Isotopic Evidence for a Terrestrial Source of Organic Compounds Found in Martian Meteorites Allan Hills 84001 and Elephant Moraine 79001

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Stepped-heating experiments on martian meteorites Allan Hills 84001 (ALH84001) and Elephant Moraine 79001 (EETA79001) revealed low-temperature (200 to 430 degrees Celsius) fractions with a carbon isotopic composition $\delta^{13}C$ between −22 and −33 per mil and a carbon-14 content that is 40 to 60 percent of that of modern terrestrial carbon, consistent with a terrestrial origin for most of the organic material. Intermediate-temperature (400 to 600 degrees Celsius) carbonate-rich fractions of ALH84001 have $\delta^{13}C$ of +32 to +40 per mil with a low carbon-14 content, consistent with an extraterrestrial origin, whereas some of the carbonate fraction of EETA79001 is terrestrial. In addition, ALH84001 contains a small preterrestrial carbon component of unknown origin that combusts at intermediate temperatures. This component is likely a residual acid-insoluble carbonate or a more refractory organic phase.

Last year, McKay *et al.* (1) reported on a number of pieces of evidence pointing to the possibility of biogenic fossils in the orthopyroxenite ALH84001. This meteorite, together with EETA79001 and other martian meteorites, form a class of rare achondrites that were apparently ejected from the surface of Mars (2). Most of them crystallized from magmas between 180 million years ago (Ma) and 1.3 billion years ago (Ga) and have shock ages of about 180 Ma (2). With an age of crystallization of about 4.5 Ga (3) and a shock age of 3.9 to 4.3 Ga, ALH84001 is much older than other recognized martian meteorites (4). Thus, the results of McKay *et al.* (1) suggest that ALH84001 not only may contain evidence of life on Mars but would imply evidence for the evolution of life early in the history of our solar system. Since the paper of McKay *et al.* (1), there has been much discussion as to the nature and origin of the organic material found in martian meteorites, particularly that found in ALH84001 and EETA79001. Here we used ^{14}C and ^{13}C as tracers to determine the origin of the carbonate mineral and organic carbon components of ALH84001 and EETA79001. These isotopes have been shown to be important tools for determining the provenance of carbonates (5–10) and organic phases (11–13) in previous studies.

ALH84001 and EETA79001 fell to Earth 13 ± 1 and 12 ± 2 thousand years ago (ka), respectively, based on the level of cosmic-ray–produced ^{14}C extracted from silicate minerals found in these rocks (9, 14, 15). This ^{14}C was produced principally by spallation reactions on ^{16}O, which occurred during irradiation by cosmic rays while the meteorites were in space (14, 15). Spallation production of ^{14}C from nuclei heavier than oxygen is not significant (14). The same process produced a significant although substantially smaller amount of ^{14}C in carbonate minerals (16, 17) that were present in the meteorites possibly as a result of aqueous alteration on Mars (2). In contrast, organic material originating from Mars should contain a negligible amount of ^{14}C from either spallation or thermal neutron capture reactions occurring in space (18). Thus, the indigenous organic components of ALH84001 and EETA79001 are expected to have had low ^{14}C activities when they fell to Earth. Once on Earth, however, if these meteorites incorporated either organic contaminants or terrestrial carbonate weathering products, the initial ^{14}C composition of these components may have increased. This effect would be greatest for recent contamination. Alteration occurring since 1955 could produce especially large ^{14}C concentrations due to the incorporation of bomb radiocarbon (19). Thus, ^{14}C can be used as a label to support interpretations of the stable carbon and oxygen isotope abundances and can potentially identify a material as extraterrestrial or terrestrial. It has been used to examine the "white druse" deposits on the EETA79001, which potentially represent martian weathering (6, 7, 20) but may instead be terrestrial weathering products (17).

