

Review



Cite this article: Alexander CMO'D. 2017 The origin of inner Solar System water. *Phil. Trans. R. Soc. A* **375**: 20150384.
<http://dx.doi.org/10.1098/rsta.2015.0384>

Accepted: 5 September 2016

One contribution of 9 to a Theo Murphy meeting issue 'The origin, history and role of water in the evolution of the inner Solar System'.

Subject Areas:

Solar System

Keywords:

water, volatiles, terrestrial planets, asteroids, Grand Tack, chondrites

Author for correspondence:

Conel M. O'D. Alexander

e-mail: calexander@carnegiescience.edu

The origin of inner Solar System water

Conel M. O'D. Alexander

Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road NW, Washington, DC 20015, USA

 CMODA, 0000-0002-8558-1427

Of the potential volatile sources for the terrestrial planets, the CI and CM carbonaceous chondrites are closest to the planets' bulk H and N isotopic compositions. For the Earth, the addition of approximately 2–4 wt% of CI/CM material to a volatile-depleted proto-Earth can explain the abundances of many of the most volatile elements, although some solar-like material is also required. Two dynamical models of terrestrial planet formation predict that the carbonaceous chondrites formed either in the asteroid belt ('classical' model) or in the outer Solar System (5–15 AU in the Grand Tack model). To test these models, at present the H isotopes of water are the most promising indicators of formation location because they should have become increasingly D-rich with distance from the Sun. The estimated initial H isotopic compositions of water accreted by the CI, CM, CR and Tagish Lake carbonaceous chondrites were much more D-poor than measured outer Solar System objects. A similar pattern is seen for N isotopes. The D-poor compositions reflect incomplete re-equilibration with H₂ in the inner Solar System, which is also consistent with the O isotopes of chondritic water. On balance, it seems that the carbonaceous chondrites and their water did not form very far out in the disc, almost certainly not beyond the orbit of Saturn when its moons formed (approx. 3–7 AU in the Grand Tack model) and possibly close to where they are found today.

This article is part of the themed issue 'The origin, history and role of water in the evolution of the inner Solar System'.

1. Introduction

The origin of Earth's water has, of course, tremendous astrobiological significance, but it also has considerable

Table 1. The orbital semi-major axes (astronomical units), sizes and estimated bulk H and N isotopic compositions of some of the largest objects in the inner Solar System. The isotopic compositions are given as both absolute ratios and delta values (relative to SMOW (standard mean ocean water) and air for H and N, respectively) because of the differing preferred usages in the astronomical and geochemical communities.

	orbit (AU)	radius (km)	D/H $\times 10^{-4}$	δD (‰)	$^{15}\text{N}/^{14}\text{N} \times 10^{-3}$	$\delta^{15}\text{N}$ (‰)
Venus ^a	0.72	6052	160 \pm 20	\sim 100 000	3.66 ^{+0.95} _{-0.62}	-4 ⁺²⁵⁸ ₋₁₆₉
Earth [1]	1.0	6371	1.49 \pm 0.03	-43 \pm 20	3.68	0
Moon [2–8]	1.0	1737	1.40 to 1.85	-100 to 190	3.67 to 3.78	-2 to 27
Mars ^b	1.52	3390	\leq 1.99	\leq 275	3.70	7
Vesta [9–11]	2.36	263	1.31 to 1.50	-162 to -34	<3.61	<-18

^aVenusian atmosphere [12,13].

^bMartian interior [14,15].

Table 2. The average bulk H and N isotopic compositions of analysed CI, CM, CR and Tagish Lake samples, along with the bulk solar compositions, the average H isotopic compositions of H₂O and N isotopic compositions of HCN/NH₃ in Oort Cloud (OCC) and Jupiter family (JFC) comets, and the range of isotopic compositions in the envelopes of forming protostars (PS). For the averages, the uncertainties are the 1 σ standard deviations of the samples.

	D/H $\times 10^{-4}$	δD (‰)	$^{15}\text{N}/^{14}\text{N} \times 10^{-3}$	$\delta^{15}\text{N}$ (‰)
CI [23–25]	1.68 \pm 0.01	78 \pm 7	3.83 \pm 0.02	42 \pm 5
CM [23–25]	1.59 \pm 0.20	-53 \pm 130	3.84 \pm 0.24	44 \pm 66
CR [23–25]	2.57 \pm 0.21	652 \pm 134	4.32 \pm 0.03	175 \pm 8
Tagish Lake [23–25]	2.32 \pm 0.13	495 \pm 83	3.91 \pm 0.03	61 \pm 7
Bulk solar [26,27]	0.21 \pm 0.05	-865 \pm 32	2.27 \pm 0.03	-382 \pm 8
OCCs [28–36]	2.88 \pm 0.71	851 \pm 161	6.81 \pm 0.41	853 \pm 32
JFCs [32,35,37,38]	3.64 \pm 2.61	1218 \pm 1675	6.97 \pm 0.25 ^a	896 \pm 19 ^a
PS [39–41]	10–100	5500–63 000	3.44–6.25	-64 to 700

^aThe average JFC N isotopic composition does not include the outlier comet 73P whose $^{15}\text{N}/^{14}\text{N} = 4.65 \pm 0.69 \times 10^{-3}$.

significance for understanding how the terrestrial planets formed and more generally for the early evolution of the Solar System. Much of the debate about the origin of water in the inner Solar System has tended to focus on the abundance and isotopic composition of H, and that is the case here. However, as will become apparent, it is important to also consider the abundances and isotopic compositions of other volatile elements, such as C, N and the noble gases, as they will have been accreted along with the H/H₂O in the same potential source materials.

Table 1 gives the sizes and estimated bulk H and N isotopic compositions of the largest objects in the inner Solar System that are known to have accreted at least some water when they formed. Mercury does have small amounts of water at its surface, but it is almost certainly exogenous [16]. The largest asteroid, Ceres, contains water in its interior [17], as do some smaller asteroids (e.g. [18–22]), but their H isotopic compositions have not been measured.

