ISOTOPICALLY LIGHT CARBON IN ALH 84001: MARTIAN METABOLISM OR TEFLON CONTAMINATION? I.P.Wright[1], M.M.Grady[1,2] and C.T.Pillinger[1]. [1]Planetary Sciences Research Institute, Open University, Walton Hall, Milton Keynes MK7 6AA, UK (i.p.wright@open.ac.uk); [2]Natural History Museum, Cromwell Road, London SW7 5BD, UK (m.grady@nhm.ac.uk).

Abstract: In light of the potential importance of ALH 84001 (A84) as a probe into the existence of life beyond the Earth, an investigation has been conducted into the carbon compounds associated with various fractions of the meteorite. During this study an intriguing carbon-bearing component has been discovered. On the basis of C content it could be a carbonate, while combustion characteristics are compatible with organic material or carbonate. The carbon isotopic composition is extremely unusual, having $d^{13}C$ of about -65‰, which is in stark contrast to that of the majority of carbonate minerals (ca. +40‰). At face value the results would seem to necessitate the action of living organisms, since purely inorganic processes within a planetary setting are unlikely to produce a carbon isotopic fractionation of 100‰. Clearly before attempting to interpret the results within the framework of a martian biotic system, it is appropriate to eradicate any doubts regarding terrestrial contamination. A $d^{13}C$ value of -65‰ is not normally encountered in contaminants; however, it would appear that teflon (of terrestrial, rather than martian, origin) could be responsible.

To understand the presence of isotopically light carbonates in A84 [1,2] we have analysed the carbon stable isotopic compositions of individual orange-colored grains (hand-picked from a lightly crushed fragment of A84,106). The grains were analysed using a combination of stepped-combustion [3] and highly sensitive static mass spectrometry [4]; in this way grains of just a few micrograms could be determined. A total of 3 individual grains have been analysed thus far, giving a range of carbon contents and isotopic compositions. Indeed one of the grains appeared to contain practically no carbonate (casting some doubt over using orange coloration as the only selection criterion). Of most interest was an analysis of a composite of 5 individual grains (total mass 420.5 mg), four of which are considered to have come from the same location within the sample. Rather than being pure orange in color, the grains were speckled black and orange (from the rim of a carbonate globule?). Upon analysis the $d^{13}C$ values started to trend from around -25‰ up to +4.2‰ as the temperature was increased to 425_C (in common with other analyses of A84). But then, over the next 4 steps (up to 525_C), $d^{13}C$ changed markedly, down to -61.8‰. The overall bulk $d^{13}C$ was -54.9‰.

The main carbon release in this sample, known as grain(s)-2, is from 450-550_C, which is compatible with it being from the thermal decrepitation of a carbonate. Indeed, this is the temperature range over which the major, ^{13}C-rich carbonates in A84 decompose [5]. The overall carbon content of grain(s)-2 is equivalent to 11.9 wt%. This suggests that the sample *could* be a practically pure carbonate mineral (12 wt% C in the case of calcite, for instance). We have no evidence to refute this possibility, however it cannot be isotopically pure since $d^{13}C$ varies from +4.2 to -61.8‰. Comparison of the carbon yield profile with those from pure carbonate minerals shows no exact match - calcite and siderite decrepitate at higher and lower temperatures respectively (magnesite provides the closest fit). What tends to mitigate against identification as a pure carbonate is the fact that the isotopic composition remains light up until the highest temperature of the experiment ($d^{13}C$ of -60.6‰ for one step at 800-1200_C). If, as the total yield suggests, the sample was pure carbonate then we would have expected a relatively straightforward extraction, with no residual carbon above 700_C.

Another possibility is that the isotopically light carbon is released from a refractory organic material, analogous to terrestrial kerogen. In this regard we note that organic materials mixed within a mineral matrix can undergo extended combustion to high temperatures. Furthermore, kerogenous separates from terrestrial sediments have combustion temperatures of about 400-500_C. It is noteworthy that samples from the Fortescue Group, Western Australia (for instance), have $d^{13}C$ values of about -55‰; while there is disagreement as to the reason for light carbon in these samples there is, however, universal agreement that it is the result of biological activity. So, it is possible that grain(s)-2 might contain some "normal" ^{13}C-rich carbonate (which explains the initial rise in $d^{13}C$ to +4.2‰) mixed with a relatively larger amount of refractory organic carbon. If this is the case we can calculate that the sample would contain about 1.2 wt% C as carbonate ($d^{13}C$ = +40‰) and 10.7 wt% C as organic material (which, from mass balance considerations, would have $d^{13}C$ of ²-65‰). In other words, the sample would need to be about 30% by weight of organic materials (the black color?). In support of this possibility we note that combustion of grain(s)-2 liberated large amounts of gases more volatile than CO_2 (compatible with H_2O from the oxidation of [H] in the organics). However, from experience, it is considered that the relative "sharpness" of the carbon release (90% of total carbon from 450-525_C) is not entirely compatible with an organic complex, (generally somewhat broader release, reflecting the cross-linked bonding of the material).

