DEUTERIUM ENRICHMENTS IN PRIMITIVE METEORITES. N.J. McNaughton, J. Borthwick*, A.E. Fallick* and C.T. Pillinger. Planetary Sciences Unit, Dept. of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ and *S.U.R.R.C., East Kilbride, Glasgow G75 0QU, U.K.

Recent studies (1-4) of D/H ratios in primitive meteorites (unequilibrated ordinary chondrites, UOCs, and carbonaceous chondrites) have demonstrated the presence of large excesses of deuterium by comparision with terrestrial waters. Far greater D enrichments are found in certain carbon containing entities in the interstellar medium where they were thought to be due to ion-molecule reactions at low temperature (5). A possible conclusion is that the primitive meteorites could contain carbon or other species surviving from the earliest events taking place during the birth of the solar system in a dark molecular cloud. It is important to establish the frequency with which D enrichments occur, the nature of D-rich phases, their petrographic location and any relationship between the D-containing species in carbonaceous chondrites and UOCs. Such investigations are likely to have considerable bearing on the synthesis of meteorite organics and aid the understanding of future analyses of the most primitive solar system materials including cometary dust and gas.

Our initial study concerned Bishunpur, Semarkona and Krymka, generally accepted as the least metamorphosed UOCs (2). Bulk specimens of the former two samples released water between 200 and 750°C with variable δD_{SMOW} values up to +3000‰, whilst water from the third had a δD of only +54‰. Chainpur, a sample considered by Robert et al. (1) afforded water of δD = +200‰ but when subjected to a separation study and investigated by stepwise heating, fractions whose δD exceeded +4400‰ were recognised. All the above samples are LL group meteorites. We have now extended the survey to include ALHA 77299 and Tieschitz both only moderately unequilibrated but nevertheless relatively carbon rich, possibly an important criterion since D in carbonaceous chondrites is associated with acid insoluble residues (4). The former is an H group meteorite whilst the latter was recently reported as having closer affinities to L or LL rather than H although it has long been considered an example of the latter type (6). When subjected to our previously described extraction procedure neither sample provided water of exceptional deuterium content having δD values of -25.6‰ and -76.5‰ respectively. We have now also performed a stepwise heating experiment using our published extraction method on a bulk sample of Bishunpur. The amounts of water released and the isotopic compositions are listed in Table 1. The release patterns closely resemble that reported by Robert et al. for Chainpur (1) and the rapid increase in D/H ratio up to 750°C parallels the carbon isotopic changes observed from the sample during step-wise combustion (7) although it must be appreciated that the extraction techniques used were appreciably different. Rather surprisingly none of the deuterium isotopic compositions approaches the values we earlier obtained for Bishunpur total extracts over the temperature interval 200-750°C. The weighted average δD for the step-wise heated sample is +419‰.

The results of the step-wise heating experiment tend to confirm our suspicion that a minor very D enriched phase may be sporadically distributed in Bishunpur which is notably inhomogeneous. Such a conclusion is important to verify and it is desirable to demonstrate the reproducibility of our technique. One possible flaw in the method used up to now is that only H_2O is collected; any H_2 or CH_4 formed during the pyrolysis is lost during the pump out of non-condensible gases. Accordingly the procedure has been modified along the lines employed by us for carbon isotopic analysis (8).

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Extractions are performed in a sealed quartz glass tube in the presence of CuO with rapid removal of H_2O cryogenically. The new technique has been tested on three small samples (ca. 3mg each) of Orgeuil and is remarkably reproducible (Table 2). As a test sample, Orgeuil has the added advantage of having been studied by other groups and the δD of extracted water is consequently reasonably well established. Our values of δD +191 to +199‰ falls mid way between those found in the literature (3,4) although our yields are slightly low compared to published figures and may indicate a systematic error in calibration. We intend to perform a reproducibility test on Bishunpur using the new technique in the near future.

In establishing the exact procedure for a combustion method, several slightly different approaches were tried which, for a variety of reasons, were less satisfactory than that finally adopted. Unfortunately there is no appropriate model material for trial experiments so small samples (usually ca. 3mg) of meteorite had to be employed. Nevertheless these studies have afforded some qualitative data on carbonaceous chondrites which may be compared to published analyses. Thus, we have obtained water with δD=+191.6‰ from the type 1 chondrite Alais, and δD=+528‰ from the unique sample Renazzo. Experiments performed by corresponding procedures on Orgeuil gave water of δD=+156.3‰ and +98‰ respectively. A 30 mg sample of Semarkona combusted by a preliminary procedure produced water of δD=+1349‰.

In the near future we hope to continue the survey of primitive meteorites using combustion rather than pyrolysis to perform more stepwise heating experiments and to investigate separates from the most D-rich UOCs. We thank Drs. R. Hutchison, R. Clarke and S.O. Agrell for samples, Dr. P.K. Swart for valuable discussions on technique development and Miss M.M. Grady for sample preparation.

References.

(1) Robert et al. (1979) Nature, 282, 785. (2) McNaughton et al. (1981) Nature 294, 639. (3) Kolodny et al. (1980) EPSL 46, 149. (4) Robert & Epstein submitted to GCA. (5) Brown and Rice in press Proc. Ro. Soc. (6) Wlotzka (1981) Abs. 44th. Meteoritical Society Meeting p.156 (7) Swart et al. this volume. (8) Grady et al. (1981) Abs. 44th. Meteoritical Society Meeting p.28.

Table 1: Step-wise heating results for H_2O collected from the pyrolysis of 100.33 mg of Bishunpur.

Temp Step (°C)	δD_{SMOW} (‰)	Yield (μ moles H_2)
200 - 300	+85	4.8
300 - 450	+234	5.6
450 - 750	+1330	2.2
750 - 1000	+1331	0.7
200 - 1000	+419*	13.3*

* calculated bulk sample value

Table 2: Results for water collected from combustion (200-1000°C) of ~ 3mg aliquots of Orgeuil.

Sample	δD_{SMOW}	H_2O (wt %)
1	191.0	4.4
2	199.1	4.2
3	191.5	4.5