

**FURTHER INVESTIGATION OF ISOTOPICALLY LIGHT CARBON IN ALH 84001.** I.P.Wright<sup>1</sup>, S.Assanov<sup>1</sup>, A.B.Verchovsky<sup>1</sup>, I.A.Franchi<sup>1</sup>, M.M.Grady<sup>1,2</sup> and C.T.Pillinger<sup>1</sup>. <sup>1</sup>Planetary Sciences Research Institute, Open University, Walton Hall, Milton Keynes MK7 6AA, UK (i.p.wright@open.ac.uk); <sup>2</sup>Natural History Museum, Cromwell Road, London SW7 5BD, UK (m.grady@nhm.ac.uk).

Attempts to comprehend the carbon chemistry and stable isotopic composition of components in ALH 84001 (hereafter A84) have involved use of stepped combustion to determine the overall carbon inventory [1–3] acid-dissolution techniques to analyse for carbonates [4,5], organic analyses for selective determination of individual classes of compounds [6,7] and latterly, ion probe and STXM measurements to investigate small-scale detail [8,9]. It is clear that a completely coherent picture, within which the results from all investigations of carbon are understood, remains to be obtained. In order to provide additional constraints, we have conducted a series of stepped pyrolysis experiments on bulk samples of A84. In many ways pyrolysis experiments give results that are inferior compared to equivalent stepped combustions. However, one of the reasons for the present effort was to try and clarify the situation regarding isotopically light carbon in A84 [10]. The rationale here is that organic compounds will pyrolyse to give species such as CO, CO<sub>2</sub> and CH<sub>4</sub>, whereas a contaminant such as teflon, would not.

Samples of A84 have been pyrolysed in a stepwise manner (from room temperature to 1200°C) in three different extraction systems. The first allows qualitative (and semi-quantitative) analyses of all gas species—i.e. a conventional evolved gas analysis. The second system is the one more usually used for our high-sensitivity stepped combustion analyses [11], suitably modified to allow pyrolysis—from this experiment we measured  $\delta^{13}\text{C}$  values of the sum of evolved CO and CO<sub>2</sub>. In the third device we measured the isotopic composition of evolved methane [12]. Note that all three extraction systems and associated instruments are optimised to work with small samples—in consequence the *total* amount of A84 used for the 3 separate analyses was less than 12 mg.

Strictly speaking it is unlikely that results from one experiment can be compared with another (because of subtle differences in each extraction procedure). However, in general terms it is apparent that most of the carbon in A84 is liberated as CO and CO<sub>2</sub>, with only a minor contribution from CH<sub>4</sub>. On the basis of the evolved gas analysis, the CO<sub>2</sub> release is seen to occur over the same temperature range as CO (with the ratio of [C] as CO<sub>2</sub>/CO being between 3 and 6 for different steps, across the major release). The major release of CO<sub>2</sub> arises from carbonate

breakdown, while CO is probably the result of the interaction of [C] with oxygen from silicates, carbonates, or other minerals (the [C] is assumed to be organic in nature). The overlapping of the releases of CO<sub>2</sub> and CO results in a maximum  $\delta^{13}\text{C}$  value for CO<sub>2</sub>+CO of +32.3‰, as opposed to about +40‰ which would have been expected for pure carbonates. This effect is not unexpected and indeed is one of the reasons why combustions are often preferred. The rest of the carbon isotopic data from the CO<sub>2</sub>+CO experiment are fairly well understood within the framework of what is already known. However, we draw attention to one step (200–300°C) which gave a large a large release of gas (i.e. 12.2% of the total carbon) and which had a  $\delta^{13}\text{C}$  value of –37.7‰. It is difficult to judge the significance of this result. While it is clearly very different from the rest of the non-carbonate carbon (having  $\delta^{13}\text{C}$  of around –25‰), it may be an artefact of the experiment (kinetic isotope fractionation resulting from pyrolysis at low temperature?). We have to learn more about the performance of our system with respect to pyrolysis before we can be sure of the relevance of this result.

