scott et al. 2009). This is consistent with the fact that there are a small number of V-type asteroids, unrelated to Vesta, that are distributed throughout the asteroid belt (Lazzaro et al. 2000; Sunshine et al. 2004; Moskovitz et al. 2008; Duffard and Roig 2009), the most distant having semi-major axes of ~3.1 AU.

The signature feature of the CI and CM chondrites is that they have undergone extensive aqueous alteration and contain abundant phyllosilicates. This is also true for some CR chondrites. There is spectroscopic evidence that at least 60–70 % of C-complex asteroids experienced some aqueous alteration and that this fraction is fairly uniform across the asteroid belt (Jones et al. 1990; Rivkin 2012; Fornasier et al. 2014; Rivkin et al. 2015). The majority of these belong to the Ch- and Chg-types that are spectroscopically similar (having 0.7 μm and ‘sharp’ 3 μm absorption features) to the CM chondrites (Rivkin et al. 2015; Takir et al. 2015). Those asteroids with a ‘sharp’ 3 μm absorption feature but lacking the 0.7 μm absorption features could be similar to either CM or CI chondrites. Given the number of asteroids with similar spectra, it is possible that the CMs and CIs come from multiple parent bodies. The sources of the other carbonaceous chondrites are even less certain.

Beyond ~3.3 AU, the 3 μm absorption feature of most measured asteroids is rounded rather than sharp (Takir and Emery 2012), and this is thought to be due to the presence of ice rather than phyllosilicates (Campins et al. 2010; Rivkin and Emery 2010). This is observed for several members of the Cybele family (~3.4 AU) that are mixed C- and P- types, and the Hilda family (~4 AU) that are P-type. One C-type member of the Hildas (but not part of the collisional family) shows the ‘sharp’ 3 μm absorption feature characteristic of phyllosilicates (Takir and Emery 2012). The same is true for one member of the Cybele family, suggesting that, prior to disruption, the parent body of the Cybele family experienced at least some aqueous alteration but its water was not entirely consumed by this process. Although water ice is most commonly found in bodies beyond 3.3 AU, it is not exclusive to this outer zone. In fact, the first direct detection of ice was made on the asteroid Themis (~3.1 AU) (Campins et al. 2010; Rivkin and Emery 2010) and four of the eight active asteroids (or main-belt comets) that appear to be driven by ice sublimation are members of the Themis family, two others belong to the Lixiaohua family (~3.2 AU), and of the remaining two, one belongs to a small, young cluster (Jewitt et al. 2015). Thus, it seems likely that disruption of larger

asteroids produces fragments with surface ice. Small impacts on the surfaces of the fragments reveals buried ice that then sublimates to space, producing the observed activity, until an insulating layer of dust develops. In this respect, Ceres (~2.8 AU) is unique as phyllosilicates are widespread on its surface, it vents water from multiple, localized areas and it has surface deposits that are rich in carbonates that do not appear to be related to recent impacts (Küppers et al. 2014; De Sanctis et al. 2016). It seems possible that internal temperatures in parts of Ceres are sufficient to maintain liquid brines that occasionally escape to the surface. To date, we have no meteorites that can be linked to Ceres.

The D-type asteroids dominate the Trojan population, but <50 km diameter bodies with D-type spectra are present even in the inner belt. There is no evidence in their spectra for either ice or phyllosilicates. Nevertheless, it has been suggested that one aqueously altered chondrite, the ungrouped C2 Tagish Lake, may be related to D-type asteroids (Hiroi et al. 2001) though this has been challenged (Vernazza et al. 2013).

3.3 The stratigraphy of the asteroid belt

If the association of asteroid spectral classes with specific meteorite groups is correct then we can infer, based on meteorite chronologies, that Vesta, the V-type, E-type and S-complex asteroids all formed ~2 Ma after Solar System formation. They are also relatively volatile-poor, either because they did not accrete many volatiles or because their strong internal heating drove out almost all the volatiles they had originally contained. The fact that most C-complex asteroids exhibit affinities to the CM and CI chondrites suggests that they formed ~3.5–4 Ma after CAIs. We do not have any recognized samples of P-type asteroids in the meteorite collection, but the absence of evidence for phyllosilicates at their surfaces despite the evidence for ice on some of them seems to imply that they formed later than ~4 Ma after CAIs, by which time there was insufficient internal radioactivity to melt the ice. However, D-type asteroids do not show evidence for phyllosilicates at their surface either. Yet if the Tagish Lake chondrite is from a D-type asteroid, they did experience aqueous alteration and they formed at about the same time as the CM and CI chondrites.

To date, it is unclear how abundant CK-, CV- and CO-like parent bodies are in the Asteroid Belt and what their orbital distributions are. The best spectral matches are to the relatively rare K-type asteroids, but the matches are by no means perfect (e.g., Cloutis et al. 2012a; Cloutis et al. 2012b; Cloutis et al. 2012c). The timing of the accretion of the CK, CV and CO chondrites seems to have been between the accretion of the OCs and the CI-CM-CR and Tagish Lake chondrites. This would suggest that there may have been a delay in planetesimal formation between the accretion of the V- and S-complex asteroids on the one hand, and the accretion of most C-complex and, possibly, D-type asteroids on the other.

Thus, to first order, it appears that asteroids in the inner belt tend to have formed earlier, experienced higher internal temperatures and accreted (or retained) less volatiles than asteroids in the outer belt, the Hildas and the Trojans. One explanation for this distribution invokes a wave of planetesimal formation that slowly progressed outwards through an Asteroid Belt that was chemically zoned with the snow line located somewhere in the middle belt (e.g., Grimm and McSween 1993; McSween et al. 2002). However, it seems unlikely that conditions would have remained essentially static in the Asteroid Belt for the

1.5–2 Ma that apparently separates the formation of the OC and E chondrites from the CICM-CR carbonaceous chondrites. Nor is it clear why there would have been such an orderly and sedate progression through the asteroid belt when bodies as large as Mars were beginning to form within ~2 Ma in the inner Solar System and the cores of the giant planets must have been largely formed by ~4 Ma if they were to have sufficient time available to acquire their gaseous envelopes before the gas disk dissipated.

The OCs show clear petrologic evidence for aqueous alteration prior to metamorphism. If the LL chondrites are linked to the Flora family, this suggests that by ~2 Ma the snowline was sunward of 2.2 AU. This is consistent with model predictions for the evolution of the snowline inwards in a disk as the main heat source, transport of material through the disk and onto the star, decreases with time (e.g., Oka et al. 2011; Bitsch et al. 2015). In principle, dry planetesimals could have accreted ice inside the snowline from ice-bearing bodies that were scattered or drifted sunward (e.g., Morbidelli et al. 2015), but as discussed earlier the chondrites accreted their water and other volatiles in fine-grained matrix, not in large bodies. This then raises the question of why the OCs did not accrete water in roughly its solar abundance (water/rock \approx 1: Lodders 2003). Morbidelli et al. (2016) argue that in accretion disks gas will flow sunward faster than will condensation fronts. As a result, dry gas that has been depleted of water by ice condensation beyond the snowline will gradually flush any wet gas sunward of the snowline into the Sun. In this scenario, the chondrite matrices could then be dust that followed the gas as it migrated from the outer Solar System into the inner Solar System. The influx of dust into an Asteroid Belt that had been depleted by an earlier phase of planetesimal formation (S-complex and V-types) could potentially explain a second phase of asteroid formation (the C-complex and D-types), the general increase in matrix abundances in chondrites with their formation age after CAIs, and the distinctly different isotopic compositions of carbonaceous chondrites from other inner Solar System materials.

However, even this scenario may be too simplistic. There is growing cosmochemical evidence (Section 2.2) that the carbonaceous chondrites formed beyond the orbit of Jupiter (Kruijer et al. 2017b). At least two episodes of giant planet migration have been invoked to explain various features of the Solar System that would have scattered bodies from the outer Solar System into the Asteroid Belt (Levison et al. 2009; Walsh et al. 2011). However, giant planet migration may not even be required for scattering of outer Solar System objects into the Asteroid Belt (Raymond and Izidoro 2017). Additionally, it has been proposed that the process of terrestrial planet formation would have scattered bodies from <2 AU into the Asteroid Belt (Bottke et al. 2006). Thus, it is possible that a large fraction of the bodies in the Asteroid Belt may not have formed there. If correct, the stratigraphy of the Asteroid Belt may be a complex record of the dynamical evolution of large bodies in the Solar System rather than a remnant of planetesimal formation in the belt.

The proposed dynamical event that would have had the most dramatic effect on the Asteroid Belt is the Grand Tack of Jupiter (Walsh et al. 2011), the prime motivation of which was to explain the small mass of Mars. In the Grand Tack, an already formed Jupiter migrates inward to roughly 1.5 AU clearing out most of the previously formed planetesimals from the Asteroid Belt. At this point, a still growing Saturn catches up with Jupiter, they become trapped in a resonance and this causes them to migrate out again in tandem until the disk

dissipates. In the process of moving out again, Jupiter and Saturn force Uranus and Neptune outwards as well. One consequence of this action is that the migrating giant planets scatter planetesimals from ~5 AU to ~13 AU into the inner Solar System. These scattered bodies would have been potent sources of volatiles for the growing terrestrial planets. However, some become trapped in the Asteroid Belt, particularly the outer belt, while the inner belt is dominated by the remnants of the inner Solar System planetesimals that were scattered by Jupiter's inward migration. Based on the estimates of the accretion ages of the CR and CB chondrites, if it happened the Grand Tack must have taken place 4–5 Ma after Solar System formation. Such a timescale would also be consistent with the absence of evidence for alteration in the P-type asteroids. The sealing off of the inner Solar System by the growth of Jupiter and having the carbonaceous chondrites form in the outer Solar System may also explain why the formation of carbonaceous chondrite bodies continued for up to 2 Ma after any known inner Solar System chondrites – i.e., material migrating inwards through the disk could not pass beyond Jupiter, causing it to accumulate outside of Jupiter's orbit. It also implies that the enigmatic process of chondrule formation was much more widespread in the nebula than is often assumed (i.e., it was not confined to the inner Solar System).

The next dynamical instability, the Nice model, was invoked to explain the architecture of the Kuiper Belt and Scattered Disk, as well as providing a mechanism for the hypothesized Late Heavy Bombardment that may have occurred ~600 Ma after Solar System formation. In the Nice model, the orbits of the giant planets become unstable again and, most importantly for the purposes of this discussion, Neptune moves outwards from ~15 AU to its current orbit at 30 AU (Levison et al. 2011). In so doing, it scatters bodies from this region into the inner Solar System, some of which are implanted into the Asteroid Belt as well as becoming trapped in the Hildas and Jupiter Trojans. Levison et al. (2009) suggested that most of the D- and P-type asteroids were acquired in this way. The Oort Cloud and Jupiter family comets would also have formed in this region (Brasser and Morbidelli 2013).