Organic materials are known to combust between 200° and 400°C, below the typical breakdown temperatures of weathering carbonate minerals of 450° to 600°C (7, 8, 11). Obviously, some overlap is possible depending on combustion conditions. Wright and co-workers (11) previously reported $\delta^{13}C$ values (21) of some organic materials released by stepped combustion of EETA79001 and a preliminary study of ALH84001 (12). We will compare our results to expected ^{14}C and $\delta^{13}C$ for various possible terrestrial contaminants.

Our experiments were designed to isolate carbon from the organic, carbonate, and silicate fractions of these two meteorites and to compare the stable isotope and ^{14}C compositions of each component by means of stepped heating experiments. We performed four separate stepped combustion experiments (22). The first two used crushed bulk material of EETA79001, and the third used sieved bulk material (>250 μm) from ALH84001. For the fourth experiment, we attempted to remove the carbonate from the noncarbonate fractions in ALH84001 by etching the sample with 85% phosphoric acid for 16 hours at 50°C before the stepped heating. The residue from this etch was washed with distilled water, dried, and combusted in the same manner as the other three experiments.

Two stepped combustion experiments were performed on different samples of EETA79001 (experiments E47 and E49, see Table 1 and Fig. 1). In E47, we used three wide temperature steps of ~200°C, whereas in E49, we used increments of about 100°C. Results from the two experiments are similar, although E49 indicated release of 33 parts

Table 1. Results from stepped-combustion experiments on martian meteorite EETA79001. For experiments 47C and 49F, spallogenic ^{14}C was released. BP, before present.

Experiment	Temperature range (°C)	C (μg)	C (ppm)	$\delta^{13}C$ (per mil)	Fraction modern ^{14}C	^{14}C age (ka BP)
			0.401 g of powder			
47A	190–422	79	197	−27.77 ± 0.01	0.583 ± 0.031	4.34 ± 0.43
47B	422–600	15	38	−2.96 ± 0.03	0.444 ± 0.074	6.53 ± 1.35
47C	600–830	30	74	−16.78 ± 0.08	1.67 ± 0.013	Spallogenic ^{14}C
			0.297 g of powder			
49A	76–200	10	33	−19.4	0.228 ± 0.075	11.9 ± 2.7
49B	200–320	30	100	−28.4	0.471 ± 0.023	6.1 ± 0.4
49C	320–410	24	81	−26.7	0.493 ± 0.032	5.7 ± 0.5
49D	410–500	9	30	−12.3	0.411 ± 0.090	7.2 ± 1.8
49E	500–635	13	44	−5.3	0.593 ± 0.063	4.2 ± 0.9
49F	635–760	11	37	−27.6	1.595 ± 0.066	Spallogenic ^{14}C

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per million (ppm) of "old" carbon with a δ^{13}C of −19.4 per mil and a ^{14}C age of ~12 ka in the lowest temperature step (75° to 200°C). The corresponding temperature step was not collected during E47. Material released at these low temperatures cannot be unequivocally identified as indigenous to the meteorite (*8*, *11*, *23*), so we cannot interpret its origin.

Both experiments show the same trend of light (low δ^{13}C) carbon being released at 200° to ~400°C, with a δ^{13}C of about −25 per mil, similar to that expected for terrestrial organic carbon. As mentioned above, the carbonate mineral fraction should typically combust between 450° and 600°C (*8*, *11*, *23*). The CO_2 released between 400° and 630°C in these two experiments show δ^{13}C values of −3 to −12 per mil, which is more negative than values previously reported for carbonate from acid dissolution of EETA79001 (*6*, *7*, *17*). This result may imply some isotopic heterogeneity in the carbonate minerals or that some organic material is still combusting in this temperature range. Nevertheless, the δ^{13}C and the amount of carbon released between 400° and 630°C suggest that it was mostly derived from the degradation of carbonates. At higher temperatures (above 600° to 700°C), the spallogenic carbon component from silicate minerals is expected to be released (*14*, *24*); the increased ^{14}C abundances in these fractions is consistent with this origin.

