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Hot Idea

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Organic Compounds in Martian Meteorites May Be Terrestrial Contaminants

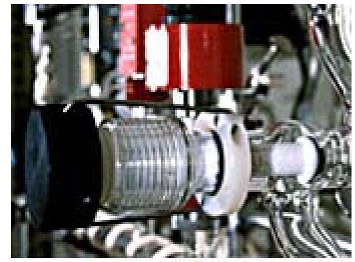

Photo by Jim Abbott.

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In 1996, David McKay and coworkers reported evidence suggesting the possibility of fossils in the martian meteorite ALH84001 (see **PSR Discoveries** article Life on Mars). This work has stimulated much discussion as to the nature and origin of organic material in ALH84001, another martian meteorite, EET79001, and other martian meteorites in general. My colleagues C. Courtney, D. A. Jeffrey, and J. W. Beck and I have been investigating the origin of the organic compounds by measuring the abundances of the isotopes of carbon (C) using accelerator mass spectrometry (AMS). Important clues to the origin of the organic material can be obtained from the amounts of ^{14}C (frequently nicknamed radiocarbon) and the relative amounts of ^{13}C and ^{12}C. Our analyses indicate that at least 80% of the organic material in ALH84001 is from Earth, not Mars, casting doubt on the hypothesis the meteorite contains a record of fossil life on Mars.

Reference:

Jull, A. J. T., C. Courtney, D. A. Jeffrey and J. W. Beck, 1998, Isotopic evidence for a terrestrial source of organic compounds found in martian meteorites Allan Hills 84001 and Elephant Moraine 79001. *Science*, **v. 279**, p. 366-369.

Radiocarbon

Carbon has two stable isotopes with 12 and 13 atomic mass units, called ^{12}C and ^{13}C, respectively. A third isotope, ^{14}C or radiocarbon, is radioactive and has a half-life of 5,730 years. Radiocarbon is used widely for dating organic material on Earth and also for tracing chemical processes. Using radiocarbon dating techniques, we determined that martian meteorites ALH84001 and EETA79001 landed on Earth: 13,000±1300 and 12,000±2000 years ago, respectively.

What can the radiocarbon in these meteorites tell us? Let's look at what we already know. ^{14}C is continuously produced in Earth's upper atmosphere by cosmic ray bombardment. The amount of radiocarbon in Earth's atmosphere is equivalent to a $^{14}C/^{12}C$ isotope ratio of about 1 part in a trillion. This is an important number because it is a standard against which values from the meteorite samples are compared.

Carbonate minerals in a small object (like in a meteoroid of less than about 1-meter radius) irradiated in space will have a $^{14}C/^{12}C$ ratio of 5.0×10^{-14} (that's 5 divided by 100 trillion!) This is only 4.3% of the ratio found in modern terrestrial carbon. Since the meteorites we're studying have been on Earth for about 13,000 years, the ^{14}C in the carbonate minerals in these meteorites has decayed further, reducing the $^{14}C/^{12}C$ ratio to about 0.9% modern. Terrestrial weathering products and organic contamination introduced after the meteorite falls would lead to higher levels approaching the level of modern terrestrial atmospheric ^{14}C. (Interestingly enough, material produced after 1950 would also contain higher levels of ^{14}C, up to 2 times modern, due to contamination of the atmosphere by nuclear testing.)

Thus, contamination of the meteorites on Earth raises the amount of ^{14}C, giving an apparent younger age. So, we are using ^{14}C as a label to help determine the source of carbon in martian meteorites, such as in ALH84001 shown here.

Accelerator Mass Spectrometry

One part in a trillion is a very small number and we must use a very specialized instrument to detect and count the very small number of atmos we're dealing with. The instrument is called an accelerator mass spectrometer. We burn the organic material in oxygen, making carbon dioxide (CO_2), which we analyze.

Photo by Jim Abbott.

Chris Courtney, Timothy Jull, and Warren Beck set up the extraction line used for martian meteorites.

Photo by Lori Stiles.

The accelerator mass spectrometer laboratory at Arizona. The large blue unit on the right is the high-voltage power supply for the ion source, which generates negative carbon ions form the sample. The large, white tank in the background is the accelerator itself. Researchers are, left to right: Timothy Jull, George Burr, Douglas Donahue, and Warren Beck.

Can we use carbon isotopes to identify the source of organic material?