Thus, the Nice model predicts a genetic link between comets and D-/P-type asteroids. This potential link will be explored further in Section 5, but petrologically the aqueously altered Tagish Lake meteorite that has been linked spectroscopically to D-type asteroids (Hiroi et al. 2001) appears to be quite distinct from comet Wild 2 (e.g., Zolensky et al. 2002; Zolensky et al. 2006; Hanner and Zolensky 2010; Blinova et al. 2014). However, the spectroscopic link between Tagish Lake and D-type asteroids has been questioned (Vernazza et al. 2013). The Nice model could not have supplied a significant amount of volatiles to the Earth because: (1) there is clear evidence that Earth had an atmosphere and hydrosphere within 30–300 Ma of Solar System formation (Mojzsis et al. 2001; Wilde et al. 2001; Avicé and Marty 2014), and (2) the material accreted by the Earth after the Moon-forming impact, which occurred ~50–70 Ma after Solar System formation (Touboul et al. 2007; Barboni et al. 2017), was too little, volatile-depleted and inner Solar System in origin (Bottke et al. 2010; Bottke et al. 2012; Walker et al. 2015; Fischer-Gödde and Kleine 2017).

Simulations by Bottke et al. (2006) suggest that significant numbers of bodies would have been scattered into the inner Asteroid Belt from the terrestrial planet region by planetary embryos. Since it seems likely that planetesimal accretion happened faster in the terrestrial planet region than further out, they proposed that all iron meteorites derived from

planetesimal cores come from bodies that were implanted into the asteroid belt in this way. They also suggested that Vesta and some fraction of S-complex asteroids could be interlopers from the terrestrial planet region.

4 Comets

Comets are undoubtedly the most primitive and volatile-rich bodies in our Solar System. Thanks to the Rosetta mission, a lot more is known about comets now than a few years ago, and once all the data are properly analysed more results will certainly come forward. At the time of writing, we can already state a few things about comets, mainly concerning their classification and origin, their accretion, and their molecular and isotopic compositions. In the following, we concentrate mostly on new results from the Rosetta mission, which does not mean that previous work on comets should be forgotten. In many ways, Rosetta confirms previous measurements, but in others has prompted the emergence of new paradigms.

4.1 Classification

It has long been known that there are two dynamically distinct families of comets: Oort cloud comets (OCC) and Jupiter family comets (JFC). Their orbits differ by their Tisserand parameters (dynamical quantities that are roughly conserved during an encounter with a planet) with respect to Jupiter (Levison 1996). OCCs generally are long or medium period comets (periods > 50 yr) with more or less isotropic inclinations with respect to the ecliptic plane, whereas JFCs have their aphelion close to Jupiter and are almost in the ecliptic plane. Both classes of comets then are sometimes subdivided into sub-families, like Encke-type comets that do not cross Jupiter's orbit, or Halley-type (HT) comets that are OCCs but have orbital periods of less than 200 yr. Because of the distinct orbits of OCCs and JFCs, it was postulated that their formation zones were also distinct: OCCs close to the giant planets (Dones et al. 2004; Brassier 2008), and JFCs outside of Neptune's orbit (Duncan and Levison 1997). JFCs are thought to have their reservoir in the scattered disk – a dynamical subclass of objects in the Kuiper Belt with highly eccentric orbits and perihelia > 30 AU. Once they are deflected into the inner Solar System, comets are captured by Jupiter.

Recently, this paradigm of two distinct formation regions for the two comet families has been challenged. Several authors have tried to classify comets according to their chemical compositions (e.g., A'Hearn et al. 1995; Mumma and Charnley 2011). However, most attempts have failed as OCCs and JFCs both have variable chemistries and their compositional characteristics cannot be tied to a specific comet family. Solar System formation models predicted that the D/H ratio in water should increase with radial distance from the Sun as temperatures decrease and mixing with processed water from the inner Solar System diminishes (e.g., Horner et al. 2007; Jacquet and Robert 2013; Yang et al. 2013). The D/H ratio in water in comets should, therefore, be an indication for their region of formation; hence OCCs should have a lower D/H ratio than JFCs. Table 5 gives an overview of D/H in comets. When a terrestrial D/H ratio was found in the JFC Hartley 2 (Hartogh et al. 2011) that was a factor of two lower than in all OCCs measured up to then, the problem was solved by considering mixing processes in the evolving accretion disk that result in a D/H ratio that does not monotonically increase with distance from the Sun (Yang

et al. 2013). However, once Rosetta found a very high D/H in water from the coma of the JFC comet 67P/Churyumov-Gerasimenko (Altwegg et al. 2015), this idea was no longer supported. Meanwhile, more D/H ratios have become available (Biver et al. 2016) showing wider spreads in the ratios for OCCs and JFCs that clearly overlap one another. This suggests that the formation zones for the two comet families overlapped over large radial distances and that they experienced different dynamical histories following accretion (Brasser and Morbidelli 2013). The D/H ratio in water, therefore, may still reflect the region of comet formation, but not the dynamical family a comet belongs to. This picture is supported by the N isotopes of HCN and CN in comets that are similarly ^{15}N -rich in both OCCs and JFCs (Table 6).

4.2 From dirty snowballs to icy dust

Another paradigm that is changing thanks to the Rosetta mission is the notion of comets as “dirty snowballs”. From the Giotto mission to comet Halley, it was already apparent that comets were probably not the dirty snowballs postulated by Oort (Oort 1986), but rather icy dust balls. The dust/gas ratios in comets has continued to be debated (e.g., Singh et al. 1992; Fulle et al. 2000). Measurements of the dust/gas ratio in comet 67P of at least 4:1 (Rotundi et al. 2015) clearly support the icy dust ball picture, although recent observations of a cliff collapse that exposed subsurface ice suggests that 67P may be more ice-rich than this (Pajola et al. 2017). The porosity of 67P is 75 % and its density is correspondingly very low ($\sim 530 \text{ kg/m}^3$), and it seems to be homogeneous down to decimeter scales (Kofman et al. 2015; Pätzold et al. 2016). The Giada instrument observed two kinds of grains: compact grains with densities of up to 4000 kg/m^3 and fluffy grains with extremely low effective densities of $<1 \text{ kg/m}^3$ (Fulle et al. 2016) that take less than 10^3 Pa to disrupt (Hornung et al. 2016). The authors proposed that the compact grains are reprocessed material from the solar nebula, whereas the fluffy grains are primitive material, probably connected to interstellar dust. These ice-free dust grains were also observed with the COSIMA (Langevin et al. 2016) instrument. The existence of these fluffy aggregates means that the cometary material has not experienced any violent collisions; collisional speeds must have been below 1 m/s. It is also postulated that the two lobes of 67P formed separately and that the shape of the comet is due to a very gentle collision of two cometesimals (Jutzi and Asphaug 2015; Massironi et al. 2015; Jutzi and Benz 2017; Jutzi et al. 2017). This bi-lobal shape has previously been found for several comets (e.g., Hartley 2; A’Hearn et al. 2011).

In terms of composition, 67P contains quite a lot of N_2 (Rubin et al. 2015a), CO (Le Roy et al. 2015) and Ar (Balsiger et al. 2015), all highly volatile species that require a low formation temperature of $\sim 25 \text{ K}$ for the comet and almost no heating of its interior. No signs of hydrated minerals have been found so far in the infrared spectra of the VIRTIS instrument (Quirico et al. 2016), which implies little or no internal radiogenic heating as would have occurred in a bigger parent body that accreted early. The presence of highly volatile species in such a porous and weak body suggests a relatively late accretion of 67P and other volatile-rich comets when the temperatures in the outer disk would have been very cold, and the abundances of radioactive heat sources would have been low.

4.3 Presolar cloud – comet connection

More information about the links between presolar cloud chemistry and cometary material comes from the detections of abundant O_2 (Bieler et al. 2015a), many S-bearing species (Calmonte et al. 2016), as well as of D_2O and HDS (Altwegg et al. 2017). The O_2 in comets 67P and Halley (Rubin et al. 2015b) has an abundance relative to water of ~ 3.8 mol.%. In 67P, the O_2 is very well correlated to water. This cannot be the result of solar nebula chemistry, but has to come from the presolar cloud, either by radiolysis or by gas phase chemistry (Taquet et al. 2016). According to Mousis et al. (2016b), O_2 can be trapped efficiently in amorphous water ice. In order to keep the correlation between water and O_2 , interstellar water ice cannot have sublimated at any stage prior to accretion by 67P. A similar conclusion may be drawn from the presence of S_2 . Sulphur in protostellar cores and dense clouds is highly depleted in the gas compared to its cosmic abundance. In diffuse clouds, however, S has a cosmic abundance in the gas (Woods et al. 2015, and references therein). It was postulated that the reason for the depletions in the dense cloud gas is that photolysis/radiolysis converts H_2S , which is predominantly formed on dust grains, into refractory S_n that stays on the grains and cannot be observed by remote sensing. The ROSINA instrument on Rosetta has detected S_2 , S_3 and S_4 (Calmonte et al. 2016) in the coma of 67P. Sublimation of S_2 occurred even at large heliocentric distances (>3 AU) and its relative abundance to the major S-bearing species H_2S remained constant for many months inbound. Once the coma became dustier, ROSINA detected not only S_2 , but S_3 and S_4 as well, and the relative abundance of S_2 to H_2S increased by more than a factor of 10. This behaviour shows that S_2 is present both in a very volatile form as well as part of the more refractory S reservoir associated dust. The detection of S_3 and S_4 clearly shows that the pathway described by Woods et al. (2015) also fits cometary material and that, therefore, S in comets and in dense clouds seem to be present in very similar forms. Once released into the gas of a cometary coma, S_2 has a very short photodissociation lifetime of ~ 250 s at 1 AU (de Almeida and Singh 1986). Its lifetime would still be short even at 30 AU as the wavelength needed for the destruction of S_2 is only 280 nm and the flux at this wavelength would probably have been sufficient even near the midplane. The presence of volatile S_2 in 67P shows that most probably the dust grain mantles formed in the dense cloud survived the accretion of the solar nebula without being heated and, therefore, retaining the S_2 . It is interesting to note that elemental S is found in CM chondrites and that it has mass independent isotopic fractionations that are most consistent with photodissociation of H_2S (Labidi et al. 2017).

