

THE ORIGIN AND EVOLUTION OF CHONDRITIC WATER. C.M.O'D. Alexander¹, K.T. Howard², R. Bowden³, M.L. Fogel³, L. Bonal¹. ¹DTM, Carnegie Institution of Washington, 5241 Broad Branch Road, Washington DC 20015, USA (alexande@dtm.ciw.edu). ²The Natural History Museum, London, SW7 5BD, UK. ³GL, Carnegie Institution of Washington, 5251 Broad Branch Road, Washington DC 20015, USA.

Introduction: Based on CI-like matrix-normalized abundances of highly volatile elements, IOM and presolar nanodiamonds, [1, 2] suggested that the matrices of all chondrites are dominated by CI-like material. This CI-like material would have included water. Indeed, [3] have suggested that matrix-normalized water contents are also fairly constant.

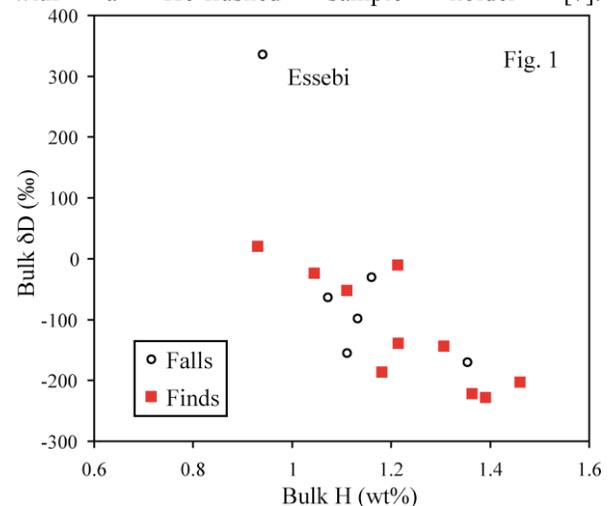
The O isotope systematics of CI-CM-CR chondrites are thought to reflect the interaction of water and anhydrous components whose compositions lay above and below the TFL, respectively. As a result, the $\Delta^{17}\text{O}$ values amongst these chondrites are measures of the water/rock ratios during alteration that either were established at the time of accretion (i.e., closed system) [4] or were the integrated fluxes in a dynamic hydrothermal system (i.e., open system) [5, 6].

If the alteration occurred in a closed system, the variable inferred water/rock ratios indicate heterogeneous accretion of at least ice, and one might expect a correlation between H content and $\Delta^{17}\text{O}$. For open system behavior, the relationship between H content and $\Delta^{17}\text{O}$ might be less straightforward. Complicating the interpretation of H and O systematics are: (1) the likelihood that significant amounts of water were consumed by oxidation of Fe and S, leading to a loss of H and D enrichment of the residual water, and (2) possible H isotope exchange between D-rich organic matter and water [7].

The favored explanation for the O isotopic composition of the inner Solar System is that there was a massive influx of ^{16}O depleted water ice from the outer Solar System. The ^{16}O depleted O isotopic composition of chondritic water is qualitatively consistent with this. This outer Solar System ice would have been accompanied by refractory and volatile organics. Indeed, the D- and ^{15}N -rich compositions of primitive chondritic organics suggest an ISM or outer Solar System origin, and amino acid synthesis in chondrites probably involved volatile HCN and NH_3 . However, the D-poor H isotopic composition of the water in CIs and most CMs indicates that it formed, or at least exchanged with H_2 , in the inner Solar System [7]. The CRs, the anomalous CMs Bells and Essebi, and the OC Semarkona contain D-rich water, but this may be due to the isotopic fractionations associated with oxidation of Fe and S [7].

To try to resolve the apparent contradictions in the H, O and organic compositions, we have begun a coordinated study of all three in bulk and at the micro-scale [8]. Here we present new bulk H elemental and isotopic abundances in a suite of 16 CMs.