The carbon dioxide from the organic and carbonate fractions of EETA79001 is composed of carbon that is 40 to 60% modern. This composition is equivalent to a conventional radiocarbon age (which assumes an initial terrestrial atmospheric composition) of 4 to 7.3 ka. Because the terrestrial age of EETA79001 was reported to be 12 ± 2 ka (*15*), the only reasonable source of the organic fraction is more recent terrestrial contamination (*9*, *17*). At this time, we cannot identify whether the contamination occurred continuously since its fall to Earth or as one or several discrete contamination events.

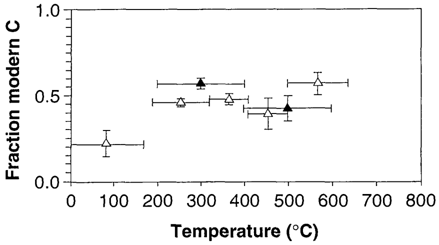

Fig. 1. Combustion experiments on martian meteorite EETA79001: total carbon released per temperature step, δ^{13}C, and fraction of modern ^{14}C. The filled symbols represent the first experiment (E47), which used 200°C temperature steps, and the open symbols, the second (E49), which used ~100°C temperature steps.

For ALH84001, we designed two different experiments. In the first (E50), we performed a stepped combustion procedure on a 0.25-g aliquot of bulk sieved material (>250 μm) (Table 2 and Fig. 2). Like EETA79001 in E49, ALH84001 released a small amount of carbon at low temperatures (75° to 200°C) with a δ^{13}C of −19.3 per mil. This sample was too small for an accelerator mass spectrometer (AMS) measurement. Material combusting at temperatures of 200° to 430°C released carbon of light δ^{13}C (−33 to −22 per mil), which is consistent with that found for combustion between 200° and 450°C in another study, identified as being derived from organic matter (*12*). One other combustion experiment (*25*) of ALH84001 reported carbon with depleted isotopic compositions (−54.9 per mil to −60.6 per mil), although the authors were uncertain whether contamination from the storage container occurred. Thus, it is unclear whether the organic material of ALH84001 is heterogeneous with respect to its stable carbon isotopic composition. In any event, the δ^{13}C of the organic carbon in ALH84001 appears to be isotopically light, with δ^{13}C between −19 per mil and −33 per mil.

Further heating from about 430°C to 600°C resulted in the release of a heavy carbon component with δ^{13}C between +32.25 and +40 per mil. This component is consistent with δ^{13}C measurements in carbonates from acid etching of ALH84001 carbonates (*9*, *10*, *26*) and ion-probe measurements of the carbonate grains of ALH84001 (*27*). The lower δ^{13}C of +32.25 per mil for the 430° to 500°C step may be the result of a residual refractory organic phase or may represent isotopic heterogeneity in the carbonates. The highest temperature fraction in this experiment (600° to 700°C) may represent a mixture of carbonate and spallogenic carbon released from the silicate minerals.

The stable carbon isotope measurements from E50 reveal an apparent difference of 55 to 75 per mil in δ^{13}C between the organic and carbonate components of ALH84001. This disparity may be even larger if the results of Wright *et al.* (*25*) can be validated. It is difficult to produce such a large difference in isotopic composition between two coexisting phases through most known mechanisms, although it is thermodynamically possible by equilibrium fractionation between CH_4 and CO_2 at low temperatures (*13*, *28*). Isotopic equilibrium between organic phases and CO_2 has a smaller isotopic fractionation factor, and the isotopic difference between the organic component and CO_2 would be correspondingly lower (*13*). The coexistence of organic and carbonate phases with such different values of δ^{13}C strongly implies that they may not have the same source of carbon.

The ^{14}C measurements from E50 reveal that, as for EETA79001, the low-temperature (200° to 300°C and 300° to 430°C) steps containing the organic carbon exhibit evidence of terrestrial contamination, with radiocarbon ages of 8.0 and 5.2 ka, respectively. This age range is younger than the terrestrial fall age of 13 ± 1 ka, implying that the bulk of the organic material in ALH84001 is contamination acquired since arrival on Earth. The radiocarbon age of the carbon from the 500° to 600°C step is older, with a radiocarbon age greater than 28.9 ka. From our criterion, this material can only be

Table 2. Results of stepped-combustion experiments on martian meteorite ALH84001.