Another link between the presolar cloud, star forming regions, and the comet compositions can be derived from the presence of D_2O and HDS. D_2O has been measured in low-mass star forming regions – the D_2O/H_2O ratio is roughly 1.2 ± 0.5 % and the HDO/H_2O ratio is on the order of 0.17 ± 0.08 % (Coutens et al. 2014). Similar values have been found in comet 67P (Altwegg et al. 2017). These high values for D_2O can be explained by dust grain chemistry in presolar clouds. Furuya et al. (2016) have shown that the ratio of $[D_2O/HDO]$ to $[HDO/H_2O]$ is a good diagnostic for the amount of reprocessing that the water experienced in the solar nebula. For values of this ratio that are $\gg 1$, the water is unprocessed, i.e., inherited from the presolar molecular cloud, whereas for reprocessed water this ratio is < 1 . In the case of 67P, the ratio is 17 (Altwegg et al. 2017), which suggests

that the comet mostly contains primordial material inherited from the presolar molecular cloud. The same conclusion holds for the high HDS/H₂S ratio measured in 67P of 0.12 % (Altwegg et al. 2017) that is indicative of dust grain chemistry (Hatchell et al. 1999).

Overall, the Rosetta data suggests that comet 67P has incorporated a significant amount of material that was formed in the presolar cloud and was little processed in the protoplanetary nebula. This would be consistent with the high D/H ratio of its water (Altwegg et al. 2015). The large range of D/H ratios amongst comets (Table 5) may then be the result of mixing of presolar material with water formed at high temperatures in the inner Solar System.

Further evidence for a link between cometary ices and the ISM, or at least evidence for low temperature ion-molecule and gas-grain chemistry, can be seen in the ¹⁵N-rich compositions of HCN and CN (Table 6). These ¹⁵N enrichments in HCN are similar to what is seen in dense, prestellar cores in molecular clouds (Ikeda et al. 2002; Milam and Charnley 2012; Hily-Blant et al. 2013). The D/H ratio ($2.3 \pm 0.4 \times 10^{-3}$) in the HCN of Hale-Bopp (Meier et al. 1998a) is almost an order of magnitude higher than its water (Table 5), but still an order of magnitude lower than observed for HCN in low mass star forming regions (Roberts et al. 2002).

4.4 Bulk compositions of comets

On arrival of Rosetta at comet 67P, several instruments detected a large heterogeneity in the coma composition (Bockelée-Morvan et al. 2015; Hässig et al. 2015; Luspay-Kuti et al. 2015). At that time, the northern hemisphere was in summer. This hemisphere experiences a long but cold summer during aphelion passage, whereas the southern hemisphere has a short intense summer of only 10 months during perihelion passage. This difference in insolation for the two hemispheres leads to different outgassing behaviours (Hässig et al. 2015; Le Roy et al. 2015) and results, over time, in different morphological changes (Feaga et al. 2007). Such heterogeneities have been observed before, e.g., for comets Hartley 2 and Temple 1 (A'Hearn et al. 2011). The heterogeneities make it difficult to derive a bulk composition for 67P. However, as the comet sheds more than 2 m from the southern hemisphere during its perihelion passage (Keller et al. 2015) and the seasonal heat wave penetrates more slowly than the erosion rate on the southern part of the comet, it is probably safe to say that the composition during the few months around perihelion best represents the bulk abundance at least of the southern hemisphere. For other comets, whose rotational axes are generally not known, any variations in composition may well be due to their seasonal evolution. The relative abundances of the major volatile species change dramatically during the orbit of 67P, even close to perihelion (Fougere et al. 2016). The same has been shown for many other comets. In addition, observing comets by remote sensing can introduce additional biases. One result from Rosetta is that for UV (Feldman et al. 2015) and optical spectroscopy (Bodewits et al. 2016) solar wind electron impact excitation of molecules plays a major role in the intensity of what is observed remotely, and the characteristics of the solar wind can be quite variable. Due to its irregular shape, 67P also shows a very pronounced diurnal variation, which can be mostly explained by variable illumination conditions (Bieler et al. 2015b). It is, therefore, not straightforward to compare abundances of different comets as

their rotational state, shape, heliocentric distance and interaction with a dynamic solar wind all strongly influence what is observed.

For many comets water is the most abundant species (>50 % of the volatiles), followed by CO and CO₂ (Mumma and Charnley 2011) and, at least in the case of 67P and Halley, O₂. The inventory of organics is very rich as can be seen from measurements at 67P (Goesmann et al. 2015; Le Roy et al. 2015; Wright et al. 2015; Altwegg et al. 2016; Calmonte et al. 2016). The data analysis is still ongoing and the assignment of species to the low-resolution mass spectra of the Ptolemy and COSAC instruments are not unique. Nevertheless, it is clear that 67P contains many hydrocarbons, oxygenated species, a complex S chemistry, as well as N-bearing species. The C-chain molecules detected by ROSINA (Le Roy et al. 2015) match the semi-volatile component of surface material detected by the Virtis instrument (Capaccioni et al. 2015; Quirico et al. 2016). The volatile inventories of 67P and other comets are similar to what is measured in presolar clouds (Mumma and Charnley 2011; Le Roy et al. 2015) and is close to what is expected based on laboratory experiments with interstellar ice analogues (For an overview see Linnartz et al. 2015 and references therein).

While the coma is clearly heterogeneous in composition, no firm statement can be made about the compositional heterogeneity of the nucleus at any given time. Some authors claim that the ice of 67P contains clathrates (Luspay-Kuti et al. 2016; Mousis et al. 2016a), but this seems to be very unlikely in view of the presence of O₂ and S₂. In order to form clathrates, all volatile species must be expelled from the amorphous ice first (Schmitt et al. 1989), even if the ice transformed without sublimation from amorphous to clathrates as postulated by Mousis et al. (2016b). This would have destroyed the very good correlation between O₂ and H₂O in the coma (Bieler et al. 2015a), and it would also have destroyed S₂ by photodissociation (Calmonte et al. 2016). We have to wait for further analysis to see if any nucleus heterogeneity exists that cannot be explained by the evolution of the outer layers of the comet. This could then shed light on the formation conditions of 67P, especially regarding whether the two lobes have different compositions because they formed separately.

4.5 Summary

With the new results from Rosetta, some paradigms about comets are changing. The most important one is that the regions where OCCs and JFCs formed probably overlapped and extended over large radial distances from the Sun. This may explain the range of D/H ratios found in cometary water, as well as some of the other compositional variations. However, care has to be taken as cometary comas can be very heterogeneous and vary with time. Evidence for a connection between the presolar cloud composition and the observed cometary chemical inventories is seen in the highly deuterated species and the complex organic chemistry, especially of S-bearing molecules. There are even indications that some presolar ice layers on dust grains have survived comet accretion. Clear signs of grain-surface chemistry, as well as of radiolysis/photolysis, are evident in the volatile inventory of 67P. There are no significant traces of mixing of the volatile material with processed material from the inner Solar System, at least for 67P. This might be somewhat different for comets with lower D/H ratios in their water, as they may have formed closer to the Sun. So far, there

have been no firm detections of CAIs or chondrules by the COSIMA instrument, although Fulle et al. (2015) claims that the compact grains they observe must have undergone modification in the solar nebula.

The very porous nature and the physical homogeneity of the nucleus down to the decimeter level, as well as the extremely fluffy, low density, low strength properties of emitted dust aggregates from 67P make violent collisions between dust grains or cometesimals in the early history of comets unlikely. These features are more compatible with comet formation by the streaming instabilities (Blum et al. 2014; Davidsson et al. 2016) or by forming in dust traps (van der Marel et al. 2015). However, it cannot be ruled out that small comets are the products of collisional disruption of larger bodies (Farinella and Davis 1996; Morbidelli and Rickman 2015). This is certainly one possible explanation for the generally elongated shapes of known JFCs (Jewitt et al. 2003). Whatever the mechanisms were for forming comets and ultimately producing their current shapes, what has become increasingly evident is that comets like 67P preserve very primitive materials that have undergone little, if any, reprocessing in the protosolar nebula.

The average D/H of water measured in comets so far is well above terrestrial. This clearly makes the notion that comets delivered all of the terrestrial water unlikely. However, it was shown by Marty et al. (2016) that, while not required, the amount of ^{36}Ar in the terrestrial atmosphere is compatible with its delivery by comets like 67P and that this could be done without changing the terrestrial D/H ratio and other volatile element abundances by much. In addition, there is isotopic evidence that ~20 % of atmospheric Xe could have come from comets like 67P (Marty et al. 2017). It has been suggested that comets are also responsible for the large enrichments in ^{22}Ne and ^{36}Ar in Venus's atmosphere (Owen and Bar-Nun 2000), although other explanations are possible (Bogard 1988). In this context, the Earth could also have acquired complex organics from comets that, if accreted after the Moon-forming impact, helped to spark life.

5 Tests of the dynamical models and constraints on the sources of terrestrial planet volatiles

5.1 Testing the dynamical models

The predictions of giant planet formation models, whether or not they involve orbital migration (e.g., the Grand Tack and Nice models), are that C-complex and P-/D-type asteroids formed in the outer Solar System, and a significant fraction will have formed in the same regions as comets. Since these asteroids are thought to be the sources of the carbonaceous chondrites, the chondrites can potentially be used to test the models, but to do this requires indicators of formation distances from the Sun. At present, the H isotopes of water are the most promising indicators of formation distance (Alexander et al. 2012). This is because there is likely to have been a radial gradient in the H isotopic composition of water in the disk. This gradient would have been the result of radial mixing between (1) water in the outer Solar System that retains a large D-rich interstellar component inherited from the presolar molecular cloud, and (2) D-poor (solar D/H) water in the warm inner Solar System produced by isotopic re-equilibration between H_2 and H_2O . While some models

predict a simple monotonic increase in D/H in water with radial distance (e.g., Horner et al. 2007), this is almost certainly a gross oversimplification (e.g., Yang et al. 2013). Nevertheless, the basic prediction that planetesimals that formed further from the Sun should tend to be more D-rich is at least consistent with the H isotopic compositions of water ice in carbonaceous chondrites, most comets and Saturn's moon Enceladus (Fig. 5, as well as Tables 4 and 5).

As previously discussed (Section 2.5), the estimates of the H isotopic compositions of OH/water in CI and CM chondrites, as well as Tagish Lake, are all intermediate between the terrestrial and solar values (Table 4), and quite distinct from those of any comets (Table 5). The estimate for the CR chondrite water is slightly above terrestrial and overlaps with the compositions of the least D enriched comets. However, perhaps most surprising are the OC and R chondrite compositions that overlap with those of comets. Taken at face value, this is the reverse of what was expected from the dynamical models as it would seem to imply that the OC and R chondrites formed further from the Sun than the carbonaceous chondrites and even many comets. At the very least, and counter intuitively, it is possible that the OC and R chondrites accreted more interstellar water than the carbonaceous chondrites (Deloule et al. 1998; Piani et al. 2015). However, there may be a more mundane explanation for the OC and R chondrite results related to the oxidation of Fe (Alexander et al. 2010; Alexander et al. 2012; Bonal et al. 2013). This process will have affected all the chondrites to varying degrees and it may partly explain why the CR chondrites have higher dD values than the other carbonaceous chondrites (Sutton et al. 2017).

