CARBON ISOTOPIC EVIDENCE FOR TERRESTRIAL ORGANIC COMPOUNDS FOUND IN SOME MARTIAN METEORITES; A. J. T. Jull, J. W. Beck, C. Courtney and D. A. Jeffrey, NSF Arizona Accelerator Mass Spectrometer Facility, University of Arizona, Tucson, AZ 85721.

Since the report of possible biofossils in ALH84001 (1), there has been much discussion as to the nature and provenance of organic material in Martian meteorites. Important clues to the origin of the organic material can be obtained from the ^{14}C and ^{13}C isotopic composition of carbon. We have previously reported on the $\delta^{13}C$, $\delta^{18}O$ and ^{14}C compositions of CO_2 released from acid-etching experiments of Allan Hills 84001, Nakhla and Zagami (2,3). We have shown that ^{14}C could potentially identify the carbonate as extraterrestrial. For a mean composition of 12.7% C for ALH 84001 carbonates, irradiation of this material in space in a small object will result in a ^{14}C activity corresponds to a $^{14}C/^{12}C$ ratio (atom/atom) of 5.0 X 10^{-14} or 4.3% of the ratio found in modern carbon (~1950AD). "Modern" carbon contains ~1.17 X 10^{-12} $^{14}C/^{12}C$. Using the composition of calcite for EETA79001 results in 4% modern carbon for recently-irradiated carbonates (2,3). The terrestrial ages of ALH84001 and EETA79001 have been determined to be 13±1 and 12±2 ka respectively, measured by the level of cosmic-ray-produced ^{14}C extracted from these rocks (3,4). In this time, ^{14}C in carbonates from these two meteorites to have decayed to about 0.9% modern carbon in this phase.

We can use a similar approach for organic compounds using ^{14}C as well as their stable isotopic composition ($\delta^{13}C$) to identify their source. Terrestrial organic material, which mainly originates from biogenic activity, will have levels of ^{14}C consistent with their time since removal from equilibrium with the terrestrial biosphere or atmosphere (5). In contrast, organic material exposed to radiation in space, can sometimes contain excess ^{14}C produced by the action of cosmic ray generated thermal neutrons on ^{14}N, or to a much lesser extent by neutron capture on ^{13}C. A significant amount of ^{14}C can only be produced by these mechanisms in organic materials in space, if secondary cosmic ray neutrons can become thermalized inside the parent meteoroid. As we know that all the martian meteorites so far recovered were irradiated as small objects in space with only trace water content, very few cosmic-ray generated neutrons can have been thermalized in these sized objects. Indeed, it has been shown (6) that for objects of radius less than ~50 g/cm^2 (or approximately 19 kg in mass) that the cosmic ray induced thermal neutron flux is extremely small and neutron products are not detectable. Both ALH84001 and EETA79001 were much smaller than this size (2.1 and 7.9kg recovered mass respectively), and thus the thermal neutron flux would be even lower and we can eliminate significant thermal neutron production of ^{14}C in the organic components of these objects.

Both inorganic weathering products and organic contamination introduced after the meteorite fell to Earth would lead to higher levels approaching the level of modern terrestrial atmospheric ^{14}C. Material produced after 1950AD would contain higher levels of ^{14}C (up to 2 times modern) due to contamination of the atmosphere by nuclear testing (7). Organic materials are known to combust at temperatures of between 200 and 400°C, below the typical breakdown temperatures of weathering carbonate minerals of 450° to 600°C (8,9,10). Wright et al (9) have previously reported on $\delta^{13}C$ values of some organic materials released by stepped combustion of EETA79001, and a preliminary study of ALH84001 (10). We report on stepped heating experiments on Martian meteorites Allan Hills 84001, Elephant Moraine 79001 and Nakhla. CO_2 produced by combustion in oxygen is let into a mass spectrometer to determined $\delta^{13}C$. The gas is the recovered and reduced to graphite and the ^{14}C content of the sample is determined by accelerator mass spectrometry (AMS). Results from combustion of a >500μ sieve fraction of ALH84001 are shown in figure 1, which indicates that the meteorite appears to contain carbonaceous materials of both terrestrial and extraterrestrial origin. Low temperature (200-430°C) fractions show that the organic components of both ALH84001 and EETA79001 have a $\delta^{13}C$ of between -22 and -33‰, with a ^{14}C content with 25-60% of modern terrestrial carbon, consistent with a terrestrial origin for bulk of the organics.

