

**THE ORIGIN OF WATER IN CHONDRITES AND VOLATILES IN THE TERRESTRIAL PLANET REGION.** C. M. O'D. Alexander<sup>1</sup>, R. Bowden<sup>2</sup>, M.L. Fogel<sup>2</sup>, K.T. Howard<sup>3</sup> and C.D.K Herd<sup>4</sup>. <sup>1</sup>DTM, Carnegie Institution of Washington, Washington, DC 20015, USA (alexander@dtm.ciw.edu). <sup>2</sup>GL, Carnegie Institution of Washington, Washington, DC 20015, USA. <sup>3</sup>Mineralogy Dept., The Natural History Museum, London, SW7 5BD, UK. <sup>4</sup>Dept. Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB, T6G 2E3, CA.

**Introduction:** Determining the source(s) of the volatile elements H, C and N in the terrestrial planet region is important not only for the origin of life on Earth, but also for understanding dynamical processes in the solar nebula and during planet formation. For instance, a massive influx of water ice from the outer Solar System is thought to have dramatically altered the O isotopic composition of the inner Solar System early in its history [1, 2]. The bulk and secondary mineral O isotopic compositions of ordinary (OCs) and carbonaceous (CCs) chondrites exhibit behavior that is at least consistent with accretion of <sup>16</sup>O-poor ice from the outer Solar System. In addition, chondrites and comets seem to have accreted similar suites of organic mater and presolar grains. Hence, to varying degrees, all chondrites (and comets) accreted primitive materials that were either inherited from the protosolar molecular cloud or that formed in the outer Solar System. Here, we use the H isotopic composition of chondritic water to determine its provenances.

Determining the original H isotopic composition of water in chondrites is problematic because of: (1) terrestrial contamination, (2) the often physically intimate association between D-rich organics and hydrated phyllosilicates, (3) similar release temperatures for H-bearing organics and water/OH in phyllosilicates, (4) the potential for H isotopic exchange between water and the organics during parent body alteration/metamorphism, and (5) isotopic fractionation associated with oxidation of Fe by water during alteration/metamorphism [3]. Here we adopted two approaches for estimating or placing limits on the original D/H ratios of the water in chondrites. Both use bulk H, and C elemental abundances and isotopic compositions.

**Experimental methods:** Bulk meteorite samples were crushed to <150  $\mu\text{m}$ . Aliquots were stored in desiccators for days to weeks at room temperature to minimize adsorbed water contents. Prior to analysis, the samples were quickly transferred to an autosampler and flushed with dry He for 1-2 hours, again to minimize adsorbed water. The samples were analyzed by mass spectrometry as described in [3].

**Results:** If bulk H isotope compositions are simple mixtures of D-rich organics and D-poor phyllosilicate water/OH, in a plot of H isotope values vs. C/H abundance ratio, the bulk compositions should form a line with the H isotope intercept representing the composition of the water. As can be seen in Fig. 1, the data for the CM and CR carbonaceous chondrites

exhibit the expected linear behavior, with implied  $\delta\text{D}$  values for their water of -450 ‰ and 100 ‰, respectively. The sub-parallel CM and CR trends, intersect in the region where the most primitive insoluble organic material (IOM) plots ( $\delta\text{D}\approx 3500\text{‰}$ ). This implies that the CMs and CRs share a common primitive organic component but distinct water isotopic compositions. The IOM in most chondrites is less D-rich than the most primitive material, suggesting that there has been exchange/reaction between the water and the organics.

The number of CIs and Tagish Lake samples, as well as the range of C/H ratios in them, are too limited to use the same approach as for the CMs and CRs, although their bulk compositions suggest water compositions that are similar to the CMs (Fig. 1). However, the fact that the CM and CR compositions can be explained by the mixing of water with a common organic component suggests that the water compositions can be estimated by subtracting a primitive IOM component that accounts for essentially all of the bulk C. The results of these estimates for CIs and Tagish Lake, as well as for the OC Semarkona, are shown in Fig. 2.

**Discussion:** Equilibrium and kinetic factors suggest that there would have been an increase in D/H ratios in nebular water ice with increasing formation distance from the Sun [4, 5]. If chondritic water formed in the outer Solar System, one might expect it to be D-rich, compared to the solar H isotopic composition, and similar to that in comets. To date, six Oort cloud comets have had their water D/H ratios measured and all are enriched in D by roughly a factor of two compared to Earth [6]. The D/H ratio of Enceladus, one of the moons of Saturn, is similar to the Oort cloud comets [6]. The one Jupiter family comet that has been measured, Hartley-2, has a water H isotopic composition that is similar to Earth's [6].

OC water is similar in composition to Oort cloud comets (the R chondrites are even more enriched [7]), whereas the CR water composition is like that of Hartley-2. The water compositions of the CIs, CMs and Tagish Lake are less D-rich than any known comets, implying formation much closer to the Sun. Taken at face value, these results run counter to the typically assumed order of the formation distances of the chondrites from the Sun. However, the H isotopic compositions in Fig. 2 should be regarded as upper limits as isotopic fractionation associated with oxidation of Fe by water during alteration/metamorphism

is likely to enrich residual water in D [3]. This effect will tend to be largest in chondrites with the lowest initial water/rock ratios i.e., roughly in the order OC (+R?)>CR>CM>CI≈Tagish Lake. Accurate estimates of how much water the various chondrites may have lost have yet to be made, but it seems possible that the water in all chondrites had D/H ratios that fell between terrestrial and solar. Even the current results (Fig. 2) have important implications for the origin of asteroids and the evolution of the terrestrial planet region, as is discussed below.