Experiment	Temperature range (°C)	C (μg)	C (ppm)	δ^{13}C (per ml)	Fraction modern^{14}C	^{14}C age (ka BP)
			0.268 g of powder, size >250 μm			
50A	75–200	8	30	−19.32 ± 0.06		
50B	200–300	27	101	−32.89 ± 0.01	0.372 ± 0.023	8.0 ± 0.5
50C	300–430	30	112	−23.43 ± 0.01	0.524 ± 0.019	5.2 ± 0.3
50D	430–500	38	142	+32.25 ± 0.01	0.127 ± 0.021	16.6 ± 1.3
50E	500–600	68	254	+39.96 ± 0.03	<0.027	>28.9
50F	600–700	33	123	+22.48 ± 0.05	0.125 ± 0.028	16.7 ± 1.8
			0.297 g of powder after treatment with 85% phosphoric acid			
52A	76–200	7	24	−31.9 ± 0.1	0.398 ± 0.056	7.4 ± 1.1
52B	200–300	13	40	−25.2 ± 0.1	0.226 ± 0.061	11.9 ± 2.2
52C	300–400	33	111	−26.07 ± 0.01	0.245 ± 0.025	11.3 ± 0.8
52D	400–500	15	47	−14.7 ± 0.1	<0.106	>18.0
52E	500–600	~3	13	−8.1 ± 0.1	—	
52F	600–700	~4	<3	—	—	

extraterrestrial (*18*). This age is consistent with our previous work (*9, 10*) on ALH84001 carbonates with a $\delta^{13}C$ of +40 per mil [see also (*26, 27*)] and our estimated ^{14}C composition of carbonates irradiated in space.

The preterrestrial nature of the ALH84001 carbonates is also clear from their petrology (*29*). The carbon released in the 430° to 500°C step has a higher level of ^{14}C of 12.7% modern carbon. On the basis of the $\delta^{13}C$ of this gas, it was probably generated mostly from combustion of the carbonate phases, but may also contain a small proportion of carbon from refractory organic materials. The intermediate radiocarbon age is consistent with this interpretation. Likewise, the fraction that was collected from the 600° to 700°C step appears to be a mixture of carbon derived from carbonate minerals with low ^{14}C and high $\delta^{13}C$, and possibly by release of some spallogenic ^{14}C from the silicate or minor mineral phases (see Table 2). An alternative explanation is that some small amount of organic material combusts at this relatively high temperature. A small release of spallogenic ^{14}C from the silicate or other phases below 700°C is possible, but evidence for this has not been observed (*14, 24*).

One issue not resolved in E50 was whether the organic carbon could be separated from the ALH84001 carbonate mineral fraction in a stepped-heating experiment. Thus, we performed a second experiment (E52) with ALH84001, in which we first treated a sample of crushed meteorite powder with phosphoric acid in order to remove the carbonate minerals before combustion. The CO_2 released by acid etching gave 337 ppm of carbon as carbonate, with a $\delta^{13}C$ of +37.1 per mil (Table 2 and Fig. 3). This yield can be favorably compared to the 367 ppm of carbon released between 430° and 600°C in E50; the $\delta^{13}C$ is similar to the +32.25 and +39.96 per mil obtained from the 430° to 500°C and 500° to 600°C steps, respectively, in E50. The values are also similar to the +39 to +45 per mil for acid dissolution of the coarse carbonate fraction of ALH84001 (*9, 10, 26, 27*). These results support the argument that, at least to first order, stepped combustion can be used as a means of separating the organic carbon and carbonate fractions of carbon in ALH84001, as shown previously (*11, 12, 23*).