No other sample analysed using the same or related instruments has ever given a carbon release and isotope profile quite like that of grain(s)-2; thus, we decided to evaluate the possibility of contamination. The only material that the sample could have reasonably been exposed to is teflon (or other fluoropolymers). Indeed, the vacuum system in which the sample was analysed comprises several valves with teflon seals (not that several thousand previous analyses had given us any cause for concern). But what was considered potentially problematic was that a previous bulk analysis of DuPont teflon foil, used for Euromet sample bags, gave an apparent $d^{13}C$ of -58.7‰ [6]. We decided to re-open the case on teflon (why should it be so isotopically light anyway?) and combusted 3 new samples at 1000_C according to the sealed-tube method [7]. The samples were: Euromet foil, foil from the Lunar Receiving Laboratory (ca. 1972) and a piece of one of the valves from our extraction system. We obtained $d^{13}C$ values of -48.4, -55.3 and -58.5‰ respectively, with corresponding yields that suggest complete combustion. But on reflection this raises an interesting question - why does teflon, $-(C_2F_4)-_n$, burn? And, are the products CO_2 and F_2? Thermodynamically the oxidation of $-(C_2F_4)-_n$ seems unlikely. Indeed, several stable isotope laboratories around the world use fluorine (F_2) or fluorine-containing species (CF_3, BrF_5) to displace oxygen from compounds, including CO_2, for analysis (on account of F_2 being more oxidising than O_2 itself).

Upon further investigation it transpires that in the sealed-tube experiments, species other than CO_2 are released during the combustion. In fact, visual inspection of the tubes (made of silica glass) showed them to have turned yellow and become etched. The mass spectra of the released gases show, in addition to CO_2, evidence for SiF_4 and C_2F_4. Unfortunately, these fluorinated gases are impossible to separate from CO_2 using the cryogenic methods that accompany sealed-tube combustions. Of concern for isotope measurements is that SiF_3^{2+} (*m/z* 42.5, 43 and 43.5) and C_2F^+ (*m/z* 43,44) can interfere and produce apparently high 44/45 ratios (erroneously interpreted as light carbon). Reluctantly we elected to treat a piece of valve teflon to stepped-combustion in our high-sensitivity system (reluctant since stepped-combustion analyses of teflon in other systems produced deleterious effects). Curiously the stepped combustion experiment appeared to progress quite "cleanly", 34.7 mg of teflon burning to yield 24.47 wt% C. The overall $d^{13}C$ was -47.5‰, which compares with -58.5‰ from the sealed-tube experiment. Several things conspire to make us believe that the stepped-combustion experiment gives more reliable results than those from the sealed-tubes - so, the ostensibly light values recorded from the latter technique [also, 6] are considered to be in error.

But can the isotopically light carbon in grain(s)-2 be ascribed to teflon contamination and if so, can it be understood? The yield profile of teflon is certainly compatible with that from grain(s)-2 (95% of total carbon released from 450-525_C). However, the 10.7 wt% light C recorded from grain(s)-2 requires that 45% of the original sample mass was teflon. It is inconceivable that this amount could have been hand-picked along with the sample - in which case, we do not suspect a generalised teflon contamination of A84. So, could teflon have been added during loading of the sample, or is it from the extraction system itself? It is possible, but then we would have to explain the difference in $d^{13}C$ between teflon (-47.5‰) and grain(s)-2 (-65‰).

In conclusion, we have analysed an interesting component in a carbonate-rich fraction of A84, characterised by a relatively sharp carbon release (450-550_C) and $d^{13}C$ of ²-65‰. If indigenous it seems inescapable that it results from biological activity. By analogy with the Earth, it would necessarily implicate a mixed methanogenic/methylotrophic bacterial community. Unfortunately, as yet, we cannot rule out the possibility of teflon contamination, but at least we have a good knowledge of the potential effects that such materials can cause.

References: [1] Jull, A.J.T. et al. (1996) *J. Geophys. Res.*, (in press); [2] Wright, I.P. et al. (1997) *Lunar Planet. Sci., XXVIII*, (this volume); [3] Carr, R.H. et al. (1986) *J. Phys. E: Sci. Instrum., 19*, 798-808; [4] Prosser, S.J. et al. (1990) *Chem. Geol., 83*, 71-88; [5] Grady, M.M. et al. (1994) *Meteoritics, 29*, 469; [6] Wright, I.P. et al. (1993) *J. Geophys. Res., 98*, 3477-3482; [7] Grady, M.M. et al. (1982) *J. Geophys. Res., 87*, A289-296.