Bulk water abundances and D/H ratios of unequilibrated ordinary chondrites. H. Grant¹, R. Tartèse¹, R. H. Jones¹, Y. Marrocchi² and L. Piani², ¹Department of Earth and Environmental Sciences, The University of Manchester, Manchester, M13 9PL, UK (https://neen.grant@postgrad.manchester.ac.uk), ²CRPG, CNRS, Université de Lorraine, UMR 7358, Vandoeuvre-lès-Nancy, 54501, France.

Introduction: Investigations into the origin and evolution of water in the early Solar System tend to focus on the water- and organic-rich carbonaceous chondrites (CCs), despite evidence for the presence of water both in ordinary chondrite meteorites (OCs) [e.g. 1-4] and their parent bodies [5]. Of particular interest are the unequilibrated ordinary chondrites (UOCs), considered to be some of the most pristine objects available from the early Solar System. Previous isotope studies of some UOCs suggest unusually high D/H ratios relative to CCs and the terrestrial planets [4, 6]. The scarce existing data hint at a trend of elevated water contents associated with high D/H ratios in UOCs of the lowest petrologic types, with water abundance and D/H ratios decreasing with increasing petrologic types [7]. Higher water D/H ratios in OCs compared to CCs is in apparent contradiction with current Solar System models, which suggest that water D/H ratios increased radially with distance from the Sun [8-9]. Existing bulk H isotope data on UOCs have been acquired by different methods on only a handful of samples. To further assess whether UOCs with the lowest petrological types are indeed characterized by D/H ratios higher than that of water in CCs, we selected 21 UOC samples with petrologic types lower than 4, on which we measured bulk water abundances and H isotope compositions.

Samples and Methods: We determined the water abundance and bulk D/H ratios of the following 21 UOC samples: Tieschitz, Bremervörde, San Juan 055, Sharps, Dhajala, Paposo 004, El Médano 260, Aba Panu, Ceniceros, Mezö-Madaras, Semarkona, Northwest Africa (NWA) 11752, Bishunpur, NWA 11534, Krymka, NWA 4560, St Mary's County, Chainpur, Parnallee, Ngawi, and Bo Xian. This sample set comprises of 15 falls and 6 finds, ranging from petrologic types 3.00 to 3.9. Samples that have been analyzed previously include Semarkona (LL3.00), Bishunpur (LL3.15), Chainpur (LL3.4), Parnallee (LL3.6), and Ngawi (LL3.6) [2-4, 6, 10-11].

Bulk water abundances and H isotope compositions were determined on-line on 5-10 mg aliquots of ~11-85 mg powdered samples using the Thermo Scientific EA IsoLink – deltaV IRMS System at the CRPG laboratory (Nancy, France). Samples were degassed under vacuum at 120° C for 48 h, transferred into a sealed auto-sampler pre-flushed with He, and combusted at 1450° before H₂O abundance and H isotope analysis. Of note, such a technique prevents any contact with atmospheric H, and thus potential rehydration, after the pre-degassing step (see further details in [12-13]).

Results: Bulk H₂O content varies significantly from ca. 0.05 wt. % to 1.5 wt. %. As shown in Figure 1, all except one of the samples with the highest H2O abundances are finds. The majority of the meteorites analyzed have δD values (δD corresponding to the deviation of the measured D/H ratio from the D/H ratio of standard mean ocean water in parts per thousands) between -140% and 0%, which is consistent with the H isotope composition of most terrestrial waters [15] (Fig. 1). However, five meteorites have bulk δD values significantly higher than +200%, ranging from +303% for NWA 11752 (LL3.05) up to 1460‰ for Semarkona (LL3.00). There is a general trend of decreasing D/H ratios with increasing petrologic type, apart from Ngawi and Tieschitz, which are both classified as petrologic type 3.6 (Fig. 1). Excluding the finds, the sample set displays a rough trend of decreasing bulk D/H ratios with decreasing H₂O abundance.

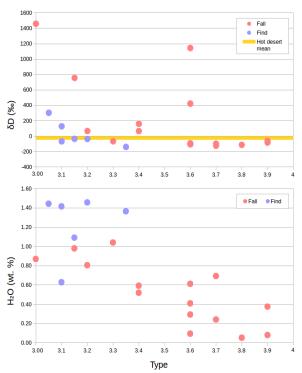


Figure 1: Bulk δD (top) and H₂O abundance (bottom) vs. petrologic types for the UOC sample set studied here. The yellow band in the top diagram, spanning from ca. -40% to 0%, represents the average H isotope composition of hot desert water [14] (where all the finds were recovered).