Figure 5 plots the estimated water isotopic compositions of the carbonaceous chondrites, comets, and Saturn's moon Enceladus as a function of the radial distance from the Sun, either in their current location (Saturn's moons and chondrites) or approximately where they are thought to have formed (comets). The H isotopic composition of CH₄ in Titan's atmosphere (Nixon et al. 2012) is also plotted, although it is unclear how closely it reflects the isotopic composition of the water that Titan initially accreted. The formation locations of the two classes of comets are unknown, but are likely to have been in the region of the current orbit of Neptune (e.g., Brassier and Morbidelli 2013). Hence, they have both been given nominal formation locations of ~25 AU. If Enceladus and Titan formed from Saturn's subdisk, this would presumably have been towards the end of Saturn's growth that in the Grand Tack model would have been when Saturn was between roughly 3 AU and 7 AU (arrowed) rather than at its current orbital radius of ~10 AU. Again, it is clear that, with the possible exception of the CRs, the carbonaceous chondrites had significantly lighter initial water H isotopic compositions than those of comets and Enceladus. Consequently, it is tempting to infer that water beyond somewhere between 3–7 AU was enriched in D relative to the bulk Earth and somewhere between 3–7 AU there was a steep decrease in the isotopic composition of the water in the disk.

There are at least two caveats to this line of reasoning. First, if Saturn's moons formed in its subdisk, their compositions will reflect the composition of the subdisk when they formed and not necessarily that of the surrounding nebula. During the main phase of Saturn's growth, the subdisk will have been very hot, erasing any intermolecular isotopic fractionations inherited from the nebula material it accreted. The subdisk will have cooled as

accretion slowed and the protoplanetary disk dissipated. Whether at this stage conditions (e.g., temperature) and timescales would have produced larger isotopic fractionations than were present in the disk at Saturn's location is not known but seems doubtful. If correct, Saturn's moons provide lower limits for the isotopic compositions of planetesimals that formed in its neighborhood. However, it is also possible that Enceladus formed from the debris of a tidally disrupted planetesimal of unknown origin that was captured by Saturn (Crida and Charnoz 2012), in which case it cannot be used to constrain the H isotopic gradient in water in the outer Solar System.

Nitrogen isotopes might provide some further constraints on the formation distances of planetesimals (Alexander 2017). The N_2 - NH_3 system in the nebula might have behaved in an analogous way to the H_2 - H_2O system, although N_2 is less chemically reactive than H_2 and there has been no detailed isotopic modeling of the N system in the nebula. Nevertheless, the N isotopic compositions of the bulk chondrites are less ^{15}N enriched than HCN or NH_3 in comets, as well as Titan's atmospheric N_2 (Niemann et al. 2010) that may have originally been accreted as NH_3 (Mandt et al. 2014). Hence, when the N isotopes are plotted against radial distance (Fig. 6) there is a similar pattern to that for H isotopes (Fig. 5), with outer Solar System bodies being more enriched than the chondrites in ^{15}N . However, to truly compare like with like we should be using HCN/ NH_3 compositions in chondrites not their bulk compositions. There is little HCN, NH_3 or ammonium salts in chondrites, and what there is has not been extensively studied. However, the CI, CM, and CR chondrites do contain amino acids that are thought to have formed in their parent bodies via Strecker-cyano synthesis that would have involved HCN and NH_3 . The N isotopic compositions of these amino acids, as well as a few measurements of NH_3 and other N-bearing soluble organic compounds, have a similar range to the bulk chondrites (Epstein et al. 1987; Pizzarello et al. 1994; Engel and Macko 1997; Pizzarello and Holmes 2009; Elsilá et al. 2012).

The amino acids and other N-bearing compounds that probably formed from HCN/ NH_3 show that, like comets, at least some fraction of the ice accreted by chondrites contained highly volatile compounds. The ubiquitous presence of carbonates in aqueously altered chondrites suggests that the ices, as in comets, also contained CO/ CO_2 (Alexander et al. 2015). However, on balance, the combination of H and N isotopes in carbonaceous chondrites suggest that they did not accrete in the formation locations of most comets and probably not beyond the formation locations of Saturn's moons, which in the Grand Tack model would have been between ~ 3 AU and ~ 7 AU. It should always be borne in mind that our meteorite collections probably do not sample all asteroid types. Nevertheless, if there was a Grand Tack it appears that it did not scatter many bodies into the asteroid belt from as far out as envisaged in the model. On the other hand, the meteoritic data are equally consistent with the chondrites having formed more-or-less where their parent bodies are presently located in the asteroid belt. Nor is there evidence in the meteorite collection, particularly from the Tagish Lake meteorite, for scattering of P-/D-type asteroids from the comet forming regions beyond 15 AU as required by the Nice model. Raymond and Izidoro (2017) have argued that scattering of outer Solar System planetesimals from as far out as 20 AU into the inner Solar System, including implantation into the Asteroid Belt, is an inevitable consequence of giant planet formation, irrespective of whether there was a Grand

Tack. Again, the isotopic evidence does not seem to be consistent with a large fraction of objects that were implanted in the asteroid belt coming from beyond the orbit of Saturn, unless we are being misled by the moons of Saturn about the nature of the H and N isotopic gradients in the nebula.

5.2 Sources of volatiles for the terrestrial planets

When the terrestrial planets formed, they will have accreted bulk planetesimals and comets, not just their water. So, in trying to constrain the sources of the volatiles in the Earth it is important to compare bulk compositions. For the comets, this is problematic as what can be measured in their comas remotely may not be representative of their bulk compositions. For instance, refractory organic matter may make significant contributions to the bulk H and N contents of comets, and N₂ may also be an important component of the N budgets. The abundances and elemental and isotopic compositions of the refractory organics and N₂ in comets are poorly known. For the organics, the similarities between Halley CHON particles, and IOM in primitive meteorites and IDPs suggest that the cometary organics are probably significantly more D-rich than their water, but will not be as ¹⁵N-rich as their HCN and NH₃. Mass balance would suggest that as the major N-bearing component in the nebula, the N₂ in comets should be close to the bulk solar value, which is highly depleted in ¹⁵N relative to the Earth (Marty et al. 2011). Hence, the H isotopic compositions measured in cometary water should be regarded as minimum estimates for their bulk D/H, while the N isotopic compositions of HCN/NH₃ should be regarded as upper limits for their bulk ¹⁵N/¹⁴N. Even with the chondrites one has to be somewhat cautious because there is no guaranty that they faithfully represent the bulk compositions of their parent bodies. For instance, as discussed earlier, their parent bodies may have retained some ice and other volatiles that the meteorites will have lost when they were small bodies prior to being captured by the Earth.

There are also considerable uncertainties and disagreements in the estimates of the volatile budget of the Earth (e.g., Marty 2012; Halliday 2013). Nevertheless, Marty (2012) has argued that the volatile budget of the Earth (H, C, noble gases, Cl, and I) can be explained by addition of ~2–4 wt.% CI/CM-like material. Hydrogen and N isotopes (Fig. 7) also suggest that CI/CM-like material, rather than comets or other chondrites, are the dominant source of Earth's volatiles (Alexander et al. 2012). The bulk CI and CM H and N isotopic compositions are not identical to the Earth's, which could be explained either by the CI/CM-like planetesimals retaining some isotopically light ices and other volatiles, or by accretion of ~10% of solar H and N. The interior H and N isotopic compositions of Mars (Mathew and Marti 2001; Usui et al. 2012; Hallis et al. 2017) are also consistent with CI/CM-like sources.

That CI/CM-like bodies were the major sources of volatiles (except perhaps some of the noble gases) for the terrestrial planets is at least consistent with the fact that CI/CM-like bodies are the most abundant type of asteroid. The terrestrial planets probably acquired their volatiles either by: (a) scattering of volatile-rich objects from the Asteroid Belt into their formation regions, as in the 'classical' model (Chambers 2001; Raymond et al. 2009), or (b) the accretion of outer Solar System bodies scattered into the inner Solar System (Walsh et al. 2011; Raymond and Izidoro 2017). In either case, the sources of the terrestrial planets' volatiles must be the most abundant of the volatile-rich asteroid types.

6 Summary and conclusions

The evidence from meteorites is that planetesimal formation in the inner Solar System began very early (~0.1–0.3 Ma after CAIs) and continued for at least 2 Ma (formation of OC and R chondrites). Planetesimals that formed earlier than ~2 Ma after CAIs would have contained sufficient short-lived ^{26}Al to have experienced extensive melting and in most cases differentiation into a silicate crust/mantle (achondrites) and iron core (magmatic iron meteorites). Spectroscopic comparisons suggest that the OC and R chondrites come from S-complex asteroids that dominate the inner Asteroid Belt. The evidence for water in the OC and R chondrites indicate that the snowline had migrated to within ~2 AU of the Sun by ~2 Ma after CAIs, assuming that the S-complex asteroids formed roughly where they are found today.

The carbonaceous chondrites have been spectroscopically linked to the C-complex and P-/D-type asteroids. The various carbonaceous chondrites parent bodies formed between roughly 2 Ma and 4 Ma after CAIs. At present, it has yet to be firmly established whether they formed in the inner or outer Solar System, although there is new isotopic evidence that suggests that they formed beyond the orbit of a growing Jupiter. Planetesimal formation may have continued beyond ~4 Ma after CAIs. However, the lack of a sufficiently strong radiogenic heat source to drive lithification (at a minimum this requires melting of ice) means that these bodies would not be consolidated enough to produce meteorites. Most C-complex asteroids show spectroscopic evidence for the presence of phyllosilicates, indicating that they, like the carbonaceous chondrites, formed within ~4 Ma of CAIs. There are asteroids without clear spectroscopic evidence for phyllosilicates, most notably the P- and D-types, that could have formed after ~4 Ma, but spectroscopic linking of the heavily altered ungrouped Tagish Lake chondrite to the D-types calls this into question. The absence of implanted solar wind in unbrecciated chondrites indicates that the solar nebula dissipated later than ~4 Ma after CAIs.