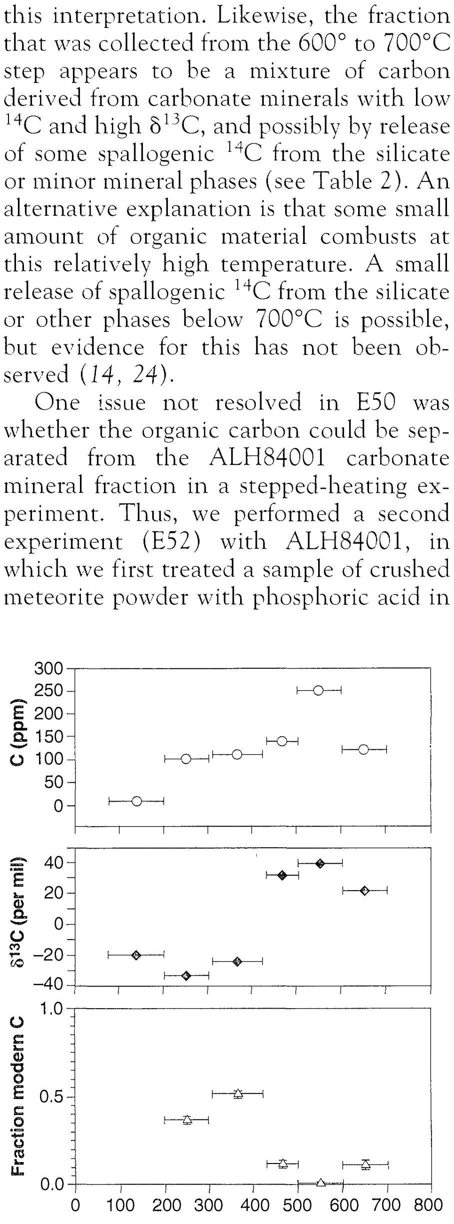

Fig. 2. Combustion experiments on ALH84001 (>250 μm) (E50): total carbon released per temperature step, $\delta^{13}C$, and fraction of modern ^{14}C.

The results of E52 confirm the previous observation that the organic material combusting between 75° and 400°C is isotopically light, with $\delta^{13}C$ of −31.9 to −25 per mil, and has radiocarbon ages consistent with a primarily terrestrial origin. No change in stable isotopic composition of these low-temperature fractions was observed as a result of the acid etching; however, the radiocarbon ages for the organic fractions are somewhat older than those in E50 (7 to 12 ka versus 5.4 to 8.0 ka). This difference suggests that some of the youngest organic carbon may also have been removed by acid etching, which suggests that the contamination of ALH84001 with terrestrial organic carbon did not occur as a single discrete event, but rather as continuous contamination since its fall to Earth or as several discrete events.

For the temperature steps above 400°C, the ^{13}C-enriched carbonate was largely removed by acid etching. A relatively small amount of carbon did however remain to be combusted in the 400° to 500°C and 500° to 600°C steps, which had $\delta^{13}C$ values of −14.7 and −8.1 per mil, respectively. Not enough carbon was generated to measure a ^{14}C age at the 500° to 600°C step, but enough was collected from the 400° to 500°C step to show that it had a minimum age of greater than 18 ka. The origin of this residual carbon from these two steps remains unclear. One possibility is that it represents an acid-insoluble carbonate phase, or it may alternatively represent a more refractory organic carbon component with a heavy stable carbon isotopic composition. In either case, this material is probably preterrestrial in origin, based on its radiocarbon content. If this particular acid-insoluble component is organic carbon, then it represents less than 20% of the total organic material found in ALH84001.

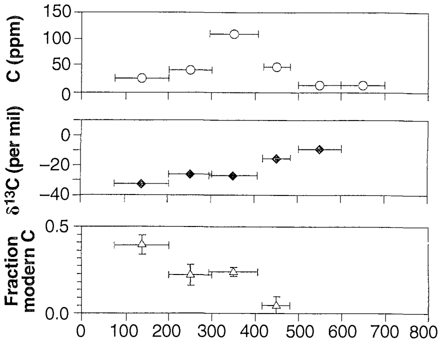

Fig. 3. Combustion experiments on acid-etched residue of bulk ALH84001 (E52): total carbon released per temperature step, $\delta^{13}C$, and fraction of modern ^{14}C.