Discussion: The primary outcome of this study is that the bulk H isotope composition of some of the lowest petrologic types of UOCs, such as Semarkona and Bishunpur, are generally consistent with elevated bulk δD values determined previously [4, 6, 10-11], and that there is a general decrease of δD values with increasing petrologic type. One possible explanation for this trend is the presence of a D-rich component in UOCs, which is progressively destroyed by heating on the OC parent bodies [4, 16-17].

However, the unusually high bulk δD values found in the two meteorites Ngawi and Tieschitz, both of which are classified as petrologic type 3.6, do not fit with this trend of decreasing δD with petrologic type. Possible explanations may be that the petrologic types assigned to these meteorites are too high, or there are issues with the analyses themselves (we note that this is unlikely, as previous studies of Ngawi yielded similar results [10]). Alternatively, here again bulk H isotope measurements may be affected by the presence of a Drich component in these two samples, and might thus not be solely representative of the water H isotope composition, as has been suggested for CC bulk D/H analyses [18].

Our new dataset confirms that the most pristine UOC falls are characterized by bulk D/H ratios much higher than those of water in CCs. This is shown in Figure 2, where previous bulk H isotope measurements of CCs are represented by red circles, bulk OCs H isotope data from the literature by orange circles, and the results from this study are shown as dark blue circles. Such elevated water D/H ratios in objects presumably formed in the inner Solar System do not conform to current models. These models predict that the Solar System formed from a molecular cloud containing deuterium-enriched water that subsequently underwent rapid isotopic exchange with D-depleted H₂ molecules in the warmer inner Solar System, resulting in low water D/H ratios in the inner Solar System, increasing with heliocentric distance from the Sun [e.g. 7-8]. If the parent bodies of OCs formed in the inner Solar System, significantly closer to the Sun than the CC parent bodies, as is currently believed, then the D/H ratios of the water accreted by the OC parent bodies ought to be lower than that of water accreted by the CC parent bodies. The bulk H isotope composition of UOCs show that this is not the case, and, in fact, the D/H ratios of some of the most pristine UOCs are more similar to those measured in a number of outer Solar System comets. Explanations as to why this may be the case will require further in situ investigations of Hbearing phases in UOCs, and possibly reassessing the existing models for the spatial and temporal evolution of the water H isotope composition in the early Solar System.

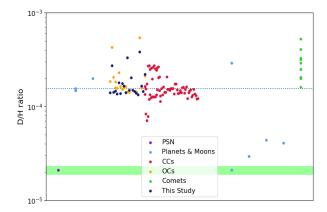


Figure 2: Plot of D/H ratios of Solar System objects. Literature OC data are orange and UOC data from this study are dark blue. Also shown are the D/H ratios of the protosolar nebula (PSN), carbonaceous chondrites, the planets spanning Earth to Neptune, and some of the comets from the outer Solar System. The x-axis loosely represents distance from the Sun, with all the comets represented at the same distance.

Acknowledgments: We acknowledge the UK Science and Technology Facilities Council for funding, and the Natural History Museum (London), the American Museum of Natural History (NYC), the Smithsonian Institution (Washington DC), and CEREGE (Aix-en-Provence) for loans of the samples studied here.

References: [1] Dobrica E. and Brearley A. J. (2014) Meteoritics & Planet. Sci., 49, 1323-1349. [2] Hutchison R. et al. (1987) Geochim. Cosmochim. Acta, 51, 1875-1882. [3] Alexander C. M. O'D. et al. (1989) Earth Planet. Sci. Lett., 95, 187-207. [4] Alexander C. M. O'D. et al. (2012) Science, 337, 721-723. [5] Jin Z. and Bose M. (2019) Sci. Adv., 5, eaav8106. [6] McNaughton N. J. et al. (1982) LPS XIII, A297-A302. [7] Robert F. and Merlivat L. (1979) Nature, 282, 785-789. [8] Yang L. et al. (2013) Icarus, 226, 256-267. [9] Jacquet E. and Robert F. (2013) Icarus, 223, 722-732. [10] Robert F. et al. (1987) Geochim. Cosmochim. Acta, 51, 1787-1805. [11] Yang J. and Epstein S. (1983) Geochim. Cosmochim. Acta, 47, 2199-2216. [12] Vacher L. et al. (2020) Geochim. Cosmochim. Acta, 281, 53-66. [13] Piani L. et al. (2020) Science, 369, 1110-1113. [14] Lécuyer C. et al. (1998) Chem. Geol., 145, 249-261. [15] Terzer S. et al. (2013) Hydrol. Earth Syst. Sci., 17, 4713-4728. [16] Alexander C. M. O'D. et al. (2010) Geochim. Cosmochin. Acta, 74, 4417-4437. [17] Remusat L. et al. (2016) Earth Planet. Sci. Lett., 435, 36-44. [18] Piani L. and Marrocchi Y. (2018) Earth Planet. Sci. Lett., 504, 64-71.