Hydrogen isotopes are fractionated relatively easily by both physical and chemical processes. For instance, the H isotopic composition of Venus's atmosphere is hugely enriched in D (table 1) due to the almost complete loss of H to space through photodissociation of H₂O [13]. On the other hand, the isotopic compositions of the other bodies are remarkably similar (table 1) given their range of sizes, formation locations and formation histories, as well as the potential sources of their water (table 2).

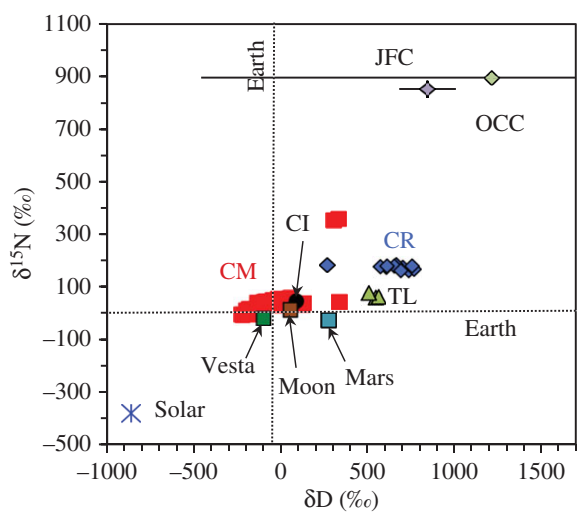


Figure 1. Comparison of the estimated bulk H and N isotopic compositions of the major inner Solar System bodies with those of the average Jupiter family (JFC) and Oort Cloud (OCC) comets and individual members of the most volatile-rich chondritic meteorites. The H isotopic compositions of Mars and the Moon are probably upper limits. The isotopic composition of N in Venus’s atmosphere is roughly terrestrial, but its H isotopes have been hugely fractionated by the loss of H to space. The sources for the isotopic compositions are given in tables 1 and 2, and Alexander *et al.* [23].

At least two mechanisms have been proposed in which solar nebula H was accreted by the Earth and other planets—adsorption of H onto grain surfaces in the nebula [42] and dissolution of H₂ by a magma ocean [43,44]. However, the H isotopic composition of the nebula is almost an order of magnitude more depleted in D than those of the major inner Solar System bodies (table 2). It has been suggested that isotopic fractionation associated with hydrodynamic escape of H₂ can explain the more D-rich compositions of the Earth and Mars. However, given their different sizes and formation histories, it would be an extraordinary coincidence if they all experienced such similar degrees of H isotopic fractionation. Also, it is not clear that hydrodynamic escape can explain the H isotopic composition of Vesta, or the abundances and isotopic compositions of other volatile elements in any of the objects (see below). Thus, it is unlikely that direct accretion of solar nebula gas can have been the major source of water for the planets and planetesimals in the inner Solar System.

At the other isotopic extreme is the D-rich interstellar ice (table 2) that the forming Solar System would have inherited from its parental molecular cloud. Again, H isotopes rule out such ices as the major source of water in the inner Solar System. However, as recent models suggest that it is not possible to produce significant D enrichments in H₂O in discs, a small amount of interstellar water may ultimately be required to explain the non-solar H isotopic compositions of the inner Solar System bodies [45,46].

This leaves comets and the parent bodies of the chondritic meteorites as the most likely major sources of water for the terrestrial planets. To distinguish between these two sources requires consideration of the isotopic compositions and abundances of other volatile elements in addition to H. The element most commonly used is N (figure 1). Again, it is clear that the isotopic compositions of the larger inner Solar System objects are distinct from the solar composition and from comets. This then leaves primitive chondritic meteorites as the most likely sources of volatiles for the terrestrial planets, in particular the CI and CM carbonaceous chondrites [23,47]. If this is correct, then, as will become apparent later, a significant fraction of the water and almost all the N in the terrestrial planets comes from organic matter and not from ice. The organic matter would also be the major source of C and noble gases.

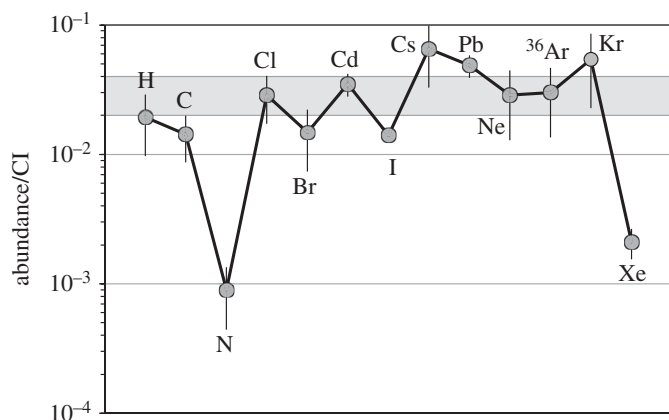


Figure 2. The Cl chondrite-normalized estimated abundances of H, C, N, noble gases and volatile lithophiles in the bulk Earth. Within the uncertainties, the volatile element abundances are consistent with a 2–4% CI contribution to a largely volatile-depleted proto-Earth. The depletions in N and Xe could be due to an underestimate of the N content of the Earth and loss of Xe from the atmosphere to space, respectively (see the text for details). The terrestrial abundances of H, C, N and noble gases are from Marty [47], and the volatile lithophile abundances are from Palme & O'Neill [51] except for I that is from Deruelle *et al.* [52]. The Cl chondrite H, C and N abundances are from Alexander *et al.* [23], while all other elements are from Lodders [53].

One note of caution in the above discussion is that the comet compositions in figure 1 are probably not their bulk compositions—the H isotopes are those of H₂O and the N isotopes are of relatively minor volatile species (HCN and NH₃). We know very little of the isotopic compositions of the refractory organic material that could make up approximately 30% of comets (e.g. [48]) and will certainly be a major contributor to the H and N budgets of bulk comets. However, if the refractory organics are anything like the organics in the most primitive chondrites and in interplanetary dust particles (IDPs) that may come from comets, they will be enriched in D and ¹⁵N relative to the terrestrial planets (e.g. [49,50]). Thus, even comets like Hartley 2 with near-terrestrial H₂O H isotopic compositions [37] are likely to have bulk compositions that are too D-rich to be the major source of the volatiles in the terrestrial planets [23].