Turning to methane, both of the experiments that were capable of recording this species showed that the gas is released at 400–600°C. The amount of methane released is extremely small, amounting to less than 1 ppm ([C] as CH<sub>4</sub>). Isotopically we are only able to measure a parameter we call  $\delta^{17}\text{M}$  [12]—unfortunately we cannot yet distinguish between  $\delta^{13}\text{C}$  and  $\delta\text{D}$ . However, if an assumption is made about one of the isotopic systems, the other can be calculated. Now, from previous work [13] it is known that in kerogen-like organic materials from carbonaceous chondrites there is a carbon isotopic fractionation between evolved CH<sub>4</sub> and CO/CO<sub>2</sub> of about 10%. Thus, if we assume  $\delta^{13}\text{C}$  of –25‰ for gaseous CO/CO<sub>2</sub> it would be anticipated that  $\delta^{13}\text{C}$  of CH<sub>4</sub> would be –35‰. On this basis,  $\delta\text{D}$  values of CH<sub>4</sub> would have to be in the range –200 to –700‰ (i.e. for the various steps of the experiment), with the average being about –300‰. Intuitively these values of  $\delta\text{D}$  seem unlikely. Consider that  $\delta\text{D}$  of water released by pyrolysis of A84 ranges from –50 to about 800‰ [14]; note that the relatively low  $\delta\text{D}$  values are obtained at low temperatures, at which no methane was observed to be released. Thus, just considering the temperature interval where methane is released, we would expect

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$\delta D$  values of water to be at least 500‰. If the hydrogen in the methane had become isotopically equilibrated with the hydrogen in the water (either during the laboratory extraction, or by some fundamental process within the meteorite) we would expect  $\delta D$  of the methane to be about 500‰. And in which case,  $\delta^{13}C$  of the methane (calculated as above) would have to be  $<-60\%$  for all steps. Even assuming a  $\delta D$  of 200‰, and taking the average value of  $\delta^{17}O$ , we still derive a  $\delta^{13}C$  value of  $-60\%$ .

At this point it is necessary to inject some caution since the quantities of methane released from A84 were very small. Indeed, the amounts were only a factor of two greater than system blanks; furthermore, the isotopic composition of the system blank is not yet understood. It appears that the methane blank arises from two components, namely organic compounds and carbon within quartz. Attempts are currently being made to constrain the characteristics of the blank so that a satisfactory correction can be applied to the sample data.

Most of the organic compounds in A84 have  $\delta^{13}C$  values which, at around  $-25\%$ , are not distinctive from similar or equivalent terrestrial materials. In other words, interpretation of the carbon isotope data from A84 is always going to be hampered by their ambiguous nature. However, it seems at least possible that within the organic complex there might be minor

components which can be distinguished by extreme carbon isotopic compositions (as first suggested by Wright et al. [10]). In light of the potential importance of establishing the presence, or otherwise, of isotopically light carbon, it is appropriate to continue searching for evidence of such components in A84. These measurements may help to constrain the life on Mars debate.

**References:** [1] Grady, M.M. et al. (1994) *Meteoritics*, 29, 469; [2] Wright, I.P. et al. (1997a) *Lunar Planet Sci.*, XXVIII (in press); [2] Wright, I.P. et al. (1997b) *Lunar Planet Sci.*, XXVIII (in press); [4] Romanek, C.S. et al. (1994) *Nature*, 372, 655–657; [5] Jull, A.J.T. et al. (1995) *Meteoritics*, 30, 311–318; [6] McDonald, G.D. and Bada, J.L. (1995) *Geochim. Cosmochim. Acta*, 59, 1179–1184; [7] Becker, L. et al. (1997) *Geochim. Cosmochim. Acta*, 61, 475–481; [8] Valley, J.W. et al. (1997) *Lunar Planet Sci.*, XXVIII (in press); [9] Flynn, G.J. et al. (1997) *Lunar Planet Sci.*, XXVIII (in press); [10] Wright, I.P. et al. (1997c) *Lunar Planet Sci.*, XXVIII (in press); [11] Yates, P.D. et al. (1992) *Chem. Geol. (Isotope Geosci.)*, 101, 81–91; [12] Morse, A.D. et al. (1996) *Rapid Comm. Mass Spec.*, 10, 1743–1746; [13] Kerridge, J.F. et al. (1987) *Geochim. Cosmochim. Acta*, 51, 2527–2540; [14] Leshin, L.A. et al. (1996) *Geochim. Cosmochim. Acta*, 60, 2635–2650.