Primitive anhydrous IDPs may come from bodies that formed later than ~4 Ma after CAIs, but at present we have no way to date when they formed. It has often been suggested that primitive IDPs come from comets. Certainly, the abundances of highly volatile species in comets suggest that they formed late and/or as small bodies. There also seems to be many common features between chondrite matrices, IDPs and comet dust. These include an abundance of fine-grained crystalline and amorphous silicates, refractory organic matter, presolar grains and water. The presence of carbonates and amino acids in chondrites suggests that the ices they accreted contained CO/CO_2 and NH_3/HCN , just like comets. However, the lower abundance of organic matter in chondrite matrices suggests that there is a continuum between it and comet dust rather than there being a direct genetic relationship. The fact that matrix abundance tends to increase with accretion age after Solar System formation could reflect the transport of more primitive dust into the inner Solar System whose dust content was being progressively depleted by planetesimal formation and accretion onto the Sun. Alternatively, it might reflect progressive planetesimal formation at increasing distances from the Sun in a compositionally zoned disk.

The elemental fractionations in chondrites can be explained by mixing of volatile-depleted chondrules and refractory inclusions with volatile-rich matrix that had a CI-like bulk composition. To first order, this also accounts for the bulk C, N and H abundances of chondrites at the time of accretion, although subsequent parent body processes have modified these abundances in most chondrites. Interestingly, water abundances in chondrite matrices and comets appear to be less than would be expected assuming a bulk solar composition. The cause of this depletion is unclear but would have implications for planetesimal and planet formation if it is representative of the dust composition beyond the snowline since it would imply a lower than predicted dust surface density in the disk.

The H isotopes of water and N isotopes of HCN and NH₃ support the evidence for a continuum between chondrites and comets rather than a direct genetic relationship. The D/H ratio in water in the nebula is thought to have increased with distance from the Sun due to mixing between interstellar ice and water that had been re-equilibrated with H₂ in the inner Solar System. Comets exhibit a range of water D/H ratios but, with a few exceptions, they are all enriched in D relative to the bulk Earth and solar compositions. On the other hand, the CI and CM chondrites, as well as Tagish Lake, have estimated water D/H ratios that are significantly depleted relative to Earth. Nevertheless, they are still enhanced relative to the bulk solar composition, indicating that these chondrites accreted some interstellar water but most of it had been re-equilibrated in the inner Solar System. The H isotopic composition of water in the CR chondrites does overlap with the most D depleted comets, but this elevated D/H ratio may have been the product of parent body processes. Parent body processes may also explain the very D-rich water compositions of the OC and R chondrites.

As with the D/H in water, the N isotopes of the HCN and NH₃ in comets are enhanced in ¹⁵N relative to the Earth and the bulk solar composition, and this enhancement is thought to be an interstellar signature. Amino acids in chondrites are thought to be the products of reactions involving HCN and NH₃, and are also enriched in ¹⁵N although not as much as in comets. Thus, the isotopic compositions of H in water and N in HCN/NH₃ indicate that chondrites did not form in the same regions as comets, but probably formed sunward of comets where the abundance of unprocessed interstellar material was lower.

In terms of the major sources of volatiles to the terrestrial planets, the addition of 2–4 wt.% CI and CM chondrites give the best fits to the abundances and isotopic compositions of H, C and N. This would also account for much of the Earth's noble gases, but comets may have been a significant source of Ar and Xe for the Earth, and Ar and Ne for Venus. A minor contribution to the Earth from solar H and N may be required to explain their isotopic compositions, although how this material was accreted is unclear. Differentiated planetesimals are often not considered as significant sources of Earth's volatiles. However, two groups of achondrites have been shown to contain water that was either retained during melting and differentiation, or was accreted late as their parent bodies cooled and began to solidify.

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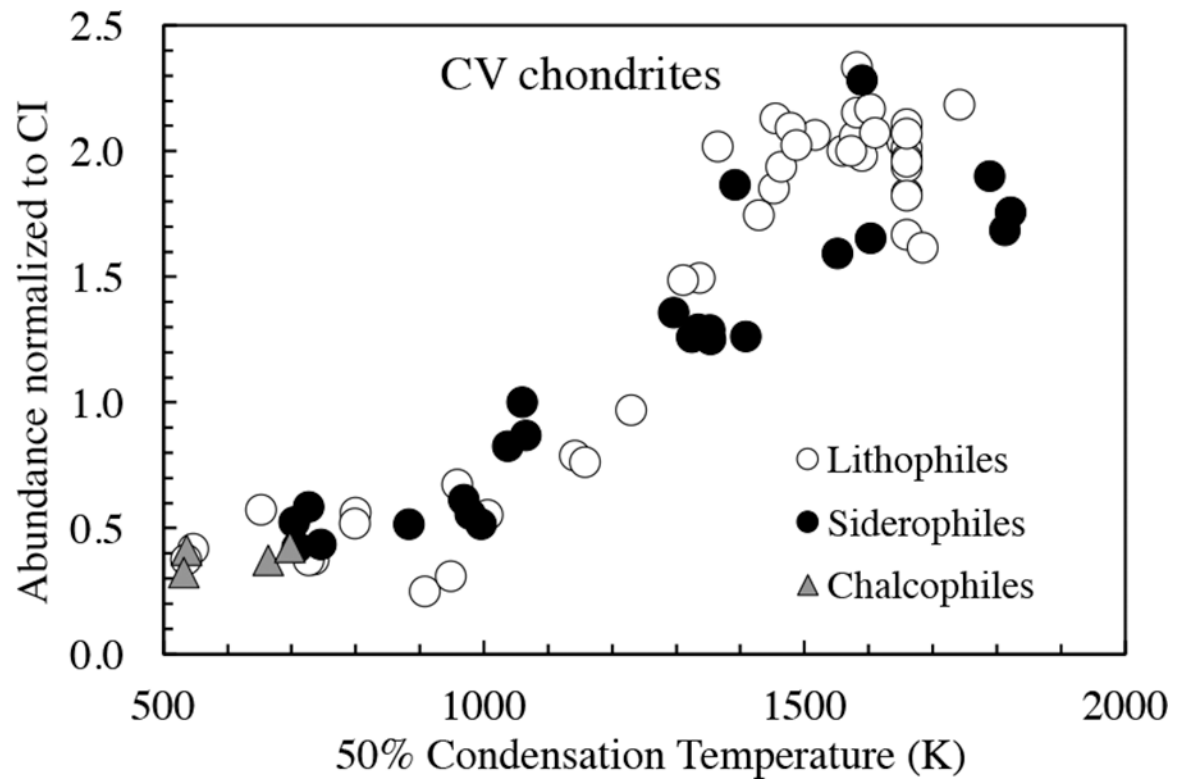


Figure 1. The CI normalized elemental abundances of bulk CV chondrites as a function of 50% condensation temperatures (Lodders 2003) and divided into their chemical affinities.

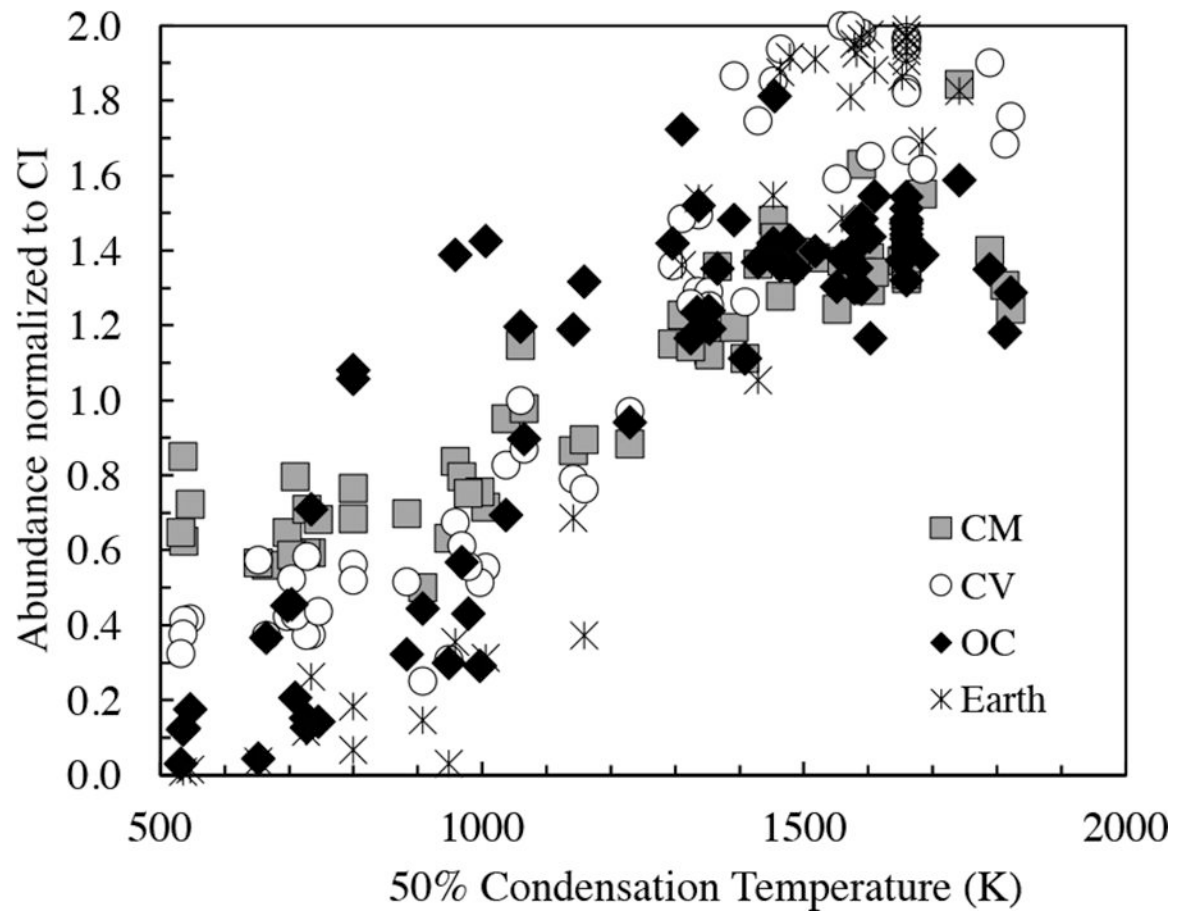


Figure 2. The CI normalized elemental abundances of bulk CM, CV and OC chondrites, as well as the estimated abundances of lithophile elements in bulk Earth, as a function of their 50% condensation temperatures (Lodders 2003).