Another interesting phenomenon observed in the experiments on ALH84001 is a shift to combustion at lower temperature for the acid-etched material. It is possible that the acid etching generated activation sites on the various components, which lowered the activation energy for oxidation reactions. In any case, this phenomena does not change our overall interpretation of these experiments: The organic material in EETA79001 and ALH84001 is predominantly terrestrial contamination. The apparent radiocarbon ages of 4.2 to 11 ka are consistent with several discrete contamination events over the last 12 to 13 ka producing a mixture. Contamination by petroleum products such as from Teflon (*25*) or plastics during handling is unlikely, because these materials would not contain ^{14}C. Our results also support the earlier conclusion of Jull *et al.* (*17*) that the carbonates in EETA79001 are terrestrially altered and that, indeed, these carbonates are of similar vintage to the terrestrial organic contamination. In the case of ALH84001, there is a refractory preterrestrial carbon component, which if organic, represents about 20% of the organic carbon in the rock. This phase is identified as being indigenous on the basis of low ^{14}C. In addition, it is undisputed, based on earlier work, that the carbonate spheroids in ALH84001 are preterrestrial, on the basis of petrography and isotopic composition (*10, 26, 27, 29*).

McKay *et al.* (*1*) studied organic material in ALH84001 only in the form of polycyclic aromatic hydrocarbons, which represents less than 1 weight % of the organic material in this meteorite. The small size of this fraction precludes ^{14}C measurements. However, our results tend to support the interpretation of Wright *et al.* (*11*), Becker *et al.* (*30*), and Bada *et al.* (*31*) that organic material in these Antarctic meteorites is predominantly a contamination effect.