Additional constraints on the sources of the terrestrial planet volatiles come from volatile abundances, as well as the isotopic compositions of other elements that vary between the chondrite groups (e.g. O, Ti, Cr, Os, Ru and Mo). The abundances of H, N and other volatiles in most types of chondrite are so low that they cannot have supplied the volatiles to the Earth, Moon and Mars without violating other bulk chemical and isotopic constraints. Of the potential chondritic sources, only the CI and CM carbonaceous chondrites are able to roughly reproduce the H and N isotopes (figure 1), as well as the relative abundances of H, C, volatile lithophiles and the noble gases (figure 2). About 2–4 wt% of CI/CM-like material would be needed to account for Earth's volatile budget [47], a small enough amount that it would avoid violating other elemental/isotopic constraints. However, the CI/CM-like material would have to have been accreted prior to the end of core formation, normally assumed to coincide with Moon formation. This is to avoid disagreement with the isotopic compositions of the highly siderophile elements in the Earth's mantle and because the estimated mass of material accreted after the Moon-forming impact, approximately 0.5 wt% in the so-called Late Veneer, is too small (e.g. [54]). Relative to the chondrites, N and Xe are notably depleted (figure 2) in estimates of the bulk Earth [47,55]. Xenon may have been progressively lost from the atmosphere over geologic time [56]. It cannot be ruled out that the N budget of the mantle has been underestimated [47,57,58] or that N has been sequestered into the core [47], but it is also possible that the N depletion reflects multiple episodes of impact-induced atmospheric loss [59].

2. Delivery of water to the terrestrial planets

The parent bodies of the chondrites are in the asteroid belt (approx. 2–4 AU), and the CI and CM chondrites are thought to come from C-complex asteroids that dominate the outer asteroid belt. So if the CI/CM chondrites are representative of the major sources of volatiles in the terrestrial planets, how were they delivered?

In the ‘classical’ explanation (e.g. [60]), there was a radial gradient in the volatile contents of the planetesimals of the inner Solar System that reflected the thermal gradient in the solar nebula at the time the planetesimals formed. Once the gas disc had dissipated, mutual gravitational interactions between the planetesimals and between the planetesimals and the giant planets led to scattering, collisions and growth. Growth would have been faster in the inner part of the planetesimal disc (less than 2 AU) where the density of planetesimals was higher and dynamical time scales were shorter. As the water-rich objects beyond 2 AU must have been scattered into this region, they would have tended to be accreted somewhat later.

Perennial problems with the ‘classical’ model are explaining the low mass of Mars and the structure of the asteroid belt, particularly the absence of embryo-sized objects in it. The so-called Grand Tack model was designed to overcome these problems [61]. In the Grand Tack model, interactions with the gas disc caused Jupiter to migrate in to approximately 1.5 AU, at which point a still growing Saturn caught up with it. Jupiter and Saturn then became locked in an orbital resonance that changed how they interacted with the gas disc and caused them to migrate outwards. This outward migration only stopped when the gas disc dissipated. As one might expect, the inward migration would have removed most of the existing planetesimals between approximately 4 AU and approximately 1.5 AU. Then as the giant planets migrated out again, they would have scattered some outer Solar System planetesimals (5–15 AU) into the inner Solar System. The clearing-out of most planetesimals beyond 1.5 AU ensured that a growing Mars remained relatively small and produced a low-mass asteroid belt that was crudely zoned, with inner Solar System objects dominating the inner belt and outer Solar System objects dominating the outer belt. Presumably, these outer Solar System planetesimals would have been volatile-rich and, therefore, potent sources of volatiles for the growing terrestrial planets.

If the Grand Tack model is correct, the source(s) of water in the inner Solar System could ultimately have been in the outer Solar System. The rest of this paper focuses on the meteorite record to try to distinguish between the ‘classical’ and Grand Tack models, searching in particular for indicators of meteorite formation distance from the Sun, because it is the formation distances of the volatile-rich objects that most clearly distinguish the two models.

3. Meteorites in brief

The classification of meteorites has been described in detail by Krot *et al.* [62], so it is only briefly outlined here. The major subdivision of meteorites is between the unmelted chondrites and the non-chondrites (achondrites, stony irons and irons) that come from asteroids that experienced variable degrees of melting and differentiation. The non-chondrites are very poor in H and other highly volatile elements, and so will not be discussed in detail here. Historically, the chondrites have been divided into three classes (ordinary, carbonaceous and enstatite) based on their compositions and mineralogies. These in turn have been subdivided into a number of groups: ordinary chondrites into H, L and LL; carbonaceous chondrites into CI, CM, CR, CV, CO, CB, CH and CK; and enstatite chondrites into EH and EL. The name ‘carbonaceous chondrite’ is a historical one and is a bit misleading because some ordinary and enstatite chondrites contain more C than some carbonaceous chondrites. The chondrite classification scheme is still evolving as more meteorites are found; two new classes (R and K chondrites) have been recognized, and a number of individual meteorites do not belong to any recognized group. While there are variations, the bulk compositions of the chondrites are remarkably similar to that of the rock-forming component of the solar photosphere (i.e. excluding H, C, N, O and the noble gases). Indeed, the CIs have bulk compositions that are within error identical to the rock-forming component of the Sun [53,63].

Chondrites comprise three main components: refractory inclusions, chondrules and fine-grained matrix. Refractory inclusions and chondrules formed at high temperatures (1400–1800°C) in the solar nebula. The most abundant refractory inclusions, the calcium–aluminium-rich inclusions (CAIs), are the oldest Solar System objects to have been dated and are generally assumed to mark the formation of the Solar System. Given their high formation temperatures, water and organics would not have survived refractory inclusion or chondrule formation. Consequently, at the time when the chondrite parent bodies formed, it was only in the matrix that water (as ice) and organic matter would have been present. It is also in the matrix that one finds other primitive materials, such as presolar circumstellar grains.

After formation, the chondrites experienced secondary modification (thermal metamorphism and aqueous alteration) due to the internal heating of their parent bodies by the decay of short-lived (now extinct) radionuclides and shock heating associated with impacts. A petrographic classification scheme for secondary processes divides the chondrites into six types—types 3 to 6 reflect increasing extent of thermal metamorphism, and types 3 to 1 reflect increasing degrees of aqueous alteration. By convention, the chemical classification is followed by the petrologic one (e.g. CI1, CM2, CV3).