Recently, Walsh *et al.* [8] suggested that Main Belt asteroids were derived from two sources: the S-types, generally associated with the OCs, formed *in situ*, while the C-types, normally associated with the CCs, formed either between the giant planets or from 8-13 AU. This suggestion for the origins of the asteroids is a byproduct of a model to explain the small size of Mars, but also has important implications for the origin of the volatiles in the terrestrial planets. There is isotopic evidence for differences in the provenance of the OC-EC-Rs and CCs [9], but at present no reliable indicator of where in the solar nebula the CCs and OC-EC-Rs formed.

Oort cloud comets are thought to have been derived from the giant planet region, while Jupiter family comets probably formed in the region of Uranus-Neptune (8-13 AU) and were scattered from there into the Kuiper Belt. So these two comet families are thought to have formed in the same regions that the Walsh *et al.* model [8] predicts were the sources of the C-type asteroids (and therefore the CCs). Consequently, one might expect that water accreted by the S-type asteroids that formed in the asteroid belt would have lower D/H ratios than objects that formed in the giant planet region and beyond, while C-type asteroids would have D/H ratios like those in comets.

The results in Fig. 2 show that, with the possible exception of the CRs, the CCs do not have water D/H ratios like known comets. The OCs and Rs, on the other hand, do have comet-like water D/H ratios, but as stated earlier these D-enrichments could be the result of parent body processes. These results are opposite to what the Walsh *et al.* model predicts.

**Conclusions:** There is clear evidence for H isotope exchange between water and organics in most chondrites. After correcting for this exchange, the D/H ratios of several chondrite groups have been estimated. The estimated D/H ratios of water in CIs, CMs and Tagish Lake, fall between terrestrial and solar values. The CR water is slightly heavier than terrestrial, while that of the OCs is highly enriched. All these values are probably upper limits of the initial compositions of accreted water because of isotopic fractionations associated with Fe oxidation on the parent bodies. Thus, it seems unlikely that chon-

droitic water formed in the outer Solar System in contradiction of the model predictions of [1, 2] and [8].

While not the prime focus of this abstract, if Earth acquired most of its volatiles from asteroids, the simplest explanation for its H and N isotopic composition is that most volatiles were accreted from CI-like precursors, along with a small amount of solar material. Since CI chondrites are much more volatile-rich than Earth, most of the material Earth accreted must have been as differentiated and degassed bodies.

**References:** [1] Lyons J. R., Young E. D., (2005) *Nature* **435**, 317. [2] Yurimoto H., Kuramoto K., (2004) *Science* **305**, 1763. [3] Alexander C. M. O'D. *et al.*, (2010) *Geochim. Cosmochim. Acta* **74**, 4417. [4] Drouart A. *et al.*, (1999) *Icarus* **140**, 129. [5] Mousis O. *et al.*, (2000) *Icarus* **148**, 513. [6] Hartogh P. *et al.*, (2011) *Nature* **478**, 218. [7] McCanta M. C. *et al.*, (2008) *Geochim. Cosmochim. Acta* **72**, 5757. [8] Walsh K. J. *et al.*, (2011) *Nature* **475**, 206. [9] Warren P. H., (2011) *Earth Planet. Sci. Lett.* **311**, 93.

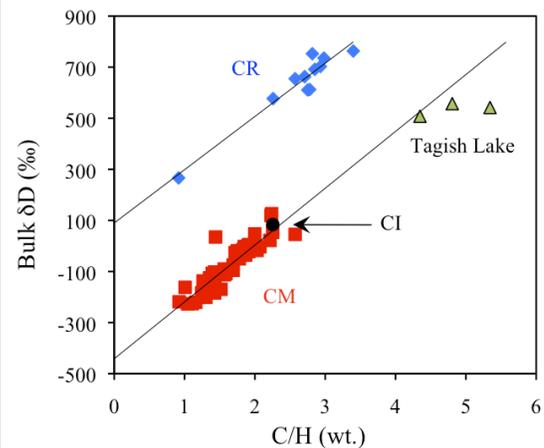


Figure 1. The bulk compositions of several CC groups, along with best-fit lines to the CRs and CMs.

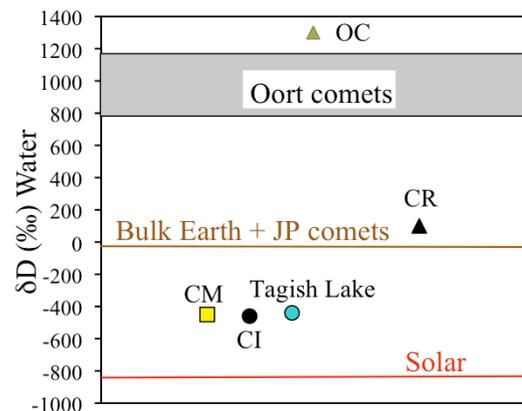


Figure 2. The estimated H isotopic compositions of water accreted by various chondrite groups.