REFERENCES AND NOTES

1. D. S. McKay *et al.*, *Science* **273**, 924 (1996).
2. H. Y. McSween, *Meteoritics* **29**, 757 (1994).
3. E. Jagoutz, A. Sorowka, J. D. Vogel, H. Wänke, *ibid.*, p. 478.
4. R. D. Ash, S. F. Knott, G. Turner, *Nature* **380**, 57 (1996); D. H. Garrison and D. D. Bogard, *Meteoritics Planet. Sci.* **32**, A45 (1997); G. Turner, S. F. Knott, R. D. Ash, J. D. Gilmour, *Geochim. Cosmochim. Acta* **61**, 3835 (1997).
5. R. H. Carr, M. M. Grady, I. P. Wright, C. T. Pillinger, *Nature* **314**, 248 (1985).
6. I. P. Wright, M. M. Grady, C. T. Pillinger, *Geochim. Cosmochim. Acta* **52**, 917 (1988).
7. R. N. Clayton and T. K. Mayeda, *ibid.*, p. 925.
8. I. P. Wright, M. M. Grady, C. T. Pillinger, *ibid.* **56**, 817 (1992).
9. A. J. T. Jull, C. J. Eastoe, S. Xue, G. F. Herzog, *Meteoritics* **30**, 311 (1995).
10. A. J. T. Jull, C. J. Eastoe, S. Cloudt, *J. Geophys. Res.* **102**, 1663 (1997).
11. I. P. Wright, M. M. Grady, C. T. Pillinger, *Nature* **340**, 220 (1989).
12. M. M. Grady, I. P. Wright, C. Douglas, C. T. Pillinger, *Meteoritics* **29**, 469 (1994).
13. K. S. Hutchins, thesis, University of Colorado (1997).
14. A. J. T. Jull, D. J. Donahue, T. W. Linick, *Geochim. Cosmochim. Acta* **52**, 1309 (1988).
15. A. J. T. Jull and D. J. Donahue, *ibid.* **52**, 1309 (1988).
16. For a mean composition of 12.7% carbon for ALH84001 carbonates, production of ^{14}C by spallation of oxygen, by irradiation of this material in a small object in space, must result in about 74 disintegrations per minute per kilogram (3.2 × 10^8 ^{14}C atoms per gram) (*9, 10*). This calculated ^{14}C activity corresponds to a $^{14}C/^{12}C$ ratio (atom/atom) of 5.0 × 10^{-14} or 4.3% of the ratio found in modern, prebomb carbon (~1950 A.D.). Using the composition of calcite for EETA79001 results in a value of 4% of that in modern carbon (*9, 10, 17*). After 13 and 12 ka (the terrestrial ages of these two meteorites), we would expect the ^{14}C in carbonates from these two meteorites to have decayed to a level about 0.9% of the modern value.
17. A. J. T. Jull *et al.*, *Lunar Planet. Sci.* **XXIII**, 641 (1992).
18. A negligible amount of ^{14}C could have been produced by spallation reactions in the organic components of these meteorites. The amount produced by spallation would not produce a significant $^{14}C/^{12}C$ ratio. No appreciable ^{14}C should have been produced while in space in the organic phases through the action of cosmic-ray–generated secondary thermal neutrons on ^{14}N or through thermal neutron capture on ^{13}C. The reason is that secondary cosmic-ray neutrons can only become thermalized inside a large parent meteoroid or in a smaller body with significant water content. Given that all of the martian meteorites so far recovered were irradiated as small objects in space with little water content, very few cosmic-ray–generated neutrons can have been thermalized. M. S. Spergel *et al.* [*Proc. Lunar Planet. Sci. Conf.* **16**, *J. Geophys. Res.* **91**, 483 (1986)] have shown that for objects of pre-atmospheric radius less than ~50 g/cm² (or approximately 19 kg in mass) that the cosmic-ray–induced thermal neutron flux is extremely small and neutron products are not detectable. ALH84001 and EETA79001 were much smaller than this size (recovered masses of 2.1 and 7.9 kg, respectively), and thus the thermal neutron flux would be even lower and we can rule out any significant thermal neutron production of ^{14}C in the organic components of these martian meteorites. Consequently, organic material indigenous to ALH84001 or EETA79001 would be expected to have very low ^{14}C abundance resulting from irradiation in space.
19. Carbonaceous material produced in equilibrium with the atmosphere after 1950 A.D. would contain higher levels of ^{14}C (up to twice the modern values) because of contamination of the atmosphere by nuclear testing [I. Levin *et al.*, *Radiocarbon* **27**, 1 (1985)].
20. J. L. Gooding, S. J. Wentworth, M. E. Zolensky, *Geochim. Cosmochim. Acta* **52**, 909 (1988).
21. The carbon isotopic compositions are determined as

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{\text{sample}}}{(^{13}C/^{12}C)_{\text{standard}}} - 1\right] \times 10^3$$

