

The Oxygen Isotopic Composition of Water Extracted from Unequilibrated Ordinary Chondrites. L. Baker, I. A. Franchi, I. P. Wright and C. T. Pillinger. Planetary and Space Sciences Research Institute, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK. (L.Baker@open.ac.uk).

Introduction: The lack of high temperature metamorphism of the unequilibrated ordinary chondrites (UOCs) means they offer a unique insight into the origin and evolution of the ordinary chondrite parent bodies. However, some thermal modification of these meteorites has occurred, and it has become increasingly apparent that fluids, most likely water, have played an important role in the alteration process. For example, alteration products in chondrule mesostasis and in the general matrix have been identified and suggest that the dominant hydrated mineral in such matrix was a smectite, possibly resembling terrestrial nontronites [1,2]. The conditions under which the ordinary chondrites were aqueously altered and the role this played on the oxygen isotopic variation in the ordinary chondrites remains poorly understood. Studies of magnetites in Semarkona [3] and density separates (i.e. mesostasis and anhydrous silicate) from a range of unequilibrated ordinary chondrites [4-6] provide evidence for the fluid phase being considerably enriched in ^{17}O . As an extension of work completed using examples of carbonaceous chondrites [7], samples of the UOCs Semarkona and Bishunpur were subjected to stepped pyrolysis in order to measure directly the oxygen isotopic composition of water evolved from hydrated minerals. Density separated samples of mesostasis [e.g. 4] contained a mixture of phyllosilicates together with glassy or feldspathic material which may have experienced partial isotopic exchange with unaltered mesostasis. Measurement of water offers the opportunity to obtain isotopic data from the phyllosilicates alone. Initial results indicate that these alteration products do indeed retain a significant positive $\Delta^{17}\text{O}$ anomaly. The magnitude of this anomaly, in excess of twice that measured in the silicate portions of these meteorites, is also greater than that observed in any carbonaceous chondrites.

Analytical technique: Measurements of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ were made on water released by pyrolysis of crushed, bulk meteorite samples of 25-47 mg, using a continuous-flow, isotope ratio mass spectrometer (Delta C, Finnigan Mat). Samples used were powdered and loaded into a platinum crucible then left overnight in a flow of dry helium prior to analysis. Water evolved from the samples was swept by a flow of purified helium directly onto the in-line fluorinating agent (CoF_3), releasing oxygen. Unwanted reaction products, mainly HF, were removed from the flow by chemical and cryogenic traps. After cryofocussing, the effluent passed

through a capillary GC column for further purification before mass spectrometer analysis. Samples were heated in a step-wise manner from room temperature to 900°C . The heating duration at each step was ten minutes. The 1σ precision of the data, as determined by repeat analysis of standard waters and an internal solid standard, are $\pm 0.30\text{‰}$ ($\delta^{18}\text{O}$) and $\pm 0.14\text{‰}$ ($\Delta^{17}\text{O}$). Details of the analytical technique are in [8].

Results: Water yields from Semarkona and Bishunpur were quite similar at 0.58 and 0.54wt% respectively. The pattern of release of this water is also broadly similar, but with a number of noticeable differences. The result from Semarkona (figure 1) is dominated by a large tailing release, peaking at 150°C , with a further smaller release superimposed upon it, centered around 700°C . The result from Bishunpur (figure 2) is also dominated by the tailing low temperature release and while the high temperature release is not as clear as that in Semarkona an additional release superimposed on the tail around 350°C is evident. The most important parameter in identifying water of an extra-terrestrial origin is its $\Delta^{17}\text{O}$ value. From both figures it can be seen that after initial values close to the terrestrial fractionation line the $\Delta^{17}\text{O}$ trace climbs more-or-less steadily to a peak of around $+2.4\text{‰}$ in Semarkona, and $+1.3\text{‰}$ in Bishunpur.

The $\delta^{18}\text{O}$ pattern is more complex, initially rising steeply from light values (-11‰ in Bishunpur). In Semarkona a peak value ($+4\text{‰}$) is attained at the start of the small high temperature release, after which it falls markedly across this small release to -4‰ . In Bishunpur a peak value of $+1\text{‰}$ is attained by 300°C , after which there is a lower plateau around -0.5‰ , corresponding to the poorly resolved release around 350°C , before climbing again to $+1\text{‰}$. There may be some evidence for a final decrease in $\delta^{18}\text{O}$ in the final steps, comparable to the marked effect seen in Semarkona, but this is unclear largely due to the poor resolution at high temperature in this experiment.