Spectroscopically, the enstatite chondrites have been linked to the Hungaria asteroids that inhabit the very inner edge of the asteroid belt, the ordinary chondrites (and the related R chondrites) have been linked to the S-complex asteroids that dominate the inner asteroid belt, and the carbonaceous chondrites have been linked with the C-complex asteroids that dominate the outer asteroid belt [64,65]. It is important to note that this spectroscopic/compositional zoning in the asteroid belt is only apparent among the larger asteroids, i.e. those asteroids that have not experienced catastrophic collisional disruption and whose orbits will not have changed much since the end of planet formation. Smaller asteroids are predominantly collisional fragments and are subject to orbital migration [66]. The relationship between S-complex asteroids and ordinary chondrites has been confirmed by two space missions to near-Earth asteroids [67–69], but the link between C-complex asteroids and carbonaceous chondrites has yet to be definitively demonstrated. Interestingly, differences in the sizes of small nucleosynthetic anomalies in bulk Ti and Cr indicate that the carbonaceous chondrites are distinct from all other inner Solar System materials (the ordinary and enstatite chondrites, non-chondritic meteorites, Earth, Moon and Mars) [70]. This is certainly consistent with the Grand Tack model, but how the nucleosynthetic anomalies were produced is not understood, and they could reflect spatial and/or temporal variations in the solar nebula.

That there could have been a temporal element to the production of the Ti and Cr anomalies is suggested by estimates of the accretion times of the chondrites. The Solar System formed with abundant short-lived radionuclides, particularly ^{26}Al . Planetesimals that formed before approximately 2 Ma after Solar System formation would have melted and differentiated, unless they were small, in which case they are unlikely to have survived to the present day. To survive impacts in space and atmospheric entry, the unmelted chondrites must have undergone a degree of lithification (rock formation from unconsolidated material). This restricts their formation to a window between roughly 2 Ma and 4 Ma after Solar System (CAI) formation, the upper limit being when there was just enough short-lived radioactivity to melt ice and enable some aqueous alteration. Unlithified bodies that formed after approximately 4 Ma could be one of the sources, along with comets, of the IDPs that are being continuously accreted by the Earth [71]. More detailed estimates of accretion times can be made using thermal models and estimates of the maximum temperatures experienced by any member of a chondrite group (figure 3). However, these estimates are at best approximate, as they must make a number of assumptions (e.g. planetesimal sizes, initial ice contents, and that the centres of all the chondrite parent bodies have been sampled). It is also possible that some chondrites (e.g. the CVs) are the unmelted crusts of differentiated objects [73,74], in which case their parent bodies must have formed much earlier than indicated in figure 3.

There is direct or indirect evidence that, with the exception of the enstatite chondrites, all chondrites accreted some water (e.g. [75]). Thus, by the time the ordinary chondrites formed, the

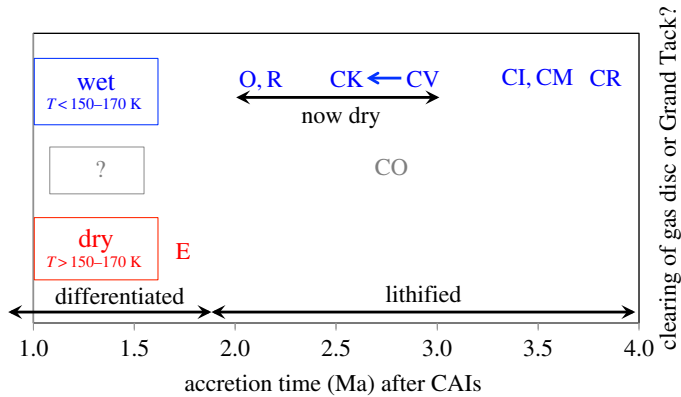


Figure 3. Estimates of the accretion times of the chondrite parent bodies (modified after [72]). All the chondrites have avoided melting, but they experienced sufficient lithification as a result of metamorphism and/or aqueous alteration to be robust enough to survive impacts and atmospheric entry. Hence, the chondrites must have formed in a window of time between when there was not quite enough short-lived radioactivity to melt and differentiate planetesimals, and when there was not enough radioactivity to even melt water ice. With the exception of the highly reduced enstatite chondrites (E) and possibly the COs, all the chondrites accreted at least some water, presumably as ice, implying accretion temperatures that were below the sublimation temperature of water ice in the nebula (150–170 K). (Online version in colour.)

ambient temperatures at approximately 2 AU had fallen below the sublimation temperature of water ice in the disc (approx. 150–170 K). Intuitively, one might expect that, as the disc continued to cool, chondrites that formed later would have accreted more ice, particularly if they also formed further from the Sun. Unfortunately, estimating how much water the chondrite parent bodies accreted is difficult. This is largely because in most chondrite parent bodies there was enough short-lived radioactivity to metamorphose and dehydrate them. Only the CI, CM and CR chondrites, along with the ungrouped carbonaceous chondrite Tagish Lake, seem to have formed late enough to have avoided extensive dehydration. Even in these meteorites, evidence for the original water is now preserved primarily as OH in phyllosilicates, hydrated amorphous silicates and, possibly, hydroxides, although some water was also consumed in the formation of anhydrous secondary minerals such as magnetite and sulfates. Estimating the initial water budgets is further complicated by the range of H₂O/OH contents seen in CM and CR chondrites [24], the possibility that water was redistributed within or lost from the chondrite parent bodies, and that any water ice that remained after alteration would have been lost when the meteorites were small objects in space prior to atmospheric entry. Nevertheless, with the notable exception of the CR chondrites, there is a general increase in matrix contents with accretion age, and because water ice was accreted with the matrix, this suggests that the water contents may also have increased with accretion age.

The conventional explanation for the apparent stratigraphy in the asteroid belt and the range of peak temperatures experienced by the chondrite groups is that there was a wave of planetesimal formation that slowly progressed outwards through the asteroid belt [76,77]. Of course, the Grand Tack model greatly increases the potential range of radial distances the chondrites may have formed over. However, at present it cannot be demonstrated that accretion age is correlated with formation distance. Nor is it clear that a monotonic increase in accretion age with formation distance is consistent with recent models that suggest that planetesimal formation should have been rapid and efficient throughout much of the disc [78–80].