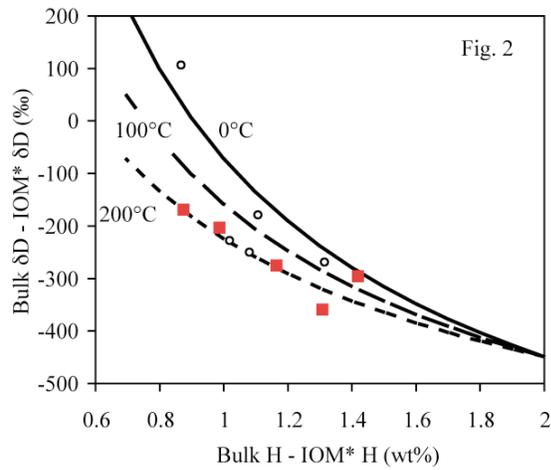
Samples and Methods: The CMs analyzed include falls and finds, and cover the entire range of alteration and bulk O isotopes observed in CMs [9]. They include: the falls Mighei, Murray, Murchison, Nogoya, Cold Bokkeveld, Essebi; and the finds QUE97990, LON94102, LEW88001, ALH85013, ALHA81002, Y791198, QUE93005, ALH83100, MET01070, SCO06043. The bulk samples were powdered and aliquots stored in a desiccator for several weeks before analysis with a Thermo Finnigan TC/EA equipped with a He-flushed sample holder [7].



Results: Figure 1 shows our results. There is a clear inverse correlation between H content and isotopic composition. Only the anomalous CM Essebi lies outside the trend. Both falls and Antarctic finds exhibit the same behavior, indicating that the trend is not due to variable alteration of the falls by Antarctic water ($\delta\text{D} < -250\text{‰}$). The alteration indices of [10-12] only weakly correlate with H content, but correlate quite strongly with δD values. No such correlations are seen in the data of [13, 14], presumably because of differences in analytical protocols.

Discussion: The inverse correlation between bulk H contents and isotopic compositions could be due to mixing of D-rich and D-poor components. Since the D-poor component is most dominant in the CMs, it is almost certainly the water/OH in hydrated silicates. An obvious candidate for the D-rich material is the organics. The insoluble organic material (IOM) is the major known organic component. Subtraction of it from the bulk compositions does not weaken the trend. The IOM in these meteorites is not as D-rich ($800 < \delta\text{D} (\text{‰}) < 1500$) as in some (e.g., Bells and CRs ~ 3000 ‰) [7]. If we assume that the lower D enrichments in

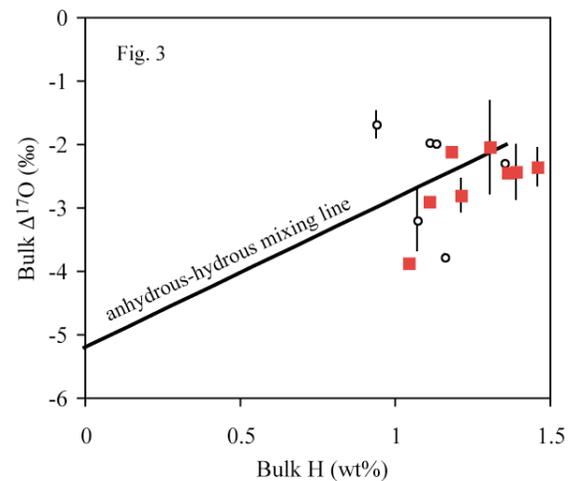
CM IOM are due to exchange with water and account for this when subtracting IOM H, the trend is still present, albeit displaced to lower δD values (Fig. 2).