Discussion: The dominant mineral in Semarkona phyllosilicates was found by [1] to be a smectite similar to nontronite, and this is reflected in the water release profile from this meteorite. Smectites are expanding clay minerals that readily accept water between their layers and as such can present a variety of levels of hydration. Under pyrolysis such clays typically produce a large low-temperature release, dominated by adsorbed water, followed by the release of inter-layer water over a range of temperatures up to 600°C . Superimposed

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upon this, starting at around 500°C, is water released from structural O-H groups. This release is generally complete by 700-800°C. $\delta^{18}\text{O}$ values climb to reach a plateau at around 400-500°C which represents the last point at which inter-layer water dominates, thereafter a sharply falling $\delta^{18}\text{O}$ trace is indicative of dominance of water from structural O-H groups containing a more coherent extraterrestrial signature, quite distinct from that at lower temperatures. Increasing $\Delta^{17}\text{O}$ values from around 0‰ also reflect the initial dominance of terrestrial adsorbed water. Subsequently, interlayer water becomes dominant and this becomes progressively less influenced by isotopic exchange with terrestrial reservoirs at increasing temperature. Consequently the signature becomes more positive reflecting a more indigenous composition. Over the last few steps, when the release is dominated by water from structural groups the $\Delta^{17}\text{O}$ values reach their peak and should be closest to the composition of parent body water from which the phyllosilicates formed (or with which they finally exchanged).

The more variable release profile of Bishunpur possibly indicates the presence of a more complex mixture of water-bearing minerals. The release around 350°C, superimposed on the large inter-layer water tail, may correspond to the release of structural water from serpentine-type minerals as typified by the Murchison meteorite [7]. However, for Bishunpur the presence of some extra-terrestrial water at low temperatures (as evidenced by the slightly elevated $\Delta^{17}\text{O}$ values) along with water release at very high temperatures confirm the dominance of smectites within this meteorite. The more complex assemblage within Bishunpur may reflect distinct, or possibly evolving conditions (declining water-rock ratio) during the aqueous alteration phase, compared to that recorded in Semarkona.

The oxygen composition of water as recorded in the structural O-H groups has a more extreme $\Delta^{17}\text{O}$ value than that of the anhydrous silicates found in the UOCs (i.e. $\sim +1\text{‰}$) – however, with a peak value of $+2.4\text{‰}$ this is comparable with the measured mesostasis separates ($+2.7\text{‰}$) [5] and significantly lower than the magnetites ($+6.9\text{‰}$) [3]. The significance of this result is unclear – however, in line with earlier conclusions [3,6] this may reflect the final oxygen isotopic composition of a fluid which had evolved, due to low water rock-ratios, from an initially highly enriched composition. The final measured value from the Semarkona sample, taken to represent the purest aliquot of structural water from indigenous smectites falls on an extrapolation of a simple model of the isotopic evolution of the water involved in the isotopic exchange in the UOC meteorites [6]. Higher resolution analyses and on-going investigation of the fractionation effects of dehydration reac-

tions will help shed further light on the significance of this relationship.

References: [1] Hutchison R. et al. (1987) *GCA* 51, 1875-1882. [2] Alexander C.M.O'D. et al. (1989) *EPSL* 95, 187-207. [3] Choi B.G et al. (1998) *Nature*. 392, 577-579 [4] Bridges J.C. et al. (1998). *EPSL* 155, 183-196 [5] Bridges J.C. et al. (1999). *GCA* 63, 945-951 [6] Franchi I.A. et al. (2001) *Phil. Trans. R. Soc. Lond.* 359, 2019-2035. [7] Baker L. et al (2002) *MAPS* 37, 977-985. [8] Baker L. et al. (2002) *Anal. Chem.* 74, 1665-1673.

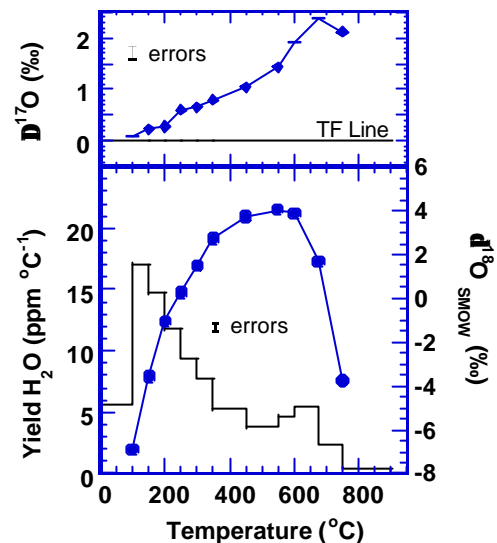


Figure 1. Yield and oxygen isotopic data of water from a 25 mg sample of Semarkona

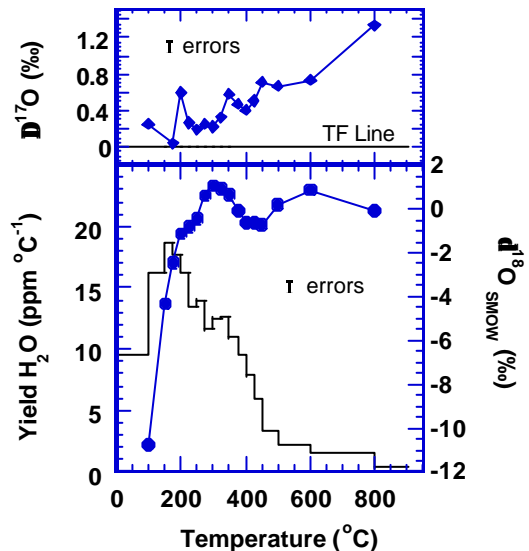


Figure 2. Yield and oxygen isotopic data from a 47 mg sample of Bishunpur