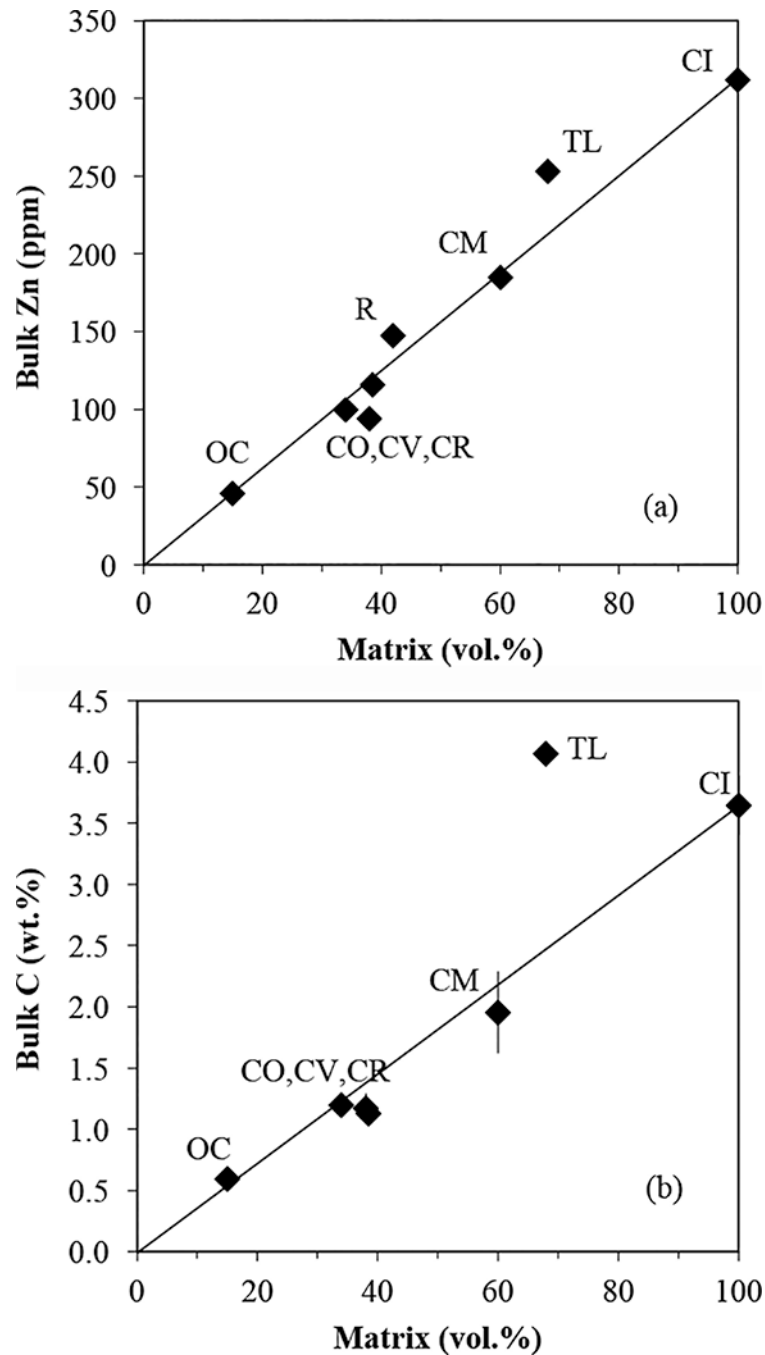


Figure 3. Matrix abundances vs. bulk Zn and C contents. In general, the abundances of Zn (Wasson and Kallemeyn 1988; Kallemeyn et al. 1991; Brown et al. 2000; Bischoff et al. 2011) and C (Alexander et al. 2012; Alexander et al. 2014a) are what would be expected if the matrices in these chondrites were dominated by CI-like material. The exception is the bulk C content of Tagish Lake (TL), but this seems to be because it is unusually rich in carbonate. The C contents for the OC, CO and CV chondrites are for the most primitive members of their groups (Semarkona, DOM 08006, and Kaba, respectively).

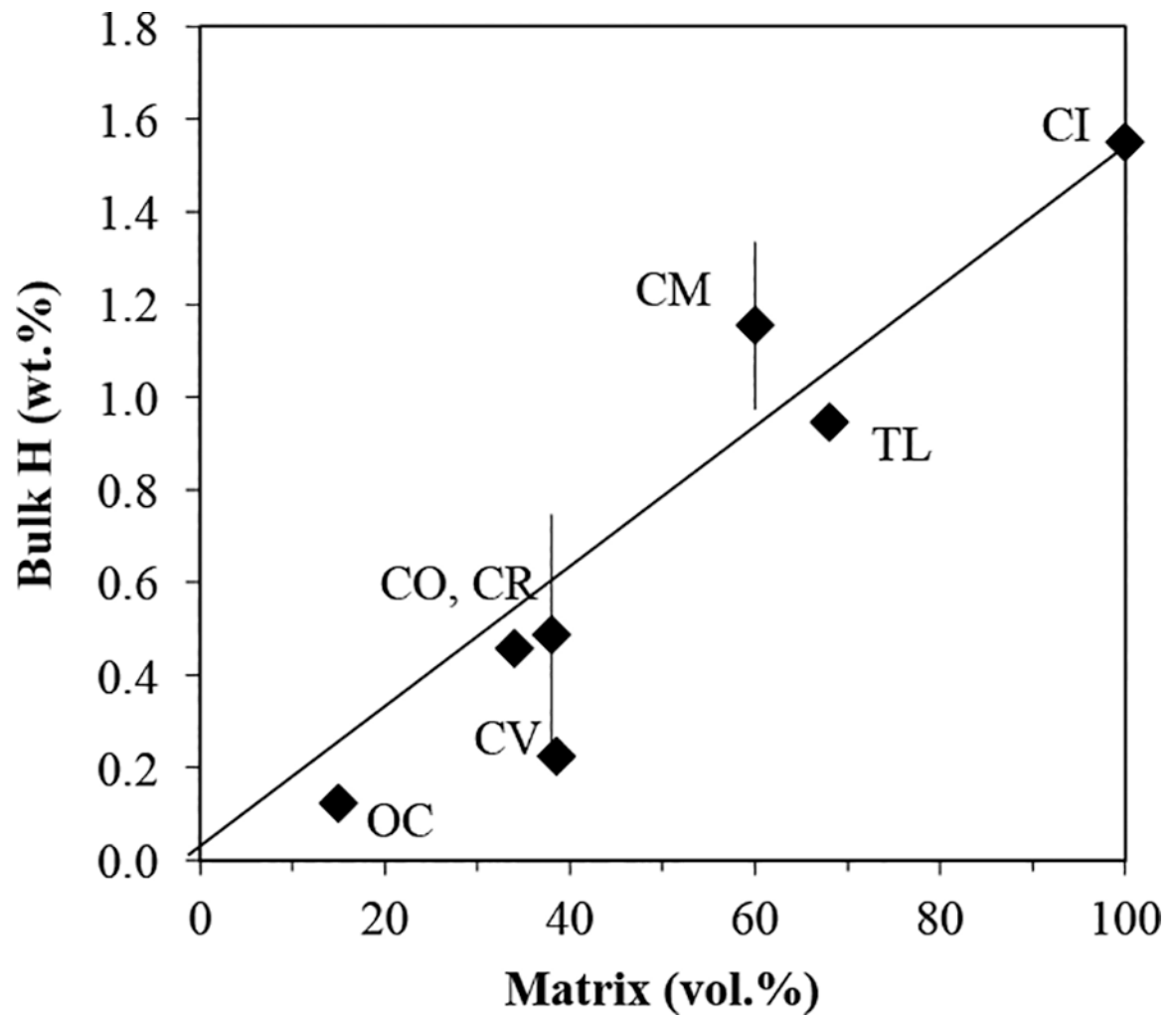


Figure 4. The bulk H (Table 3) and matrix contents for the more primitive chondrite groups. The CVs, COs and OCs are represented by the most primitive members of their groups (Kaba, DOM 08006, and Semarkona, respectively). The line is what would be predicted if the matrices of all chondrites had H contents like those of CI chondrites.

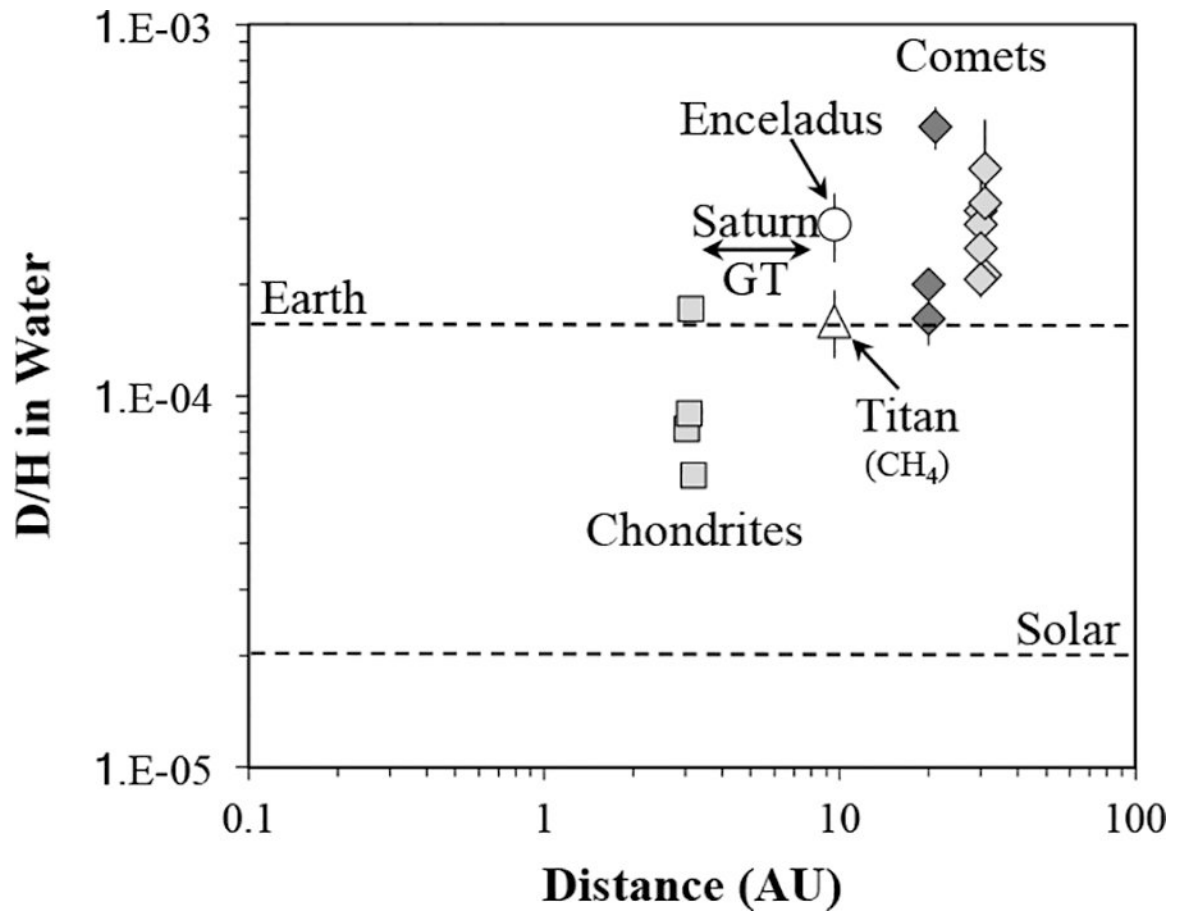


Figure 5.