4. Hydrogen isotopes: indicators of formation distance?

At present, the H isotopes of water are the most promising indicators of formation distance. This is because there is likely to have been a radial gradient in the H isotopic composition of water in

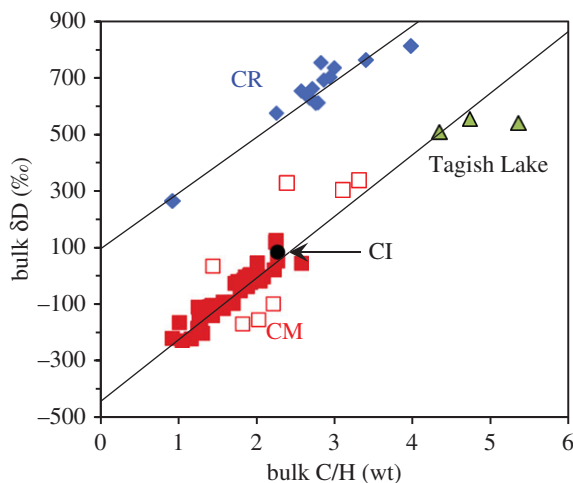


Figure 4. The bulk H isotopic compositions versus the bulk C/H ratios of CI, CM, CR and Tagish Lake carbonaceous chondrites (after [23]). The linear arrays displayed by the CM and CR chondrites reflect mixing between relatively D-poor water/OH and D-rich organic matter ($\delta D \approx 3500\text{‰}$). The y -axis intercepts of the best-fit lines to the CM and CR trends give their water/OH compositions. The open red squares are CM chondrites that were not used in the fit for various reasons (see [23]). (Online version in colour.)

the disc. This gradient would have been the result of radial mixing between water in the outer Solar System that retains a large D-rich interstellar component and D-poor (solar D/H) water in the warm inner Solar System produced by 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. [81]), this is almost certainly a gross oversimplification (e.g. [82]). 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 most comets (e.g. [38]) and Saturn's moon Enceladus [83].

Determining the initial H isotopic composition of the water accreted by the chondrites is not as straightforward as one might think. This is because the OH-bearing clay minerals in the chondrites are intimately intermixed with D-rich organic material. Not only is it not possible to physically or chemically separate the clay minerals from the organics, but there may also have been isotopic exchange between the water and the organics during aqueous alteration in the chondrite parent bodies. However, the situation is not hopeless. The CM and CR chondrites experienced a wide range in the extent of alteration, but the variation in organic contents is more restricted. Provided that (i) this range in alteration either reflects heterogeneous accretion of the ice or, more likely, a very early redistribution of water in the parent bodies before any exchange with the organics took place, and (ii) once alteration began, the meteorites remained as closed systems, then plotting bulk H isotopes versus bulk C/H should produce a linear mixing line between the original water and organic H isotopic compositions. As can be seen from figure 4, this does seem to be the case for both the CM and CR chondrites, with the y -axis intercepts giving the initial water isotopic compositions. The same exercise cannot be done for the other chondrite groups because they do not show the same ranges of alteration. However, model compositions can be estimated by subtracting a primitive organic component from their bulk compositions.

The initial water H isotopic compositions estimated in this way are shown in figure 5, along with a direct water measurement for the R chondrites [84], and compared to those of comets and Enceladus. The estimates for water in CI and CM chondrites, as well as Tagish Lake, are all intermediate between the terrestrial and solar values, and quite distinct from those of any comets. The estimate for the CR chondrite water is slightly above terrestrial and overlaps with the compositions of two of the least D-enriched comets. However, perhaps most surprising are

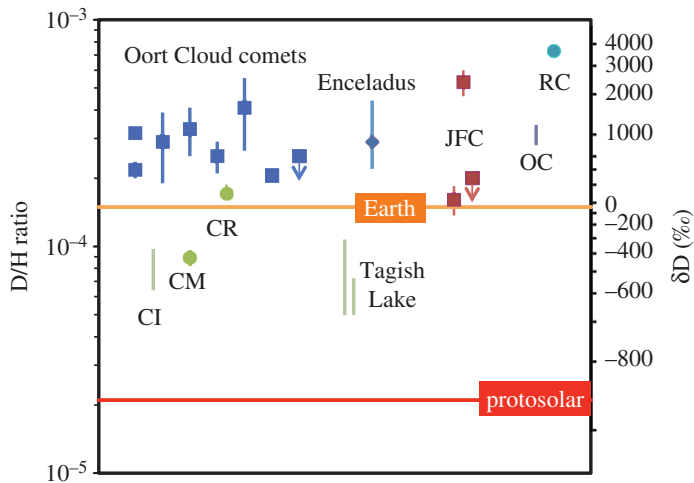


Figure 5. Comparison of the estimated H isotopic compositions of water in various chondrites with those for water in comets and Saturn’s moon Enceladus (after [23]). The CI, CM and Tagish Lake isotopic compositions are clearly distinct from those measured for outer Solar System objects. The CR composition overlaps with those of the most D-poor comets. Surprisingly, the water in ordinary and R chondrites has H isotopic compositions that resemble those of most comets and Enceladus. However, this does not necessarily mean that the ordinary and R chondrites come from the outer Solar System. It is more likely that the H isotopic compositions of their water has been fractionated by parent body processes (see the text for details). This parent body fractionation may also have affected the carbonaceous chondrites, particularly the CRs.

the ordinary and R chondrite compositions—the ordinary chondrite composition is similar to that of most comets, as well as Enceladus, while the R chondrite composition is more D-enriched than any measured comet. Taken at face value, this would seem to imply that the ordinary and R chondrites formed further from the Sun than the carbonaceous chondrites and even most comets, which would be contrary to the expectations of both the ‘classical’ and Grand Tack models. At the very least and counter-intuitively, it is possible that the ordinary and R chondrites accreted more interstellar water than the carbonaceous chondrites [85,86].