where the standard is Pee Dee belemnite.
22. For each combustion, between 0.25 and 0.40 g of meteorite powder were placed in a cleaned 9-mm Vycor glass tube, which was then evacuated. Ultrapure oxygen was introduced at a pressure of ~0.3 atm. The samples were then combusted at a series of temperature steps each lasting 20 to 30 min. The temperature was controlled by a resistance furnace and thermocouple apparatus. After each step, the evolved CO_2 was cryogenically collected and cleaned by standard radiocarbon procedures (*14, 32*). An aliquot of oxygen was added to the cell between each step. The $\delta^{13}C$ of each gas was measured with a stable-isotope mass spectrometer, cryogenically recovered from the dual inlet, and then catalytically converted to graphite over iron (*33*) for ^{14}C analysis by AMS. The AMS measurements on these graphite targets were made at the University of Arizona AMS Facility (*34*). Blanks run at each temperature step showed 3 ± 1 μg of modern C for each extraction step (*35*). For our samples, each combustion step yielded between 9 and 79 μg of C, with an average sample size of ~30 μg.
23. M. M. Grady, I. P. Wright, P. K. Swart, C. T. Pillinger *Geochim. Cosmochim. Acta* **52**, 2855 (1988).
24. U. Neupert *et al.*, *Meteoritics Planet. Sci.* **32**, A98 (1997).
25. I. P. Wright, M. M. Grady, C. T. Pillinger, *Lunar Planet. Sci.* **28**, 1591 (1997).
26. C. S. Romanek *et al.*, *Nature* **372**, 655 (1994).
27. J. W. Valley *et al.*, *Science* **275**, 1633 (1997).
28. I. Friedman and J. R. O'Niel, *U.S. Geol. Surv. Prof. Pap. 440-KK* (1977).
29. D. Mittlefehldt, *Meteoritics* **29**, 214 (1994); R. P. Harvey and H. Y. McSween Jr., *Nature* **382**, 49 (1997).
30. L. Becker, D. P. Glavin, J. P. Bada, *Geochim. Cosmochim. Acta*, **61**, 475 (1997).
31. J. L. Bada, D. P. Glavin, G. D. McDonald, L. Becker, *Science* **279**, xxx (1998).
32. R. E. Taylor, *Radiocarbon Dating: An Archaeological Perspective* (Wiley, New York, 1987).
33. P. J. Slota, A. J. T. Jull, T. W. Linick, L. J. Toolin, *Radiocarbon* **29**, 303 (1987).
34. D. J. Donahue, T. W. Linick, A. J. T. Jull, *ibid.* **32**, 135 (1990); D. J. Donahue, *Int. J. Mass Spectrom. Ion Processes* **143**, 235 (1995).
35. The blank levels we determined for a series of combustion steps gave 3 μg (75° to 200°C), 2.5 μg (200° to 400°C), and 5.6 μg (400° to 600°C) of modern carbon. Other studies on blanks in our laboratory for combustions using this line give a mean blank of 3 ± 1 μg of carbon.
36. We are grateful to the Meteorite Working Group for provision of the samples. We wish to thank A. L. Hatheway, D. Biddulph, L. R. Hewitt, and T. E. Lange for technical assistance, and K. Hutchins, G. S. Burr, D. J. Donahue, and C. J. Eastoe for many useful scientific discussions. This work was partly supported by NASA grant NAGW-3614 and NSF grant EAR 95-08413.

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Import of Mitochondrial Carriers Mediated by Essential Proteins of the Intermembrane Space

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In order to reach the inner membrane of the mitochondrion, multispanning carrier proteins must cross the aqueous intermembrane space. Two essential proteins of that space, Tim10p and Tim12p, were shown to mediate import of multispanning carriers into the inner membrane. Both proteins formed a complex with the inner membrane protein Tim22p. Tim10p readily dissociated from the complex and was required to transport carrier precursors across the outer membrane; Tim12p was firmly bound to Tim22p and mediated the insertion of carriers into the inner membrane. Neither protein was required for protein import into the other mitochondrial compartments. Both proteins may function as intermembrane space chaperones for the highly insoluble carrier proteins.

Most proteins imported to mitochondria are synthesized with a cleavable NH_2-terminal targeting sequence and are sorted to their correct intramitochondrial location by the dynamic interaction of distinct transport systems in the outer and inner membranes (*1*). The TIM system in the inner membrane consists of two integral membrane proteins, Tim17 and Tim23, which make up the inner membrane import channel. Complete translocation into the matrix is coupled to adenosine triphosphate (ATP) hydrolysis and is mediated by Tim44, mHsp70, and GrpE. However, some of the most abundant inner membrane proteins, such as the metabolite carriers, are synthesized without a cleavable NH_2-terminal presequence and therefore do not engage with the Tim23 channel. It has been suggested that import of these proteins is directed by one or more internal targeting signals (*2*), but the exact mechanism is still poorly defined. In the cytosol of the yeast *Saccharomyces cerevisiae*, chaperones escort these insoluble carrier proteins preferentially to the outer membrane receptors Tom37 and Tom70 (*3*). The carriers then move through the TOM channel in the outer membrane and insert into the inner membrane, bypassing the ATP-dependent Tim23 system, which transports proteins

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