The H isotopic compositions of OH/water in various objects as a function of radial distance from the Sun (modified after Alexander 2017). The H isotopic composition of methane in Titan's atmosphere is also shown, although it is not known how closely it reflects that of the water that Titan accreted. The locations of the asteroidal parent bodies of the carbonaceous chondrites are not known and so they have been given nominal radial distances of 3 AU. Saturn's moons Titan and Enceladus have been given their current orbital distances, although if there was a Grand Tack they may have formed between ~3 AU and ~7 AU (double arrowed). The formation locations of the comets are unknown, but are thought to have been between ~20 AU and ~30 AU (e.g., Brassier and Morbidelli 2013). The Oort (light grey) and Jupiter family (dark grey) comets are plotted at 30 AU and 20 AU, respectively, but their overlapping D/H ratios suggest that they formed in similar regions of the disk. With the possible exception of the CRs, the carbonaceous chondrite with the most D-rich water, the carbonaceous chondrites have compositions that are distinct from any measured outer Solar System body. Data sources are given in Tables 4 and 5.

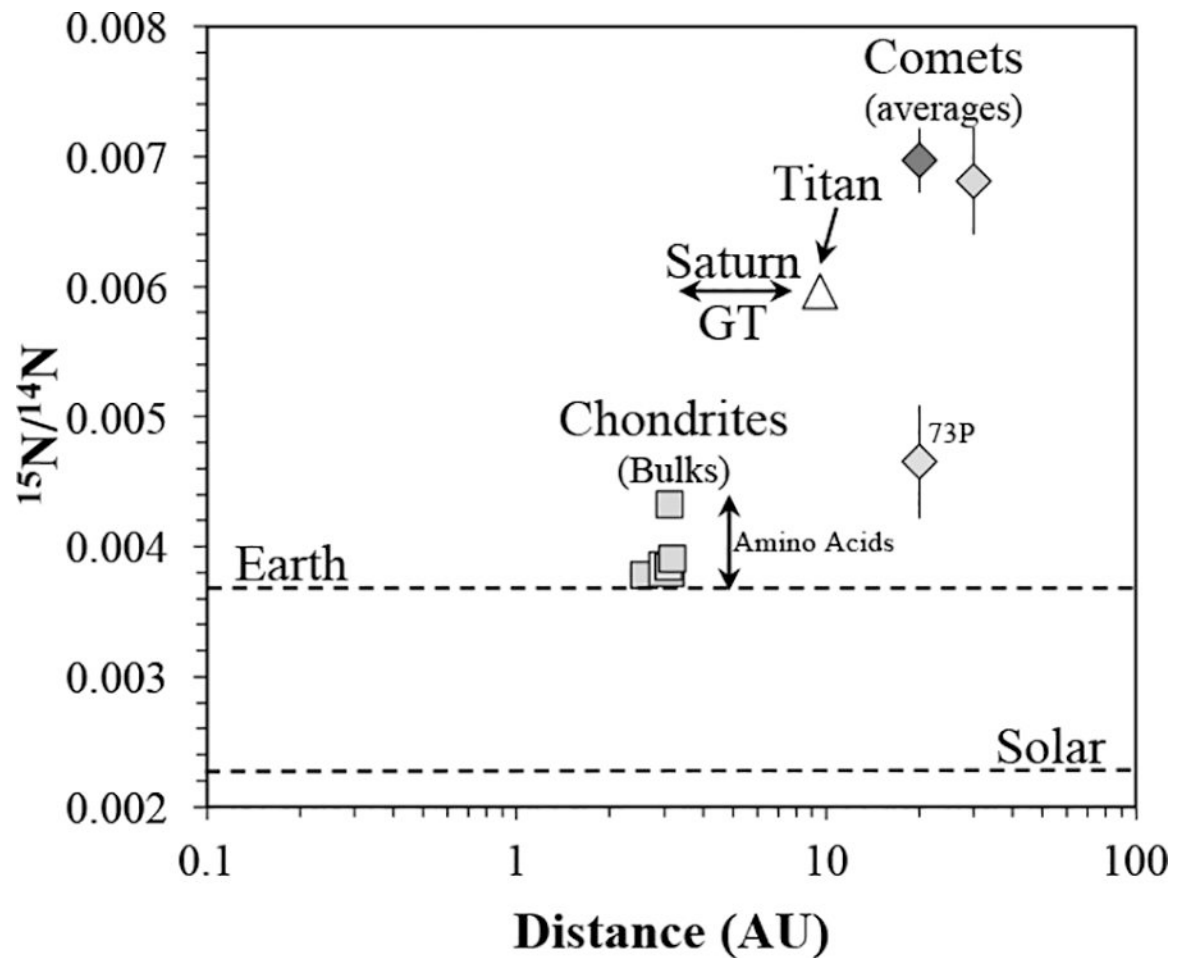


Figure 6.

The same as for Figure 6 but for N isotopes (modified after Alexander 2017). The N isotopic compositions of individual comets are generally very consistent but the uncertainties can be large (Table 6), so they have been averaged, except for the JFC outlier comet 73P. Titan's atmospheric N isotopic composition is thought to reflect that of the NH_3 it accreted (Mandt et al. 2014). The carbonaceous chondrite compositions are for bulk meteorites (Table 3). However, amino acids and other N-bearing soluble organic compounds (vertical double arrow) probably formed from HCN/NH_3 and exhibit a similar range of isotopic compositions to the bulk meteorites (see text and Table 6 for sources).

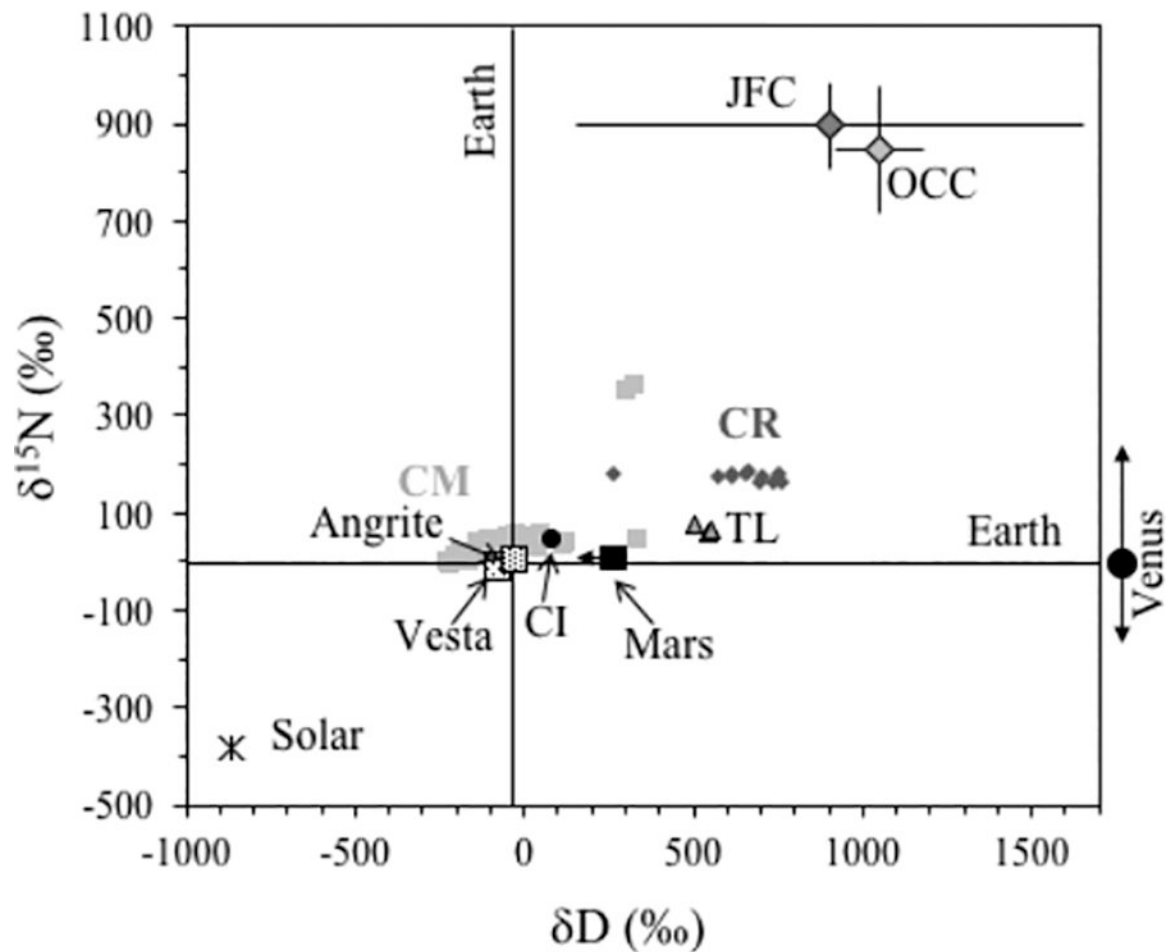


Figure 7.

Comparison of the estimated bulk H and N isotopic compositions of the major inner Solar System bodies with those of the average Jupiter family (JFC) and Oort Cloud (OCC) comets and individual members of the most volatile-rich chondritic meteorites. The H isotopic composition given for Mars is probably an upper limit. The H isotopes of the comets, based on their water compositions, are probably lower limits for their bulk compositions, whereas their N isotopes are probably upper limits (see text for details). Venus has lost almost all of its original water and its initial H isotopic composition is unknown. The sources are given in Tables 5 and 6.

Table 1.

The major chondrite classes, their groups, and their ranges of petrologic types.

Class	Groups	Types
Enstatite	EH, EL	3–6
Ordinary	H, L, LL	3–6
Rumaruti	R	3–6
Kakangari	K	3
Carbonaceous	CK	3–6
	CO, CV	3
	CI, CM, CR	1–2
	CH	Mixed chondritic & impact products
	CB	Impact products

Table 2.