However, there may be a more mundane explanation for the ordinary and R chondrite results [23,50,87]. Magnetite and other Fe^{3+} -bearing minerals are ubiquitous in the altered chondrites. Petrologic evidence indicates that the Fe in these minerals was largely derived from the oxidation of Fe metal by water. These oxidation reactions (e.g. $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$) would have produced copious H_2 . At low temperatures (less than 200°C), there is a very large equilibrium isotopic fraction between water and H_2 , which probably explains why the δD values of H_2 produced during serpentinization on Earth can be as low as -600‰ to -800‰ [88–90]. Loss of such isotopically light H_2 would have enriched the residual water in D, and the higher the initial metal/water ratio the greater the final water δD will have been. Given their low matrix contents, the ordinary and R chondrites probably did have the highest initial metal/water ratios of the chondrites measured. After correcting for the estimated water loss, the initial H isotopic composition of the ordinary chondrite water may have been similar to that of the carbonaceous chondrites [91]. However, this process will have affected all the chondrites to varying degrees and it may partly explain why the CR chondrites have higher δD values than the other carbonaceous chondrites.

Figure 6 plots as a function of radial distance from the Sun the estimated water isotopic compositions of the carbonaceous chondrites, comets and Saturn’s moon Enceladus. The H isotopic composition of CH_4 in Titan’s atmosphere [93] 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 comet are unknown, but are likely to have been in the region of

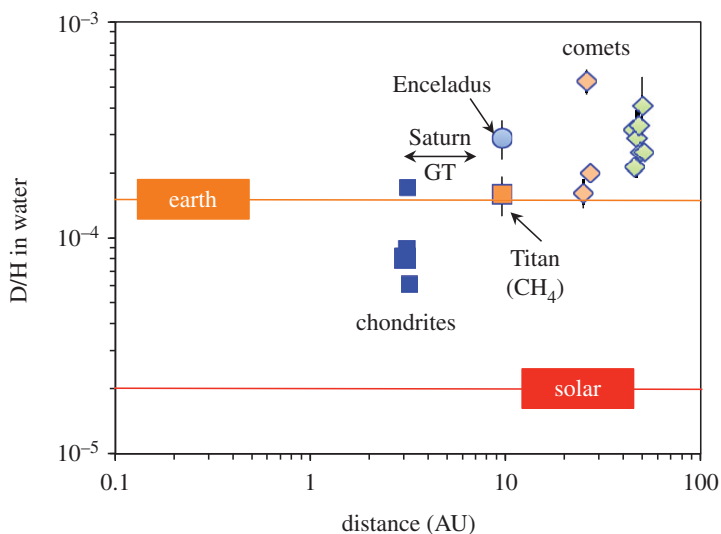


Figure 6. The H isotopic compositions of water in various objects as a function of radial distance from the Sun. The H isotopic composition of methane in Titan's atmosphere is also shown, although it is not known how closely it reflects that of the water that Titan accreted. The asteroidal parent bodies 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 approximately 3 AU and approximately 7 AU (arrowed). The formation locations of the comets are unknown, but are thought to have been between approximately 20 AU and approximately 30 AU (e.g. [92]). 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. Sources are given in tables 1 and 2, and Alexander *et al.* [23].

the current orbit of Neptune (e.g. [92]). Hence, they have both been given nominal formation locations of approximately 30 AU. If Enceladus and Titan formed from Saturn's subdisc, this would presumably have been towards the end of Saturn's growth, which in the Grand Tack model would have been between roughly 3 AU and 7 AU (arrowed) rather than at Saturn's current orbital radius of approximately 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 comets and Enceladus. Consequently, it is tempting to infer that water beyond somewhere between 3 and 7 AU was enriched in D relative to the bulk Earth and somewhere between 3 and 7 AU there was a steep decrease in the isotopic composition of the water in the disc. However, it is possible that Enceladus formed from the debris of a tidally disrupted planetesimal that was captured by Saturn [94]. If correct, this would weaken or remove the constraints on the H isotopic composition of water in the inner part of the outer Solar System.

Nitrogen isotopes might provide some further constraints on the formation distances of planetesimals. 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 more stable than H_2 and there has been no detailed isotopic modelling of the N system in the nebula. Nevertheless, as is evident from figures 1 and 7, the N isotopic compositions of the bulk chondrites are less ^{15}N -enriched than HCN/NH_3 in comets, as well as Titan's atmosphere [96], which may have originally been accreted as NH_3 [95]. Hence, when the N isotopes are plotted against radial distance (figure 7), there is a similar pattern to that for H isotopes (figure 6), with outer Solar System objects being more enriched than the chondrites. However, to truly compare like with like we should be using NH_3 compositions in chondrites not their bulk compositions. There is little NH_3 or ammonium salts in chondrites, and what there is has not been extensively studied. However, they do contain amino acids that have garnered a lot of attention and they are thought to have formed in their parent bodies via Strecker-cyano

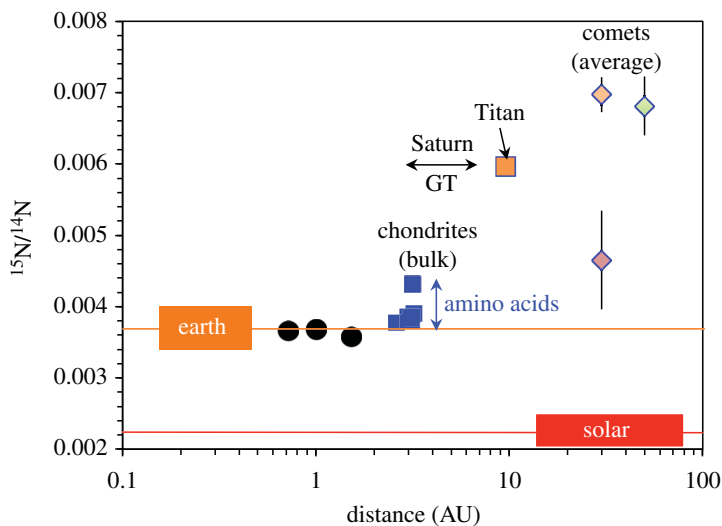


Figure 7. The same as for figure 6 but for N isotopes. The N isotopic compositions of individual comets are generally very consistent but the uncertainties can be large, so they have been averaged (table 2), except for the JFC outlier comet 73P. Titan’s atmospheric N isotopic composition is thought to reflect that of the NH_3 it accreted [95]. The chondrite compositions (carbonaceous in blue, ordinary in red) are for bulk meteorites. However, amino acids and other N-bearing soluble organic compounds (blue double arrow) probably formed from HCN/NH_3 and exhibit a similar range of isotopic compositions to the bulk meteorites (see the text for details).