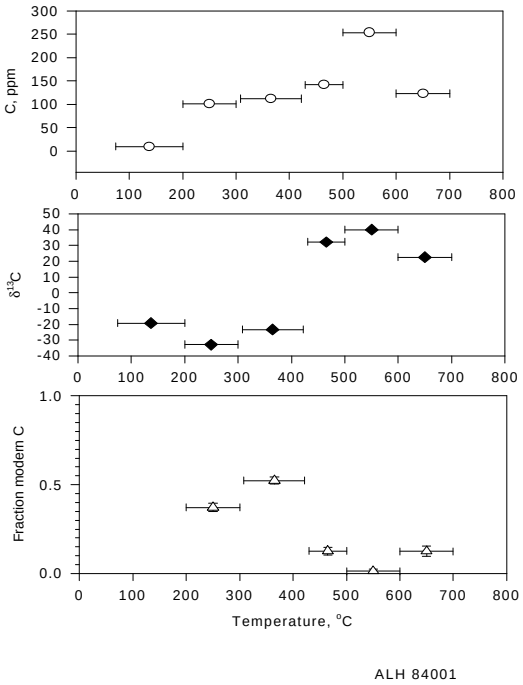

Figure 1: Combustion experiments on ALH84001, (>500μ). Three graphs are shown in each case for total carbon released per temperature step, $\delta^{13}C$ and fraction of modern (1950AD) ^{14}C.

CARBON ISOTOPIC EVIDENCE: A. J. T. Jull et al.

We have also examined gas released by combustion of ALH84001 after acid treatment to remove any carbonate (see figure 2). These studies on ALH84001 reveal that these contaminants can be understood as at least three discrete components: a.) an acid-resistant phase of approx. -25‰ and 11,000 yr age, b.) a phase partially removed by acid etching which we assume is approx -35‰ and recent ^{14}C and c.) acid etching to remove carbonate reveals there is ~50pm of a previously unidentified Martian indigenous phase combusting at 400°-500°C, with $\delta^{13}C$ of -14.5‰. This latter phase has low ^{14}C, which suggests a pre-terrestrial origin. Thus, we can assert that at least 80% of the combustible "organic" material in ALH84001 is terrestrial contamination. The apparent radiocarbon ages of 4,200 to 11,000 yr are consistent with several discrete contamination events over the last 12-13ka.

Intermediate-temperature (~400°-600°C) fractions of bulk sample combustions reveal that the carbonate mineral component of EETA79001 has exchanged with terrestrial carbon dioxide to some extent, whereas the carbonate fraction of ALH84001 is consistent with an extraterrestrial origin. The large difference in ^{14}C and $\delta^{13}C$ measurements of organic and carbonate fractions of ALH84001 indicates that it is extremely unlikely that they could have formed from a common reservoir of carbon. Our results also support the earlier conclusion of Jull et al (12) that the carbonates in EETA79001 are terrestrially-altered and that, indeed, these carbonates are of similar vintage to the terrestrial organic contamination. New experiments on Nakhla, which fell in 1911 and should have minimal terrestrial effects are under way and will be reported at LPSC.

References: 1. D. S. McKay, et al., *Science*, 273, 924, (1996); 2. A. J. T. Jull, et al. *Meteoritics*, 30, 311(1995); 3. A. J. T. Jull, et al., *J. Geophys. Res. Planets*, E102, 1663-1669 (1997); 4. A. J. T. Jull and D. J. Donahue, *Geochim. Cosmochim. Acta*, 52, 1309 (1988); 5. R. E. Taylor, *Radiocarbon Dating: An archaeological perspective*, John Wiley, New York (1987); 6. M. S. Spergel, et al., *Proc. Lunar Planet. Sci. Conf. 16th, J. Geophys. Res.*, 91, no. B4, D483 (1986) ; 7. I. Levin, et al., *Radiocarbon*, 27, 1 (1985); 8. I. P. Wright, et al. *Geochim. Cosmochim. Acta*, 52, 917 (1988); 9. I. P. Wright, et al., *Nature*, 340,220 (1989); 10. M. M. Grady, et al. *Geochim. Cosmochim. Acta*, 52, 2855 (1988); 11. M. M. Grady, et al., *Meteoritics*, 29, 469 (1994); 12. A. J. T. Jull, et al., *Lunar Planet. Sci. XXIII*, 641 (1992).

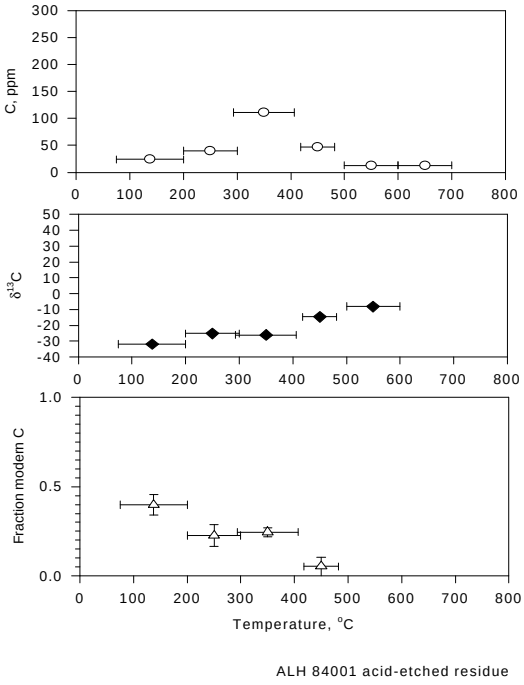

Figure 2: Combustion experiments on phosphoric-acid etched ALH84001. Three graphs are shown in each case for total carbon released per temperature step, $\delta^{13}C$ and fraction of modern (1950AD) ^{14}C.