It is possible that there is another D-rich component in the CMs that we have not yet accounted for. It is also possible that the trend is the result of the oxidation of Fe and S, and the associated loss and isotopic fractionation of H. In other words, the present extent of hydration in CMs is at least in part due to variable degrees of oxidation and not just initial water/rock ratios. To explore this possibility, we have developed a simplistic model for a fully altered, metal-free CM chondrite assuming a bulk CM composition and that only serpentine, greenalite, cronstedite, smectite-vermiculite, tochilinite and magnetite are present. This resulted in a H content that is similar to our CM1s. Assuming that Fe in the CM progenitor was only in metal, the Fe^{2+} and Fe^{3+} in the model allowed for an estimate of the original water/H content. The initial δD value of the water was then adjusted so that curves for Fe oxidation and H loss between $0^\circ C$ and $200^\circ C$ reproduced the data in Fig. 2. An alteration temperature of $200^\circ C$ is high compared to estimates for CMs, but these estimates may not record peak temperatures. An initial δD value of about -450‰ fits the data and would imply either a formation/re-equilibration temperature in the solar nebula of ~ 300 K or a $\sim 80:20$ mixture of ices with solar- ($\sim 840\text{‰}$) and comet-like ($\sim 1000\text{‰}$) H isotopic compositions. Equilibration at 300 K is likely to be slow, ruling out transient heating events (e.g., chondrule formation). Mixing of two ices could explain the relatively small $\Delta^{17}O$ of chondritic water compared to some models of the O isotopic compositions of outer Solar System ices.

Using the above alteration model, and the O isotopic compositions of the HW water and anhydrous component of [4], one can predict how H content and $\Delta^{17}O$ should vary if CMs are simple mixtures of fully hydrated and anhydrous components (Fig. 3). The

model passes through most of the data, but the data does not show the predicted correlation. The scatter may reflect the added complexity of variable degrees of oxidation at different temperatures. To test this will require determining the degree of oxidation (abundances of Fe^{2+} and Fe^{3+}) in each sample.



Conclusions: Bulk H abundances and isotopic compositions of CMs correlate with alteration indices. Current matrix-normalized water contents of CMs are not constant, but may have been during accretion. The relationship between bulk H abundances and H and O isotopic compositions is complex, probably reflecting differing degrees of oxidation of Fe and S by water, accompanied by H loss, at varying temperatures. The estimated initial water composition ($\delta D \leq -450\text{‰}$) shows that most or all of it formed/re-equilibrated in the inner Solar System. The presence of volatiles, like HCN and NH_3 , and D-rich organics in chondrites, suggests a scenario in which up to 20% of accreted ice came from the outer Solar System. This could come about if during accretion there was outward transport of material at the midplane of the solar nebula and downward diffusion of outer Solar System material from higher altitudes that was flowing sunward. However, before more quantitative modeling can be done, degrees of oxidation for each sample need to be determined and it must be established that all major H-bearing components in CMs have been accounted for.

References: [1] Alexander C. M. O'D., (2005) *MPS* **40**, 943. [2] Alexander C. M. O'D. *et al.*, (2001) *Science* **293**, 64. [3] Zanda B. *et al.*, (2009) *LPS* **40**, #1810. [4] Clayton R. N., Mayeda T. K., (1999) *GCA* **63**, 2089. [5] Young E. D. *et al.*, (1999) *Science* **286**, 1331. [6] Palguta J. *et al.*, (2010) *EPSL* **296**, 235. [7] Alexander C. M. O'D. *et al.*, (2010) *GCA* **74**, 4417. [8] Bonal L. *et al.*, (2011) *LPS* **42**, In Press. [9] Howard K. T. *et al.*, (2011) *LPS* **42**, In Press. [10] Rubin A. E. *et al.*, (2007) *GCA* **71**, 2361. [11] Browning L. B. *et al.*, (1996) *GCA* **60**, 2621. [12] Howard K. T. *et al.*, (2011) *GCA*, In Press. [13] Pearson V. K. *et al.*, (2001) *LPS* **32**, #1861. [14] Kerridge J. F., (1985) *GCA* **49**, 1707.