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 [97–101].

Bulk chondrites exhibit a range of mass-dependent and mass-independent O isotope variations, and their individual components can show even larger variations. In an O three-isotope diagram, bulk chondrites lie fairly close to the terrestrial mass fractionation line (TFL)—the TFL is defined by the equation $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$, while mass-independent deviations from the TFL are usually indicated by $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$. On the other hand, the Sun and most refractory inclusions have ^{16}O -rich compositions ($\Delta^{17}\text{O} = -28 \pm 2\%$ for the Sun) that fall far from the TFL [102]. At present, the favoured explanation for producing these large mass-independent variations is that UV self-shielding by CO, either in the protosolar molecular cloud [103] or in the outer solar nebula [104], produced ^{16}O -rich CO and ^{16}O -poor H_2O . The H_2O may have had a mass-independent anomaly as high as $\Delta^{17}\text{O} \approx 80\%$ [105]. By some still poorly understood process, fractionation of silicates and H_2O ice from CO in the gas, followed by isotopic exchange between the silicates and H_2O , would explain why all inner Solar System materials, as well as IDPs and comet Wild 2 dust, have O isotopic compositions that fall fairly close to the TFL [106–109]. Much of this exchange has to have occurred prior to accretion of the chondrite and comet parent bodies because most of their components, other than refractory inclusions, have O isotopic compositions that lie closer to the TFL than to the solar composition. The isotopic compositions of secondary minerals (e.g. magnetite and carbonates) in chondrites have relatively modest mass-independent fractionations (e.g. summary by [23] in their electronic supplementary material), suggesting that the bulk of the water that they accreted had already been re-equilibrated with silicates in the disc [110,111]. Qualitatively, this is a very similar conclusion to that arrived at from the H isotopes, i.e. most of the water had been re-equilibrated in the inner Solar System, but that a small fraction of interstellar water was present when the chondrites formed.

On balance, the combination of H, N and O isotopes in carbonaceous chondrites suggests that they did not form beyond the formation locations of Saturn’s moons, which in the Grand Tack model would have been between approximately 3 AU and approximately 7 AU. Thus, if there

was a Grand Tack, it did not scatter objects into the asteroid belt from as far out as envisaged in the original model, but 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.

5. Minor contributors to volatile budgets

If CI/CM-like planetesimals were the major sources of the terrestrial planets' water and other volatiles, were there other more minor contributors? As already mentioned, the CK, CO and CV chondrites can be ruled out because their volatile contents are too low. Figure 1 shows that, based on their bulk H and N isotopic compositions, the CR chondrites and Tagish Lake can also be ruled out. This really only leaves the CI and CM chondrites as potential representatives of the major sources of Earth's volatiles. The CIs have roughly twice the volatile contents of the CMs, and so half the amount of CI-like material would be required to reproduce the Earth's volatile budget. On the other hand, the bulk CI and CM H and N isotopic compositions are not identical to terrestrial (figure 1 and table 2), and the CI composition is further from terrestrial than the average CM composition. As there are no obvious fractionation mechanisms for producing the Earth's isotopically lighter H and N compositions from bulk CI/CM material, an additional volatile source is required. The most obvious source would be a solar component acquired either directly from the nebula or as solar wind implanted into the surfaces of accreted dust and small planetesimals. Indeed, noble gases clearly show that there is a solar component in the Earth's mantle (e.g. [112]).

The estimates of the interior N isotopic compositions of the Moon and Mars, and the upper limits we have for their interior H isotopic compositions (table 1), are both consistent with CI- and/or CM-like materials being the major volatile sources. The N isotopic composition of Venus is also consistent with CI- and/or CM-like sources for its volatiles. However, other aspects of its volatile budget seem to require additional sources. Figure 8 compares the CI-normalized volatile budgets of Earth and Venus. The Venus volatile budget assumes that the planet has fully degassed and that all of its volatiles are in its atmosphere. For elements like N, Kr and even Xe, there is a reasonable agreement between the Earth and Venus. Carbon and ^{40}Ar (produced by decay of ^{40}K) are clearly depleted in Venus's atmosphere, probably because they have not fully degassed. It is the large enrichments in ^{22}Ne and ^{36}Ar in Venus that are problematic, but might be explained by additional accretion of material rich in implanted solar wind [114] and/or cometary planetesimals [115].

The origin of the water in Vesta is an interesting problem. All the samples of Vesta that we have are igneous rocks, and the evidence for water is largely confined to trace phosphate minerals. Because they are igneous rocks from a small body, degassing of the magmas (as well as shock) could have contributed to the variability of the phosphate H isotopic compositions that have been reported (table 1, [10,11])—degassing can result in either D enrichments or depletions in the residual melt depending on the $f\text{O}_2$. In terms of its Cr, Ti and O isotopes, Vesta is clearly related to other inner Solar System objects and not the carbonaceous chondrites [70]. Nevertheless, Vesta's H and N isotopic compositions are roughly consistent with a CM/CI origin. Vesta is the second largest object in the asteroid belt and appears to have undergone wholesale melting and differentiation. Estimates for the timing of differentiation and the onset of magma ocean crystallization range from 2.2 ± 1.1 Ma [116,117] to less than or equal to $0.6^{+0.5}_{-0.4}$ Ma [118] after CAIs, and are broadly consistent with estimates of accretion times for Vesta of less than 1 Myr after CAIs [119]. As discussed earlier, this is long before the CI and CM parent bodies seem to have formed. Sarafian *et al.* [10] assumed that Vesta lost what volatiles it may originally have formed with during differentiation, and that the volatiles that are now found in it were collisionally accreted approximately 10–20 Ma later while there was still some melt present in Vesta's interior. However, it has not been definitively shown that differentiating planetesimals will fully degas them. Also, ordinary chondrites accreted matrix with primitive materials (organics, presolar grains, etc.) and water whose initial H isotopes may have resembled that in CI/CM chondrites. Thus, it should not be ruled out at this stage that the water in Vesta is primary and that CI/CM chondrites represent a