A summary of average chondrule ages and estimates of the accretion ages of chondrites and non-chondrites. The most complete set of accretion age estimates are from Sugiura and Fujiya (2014) (S+F). The ages are in millions of years after CV CAI formation.

Group/meteorite	Chondrules	S+F	Other
Non-chondrites:			
Angrites		0.5±0.4	1.5 ^a
HEDs		0.8±0.3	2.2±1.1 ^b , ≤ 0.6 ^{+0.5c} _{-0.4} , <1 ^d
Magmatic irons		0.9±0.3	1.0–1.5 ^e , 0.1–0.3 ^f
Stony irons		0.9±0.3	
Ureilites		1.0±0.3	~1.6 ^g
Acap.+Lodran.		1.3±0.3	
Aubrites		1.5±0.1	
NWA 011		1.5±0.1	
Tafassasset		1.9±0.2	
Chondrites:			
E		1.8±0.1	~2 ^h
OC	2.0 ^{+0.5i} _{-0.3} , 1.7±0.7 ^j	2.1±0.1	~2 ^{k,h} , ~1.8 ^l
R		2.1±0.1	
CK		2.6±0.2	
CO	2.0 ^{+0.3m} _{-0.2}	2.7±0.2	~2.5 ^l
CV	2–2.5 ⁿ	3.0±0.2	~2.5 ^l
CI, CM, TL		3.5±0.5	3–4 ^o
CR	3.7 ^{+0.3p} _{-0.2} , 3.7 ^{+0.9p} _{-0.9}	3.5±0.5	> 4.0 ^{+0.5p} _{-0.3}

^aKleine et al. (2012).

^bTrinquier et al. (2008).

^cSchiller et al. (2011).

^dNeumann et al. (2014); Touboul et al. (2015).

^eKruijjer et al. (2013).

^fKruijjer et al. (2014).

^gBudde et al. (2015).

^hPolnau and Lugmair (2001); Shukolyukov and Lugmair (2004).

ⁱmean age of chondrules from Kita et al. (2000); Villeneuve et al. (2009).

^jKleine et al. (2008).

^kKleine et al. (2008); Harrison and Grimm (2010); Henke et al. (2013).

^lDoyle et al. (2015).

^mselected chondrules from Kurahashi et al. (2008).

ⁿBudde et al. (2016); Nagashima et al. (2017).

^oFujiya et al. (2013).

^pSchrader et al. (2016).

Table 3.

The bulk H, C and N contents and H and N isotopic compositions of various chondrite groups. For the CI, CM and CR chondrites, the values are the averages for multiple samples and the uncertainties are the standard deviations. The large standard deviations for the CM and CR chondrite H abundances and isotopes reflect the variations in degree of alteration, and in the case of the CM isotopes the anomalous Bells meteorite. For Tagish Lake, the values are averages for several lithologies, except for H abundances and isotopes that are for the most primitive (least heated?) lithology 5b. The OC, CV and CO chondrites are represented by the most primitive and volatile-rich (i.e., least metamorphosed) members of their groups (Semarkona, Kaba, and DOM 08006, respectively), hence no uncertainties are given. The data are from Alexander et al. (2012) and Alexander et al. (2017b).

	H (wt.%)	C (wt.%)	N (wt.%)	δD (‰)	$\delta^{15}N$ (‰)
OC	0.12	0.59	0.01	1616	39
CV	0.23	1.13	0.13	14	-24
CO	0.46	1.20	0.02	0	8
CM	1.15±0.18	1.95±0.34	0.10±0.03	-53±150	44±66
CI	1.55±0.02	3.65±0.24	0.19±0.03	78±7	42±5
Tagish Lake	0.94	4.07±0.10	0.20±0.04	508	66±9
CR	0.49±0.26	1.17±0.12	0.08±0.01	651±135	175±8

The standard ratios for calculating delta values are: $D/H=1.5576\times 10^{-4}$ and $^{15}N/^{14}N=3.67\times 10^{-3}$.

Table 4.

The estimated initial ^{17}O and δD values of water in the various chondrite groups. The ^{17}O values are the highest reported for secondary minerals in any member of the group, but are still probably lower limits as it is likely that there was some isotopic exchange with anhydrous minerals prior to formation of the secondary minerals. The δD values are estimated after subtraction of D-rich organic matter from bulk chondrite compositions, except for the R chondrites that is a direct measurement of hydrated silicates.

	$^{17}\text{O}^a$ (‰)	δD^b (‰)	D/H ^b
R	3.5	3660±75	$7.26\pm 0.13\times 10^{-4}$
OC	4.8±1.7	1002±207	$3.1\pm 0.3\times 10^{-4}$
CV	-0.4±0.9		
CO	-2		
CM	1.3	-427±45	$8.7\pm 0.4\times 10^{-5}$
CI	1.7	-481±107	$8.1\pm 1.7\times 10^{-5}$
Tagish Lake	2	-550±130	$7.0\pm 2.0\times 10^{-5}$
CR		96^{+110}_{-65}	$1.7\pm 0.2\times 10^{-4}$

^(a)R - Greenwood et al. (2000); OC - Choi et al. (1998); Doyle et al. (2015); CV - Choi et al. (1997); Choi et al. (2000); Doyle et al. (2015); CO - Choi et al. (2008); CM - Rowe et al. (1994); Airieau et al. (2005); CI - Rowe et al. (1994); Tagish Lake - Leshin et al. (2001).

^(b)R - McCanta et al. (2008); others - Alexander et al. (2012).

Table 5.

The D/H ratios of water in Oort Cloud (OCC) and Jupiter Family (JFC) comets. The estimated D/H ratios for the solar nebula, bulk Earth and water in Enceladus are also provided for comparison.

	D/H	Ref.
OCCs		
1P/Halley	$3.16 \pm 0.34 \times 10^{-4}$	1
1P/Halley	2.12×10^{-4}	2
C/1996 B2 Hyakutake	$2.90 \pm 1.0 \times 10^{-4}$	3
C/1995 O1 Hale-Bopp	$3.30 \pm 0.8 \times 10^{-4}$	4
C/2002 T7 LINEAR	$2.50 \pm 0.4 \times 10^{-4}$	5
8P/Tuttle	$4.09 \pm 1.45 \times 10^{-4}$	6
C/2009 P1 Garradd	$2.06 \pm 0.22 \times 10^{-4}$	7
C/2001 Q4 Neat	$4.60 \pm 1.4 \times 10^{-4}$	8
153P/Ikeya-Zhang	$< 2.50 \times 10^{-4}$	9
C/2014 Q2 Lovejoy	$1.40 \pm 0.4 \times 10^{-4}$	10
C/2012 F6 Lemmon	$6.50 \pm 1.6 \times 10^{-4}$	10
JFCs		
103P/Hartley 2	$1.61 \pm 0.24 \times 10^{-4}$	11
67P/Churyumov-Gerasimenko	$5.30 \pm 0.7 \times 10^{-4}$	12
45P/Honda-Mrkos-Pajdušáková	$< 2.00 \times 10^{-4}$	13
Other		
Solar	$2.1 \pm 0.5 \times 10^{-5}$	14
Earth	$1.49 \pm 0.03 \times 10^{-4}$	15
Angrites	$1.53 \pm 0.04 \times 10^{-4}$	16
Vesta	$1.40 \pm 0.14 \times 10^{-4}$	17
Enceladus	$2.9 + 1.5 / - 0.7 \times 10^{-4}$	18
Titan (CH ₄)	$1.59 \pm 0.33 \times 10^{-4}$	19

¹Eberhardt et al. (1995).

²Brown et al. (2012).

³Bockelée-Morvan et al. (1998).

⁴Meier et al. (1998b).

⁵Hutsemékers et al. (2008).

⁶Villanueva et al. (2009).

⁷Bockelée-Morvan et al. (2012).

⁸Altwegg et al. (2015).

⁹Biver et al. (2006).

¹⁰Biver et al. (2016).

¹¹Hartogh et al. (2011).

¹²Altwegg et al. (2015).

¹³Lis et al. (2013).

¹⁴Geiss and Gloeckler (1998).

¹⁵Lécuyer et al. (1998).

¹⁶Sarafian et al. (2016).

¹⁷Sarafian et al. (2014); Barrett et al. (2016).

¹⁸Waite Jr et al. (2009).

¹⁹Nixon et al. (2012).

Table 6.

The N isotopic compositions of HCN and/or CN in Oort Cloud (OCC) and Jupiter Family (JFC) comets. Comet 8P/Tuttle is included in both as it has mixed orbital properties. The estimated bulk N isotopic compositions for the solar nebula, the terrestrial planets and Titan's atmosphere are also included for comparison.

	$^{14}\text{N}/^{15}\text{N}$	Ref.
OCCs		
Hale-Bopp	140±35	1
C/2002 T7 (LINEAR)	160±25	2
8P/Tuttle	150±20	3
153P/Ikeya-Zhang	140±50	4
122P/de Vico	145±20	4
C/1999 S4 (LINEAR)	150±50	5
C/1999 T1 (McNaught-Hartley)	160±50	2
C/2000 WM1 (LINEAR)	150±30	6
C/2002 X5 (Kudo-Fujikawa)	130±20	2
C/2002 V1 (NEAT)	160±35	2
C/2002 Y1 (juels-Holvorcem)	150±35	2
C/2001 Q4 (NEAT)	135±20	1
C/2003 K4 (LINEAR)	145±25	1
C/2006 M4 (SWAN)	145±50	2
C/2007 N3 (Lulin)	150±50	2
C/2012 S1 (ISON)	139±38	7
C/2012 F6 (Lemmon)	152±72	8
C/2014 Q2 (Lovejoy)	145±12	8
JFCs		
88P/Howell	140±20	5
9P/Tempel 1	145±20	9
73P/Schwassmann-Wachmann 3	215±32	10
17P/Holmes	139±25	11
8P/Tuttle	150±30	3
Other		
Venus	273±56	12
Earth	272	
Mars	280±5	13
Angrites	272±1	14
Vesta	277	15
Titan	168±2	16
Solar	441±6	17

¹Manfroid et al. (2005).

²Manfroid et al. (2009).

³Jehin et al. (2009).

⁴Jehin et al. (2004).

⁵Hutsemékers et al. (2005).

⁶Arpigny et al. (2003).

⁷NH₃, Shinnaka et al. (2014).

⁸Biver et al. (2016).

⁹Jehin et al. (2006).

¹⁰Jehin et al. (2008).

¹¹Bockelée-Morvan et al. (2008).

¹²Hoffman et al. (1979).

¹³Mathew and Marti (2001).

¹⁴Abernethy et al. (2013).

¹⁵Miura and Sugiura (1993).

¹⁶Niemann et al. (2010).

¹⁷Marty et al. (2011).