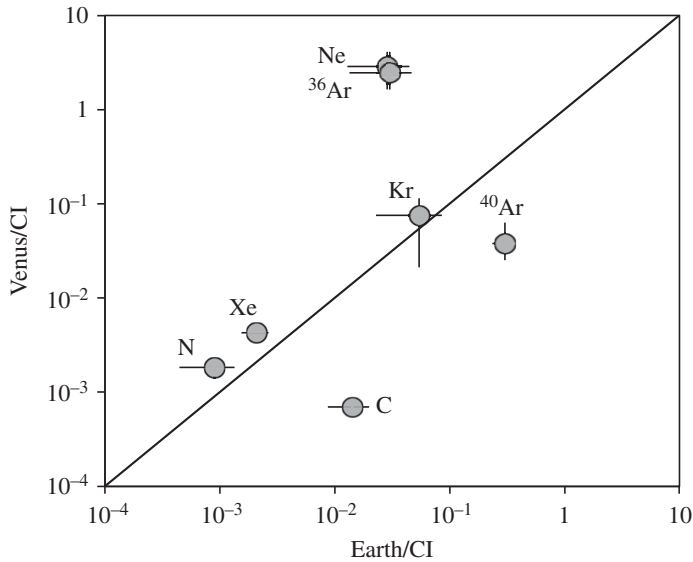


Figure 8. Comparison of the CI chondrite-normalized estimated volatile abundances in Earth and Venus. The Venus abundances assume that its interior has entirely degassed. The relative depletions in Venus's C and ^{40}Ar (from decay of ^{40}K) suggest that this was not always the case. The large relative enrichments in Ne and ^{36}Ar indicate that Venus did not have the same mix of sources as Earth (see the text for discussion). The data for the Earth are from Marty [47], and those for Venus from Fegley [113] except for Xe which is from Bogard [114] but its value is very uncertain.

primitive dust component in the disc that was widely distributed in the solar nebula even at early times. This possibility also has relevance for Mars because it may have reached roughly 50% of its current mass by $1.8_{-1.0}^{+0.9}$ Ma after CAIs [120,121], although it is possible that most of its volatiles were accreted later towards the end of its growth.

6. Summary and conclusion

Any discussion of the origin of water in the inner Solar System should not consider water in isolation, but must also consider the origin(s) of other volatiles. Of the potential sources of the volatiles for the terrestrial planets, the CI and CM carbonaceous chondrites provide the closest fit to the planets' bulk H and N isotopic compositions. For the Earth, at least, the abundances of H, C, the noble gases (except Xe) and many volatile lithophile elements are consistent with the addition of approximately 2–4 wt% of CI/CM material to a volatile-depleted proto-Earth. Other constraints require that the CI/CM material must have been accreted prior to the Moon-forming impact, and not in the post-impact Late Veneer. However, the Earth and even more so Venus show clear evidence that they also accreted some solar-like material, probably either as solar wind implanted into accreted dust/planetesimals or in cometary ices.

Hence, the origin of water in the inner Solar System largely becomes a question of the origin of the chondrites, in particular the CI and CM chondrites. Two dynamical models for delivery of volatiles to the growing terrestrial planets predict very different formation locations for the carbonaceous chondrites. In the 'classical' model, the volatiles were accreted in volatile-rich planetesimals that were scattered into the terrestrial planet region from the asteroid belt, i.e. the carbonaceous chondrite parent bodies formed roughly where they are located today. On the other hand, in the Grand Tack model, the carbonaceous chondrite parent bodies are remnants of a swarm of planetesimals that were scattered into the inner Solar System from as far out as 13–15 AU by the orbital migrations of Jupiter and Saturn.

The meteorite record can potentially distinguish between these two models if an indicator of formation distance can be found. There is evidence that the carbonaceous chondrites are

chemically distinct from all other inner Solar System materials. However, as the carbonaceous chondrite parent bodies appear to have formed after all other measured inner Solar System planetesimals, these chemical differences could be the result of temporal rather than radial variations in the disc. At present, the H isotopes of water appear to be the most promising indicators of formation distance, as they are expected to become increasingly D-rich with distance from the Sun. This radial gradient would have been due to radial mixing between outer Solar System water with a large D-rich interstellar component, and inner Solar System water that had been isotopically re-equilibrated with D-poor H₂. The estimated initial H isotopic compositions of water accreted by the CI, CM, CR and Tagish Lake carbonaceous chondrites were, with the possible exception of the CRs, much more D-poor than known outer Solar System objects (comets, Enceladus and Titan), although they do require a small interstellar component. The ordinary and R chondrites contain small amounts of water that have outer Solar System-like H isotopic compositions. However, this is likely to be largely the result of parent body processes and at least the ordinary chondrite water may have been isotopically quite similar to that in the carbonaceous chondrites.

Based on the H isotopes, if Enceladus and Titan formed around Saturn towards the end of its growth, then in the Grand Tack model the carbonaceous chondrites did not form beyond 3–7 AU. However, there are alternative formation scenarios, at least for Enceladus, that, if correct, would greatly weaken this conclusion. Nevertheless, the O isotopes of the water in chondrites also suggests that it had undergone significant re-equilibration prior to accretion, and the inferred N isotopic compositions of HCN/NH₃ in carbonaceous chondrites are also quite distinct from those of comets and Titan. Thus, on balance, it seems that the carbonaceous chondrites and their water did not form very far out in the disc, almost certainly not beyond the orbit of Saturn when its moons formed (approx. 3–7 AU in the Grand Tack model) and possibly close to where they are found today.

Competing interests. The author declares that there are no competing interests.

Funding. This work was also partially supported by NASA Cosmochemistry grant no. NNX14AJ54G.

Acknowledgements. The author would like to thank Monica Grady, Sara Russell and Chris Ballentine for the invitation to participate in the 'The origin, history and role of water in the evolution of the inner Solar System' workshop, and the Royal Society for partial funding for travel to the workshop.

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