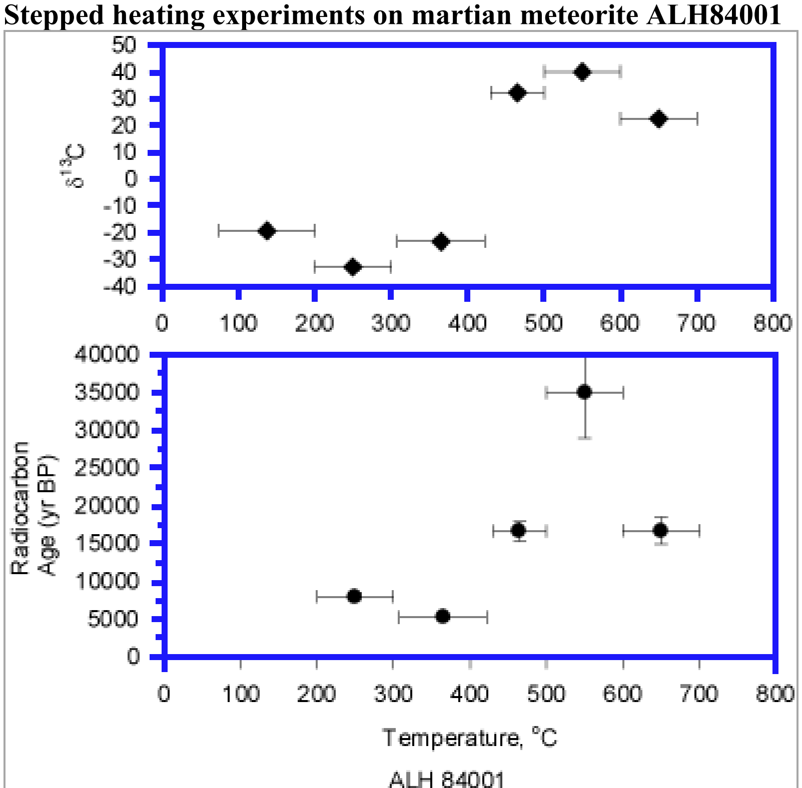
In terrestrial organic material, which originates mainly from biologic activity, ^{14}C has been decaying at a fixed rate ever since the removal of the material from contact with the terrestrial biosphere or atmosphere. Or, in other words, since the time of formation of the organic material. This is the start of the radiometric "clock." Indeed, this is how we use radiometric dating to determine the age of an old mammoth bone, for example. We know half of the ^{14}C decays in 5,730 years so, if we find half the level of radiocarbon, then the sample must be about 5,700 years old. (In real life, there are some more complications).

A potential problem with organic material exposed to radiation in space is that it might contain excess ^{14}C produced by the action of cosmic rays. Fortunately, this turns out not to be a significant source of ^{14}C in the martian meteorites, and here's why. When high-energy cosmic-ray particles interact with a rock in space, they slow down and produce many secondary particles, usually protons and neutrons. However, ^{14}C can be produced only by thermal neutrons on ^{14}N, or to a much lesser extent by a process called neutron capture on ^{13}C. These are neutrons which have slowed down to the vibrational energy of the atoms in the material. This can only happen if the meteoroid is quite large and/or contains a lot of water. Considering that all samples of these meteorites so far recovered were irradiated in space as small objects with only trace water content, then very few cosmic-ray generated neutrons can have been produced. Indeed, M. S. Spergel (City University of New York) and his coworkers at Los Alamos and Brookhaven National Laboratories showed that for objects of radius less than about 150 cm (approximately 19 kg in mass) cosmic rays produce few neutrons and neutron products are not detectable. Both ALH84001 and EETA79001 were much smaller than this size (2.1 and 7.9 kg recovered mass, respectively), and we can eliminate this source of ^{14}C in the organic components of these martian meteorites. Therefore, we proceed to use ^{14}C and the relative amounts of ^{13}C to ^{12}C to attempt to identify the source of organic material in the martian meteorites.

The AMS Results

Results of combustion experiments on martian meteorite ALH84001 are shown in the graphs below. Low temperature (200-430°C) fractions show that the organic components have a ^{13}C of between -22 and -33‰, and a ^{14}C age of 5,000 to 7,400 years. This suggests that this low-temperature fraction contains 40-60% of modern terrestrial carbon. Since this age is less than the time the meteorite fell to Earth (13,000 years ago), this is consistent with a terrestrial origin for most of the organic compounds. We found similar results for martian meteorite EET79001.

Stepped heating experiments on martian meteorite ALH84001



(adapted from Jull et al., 1998, Science, v.279, p. 366-369.)

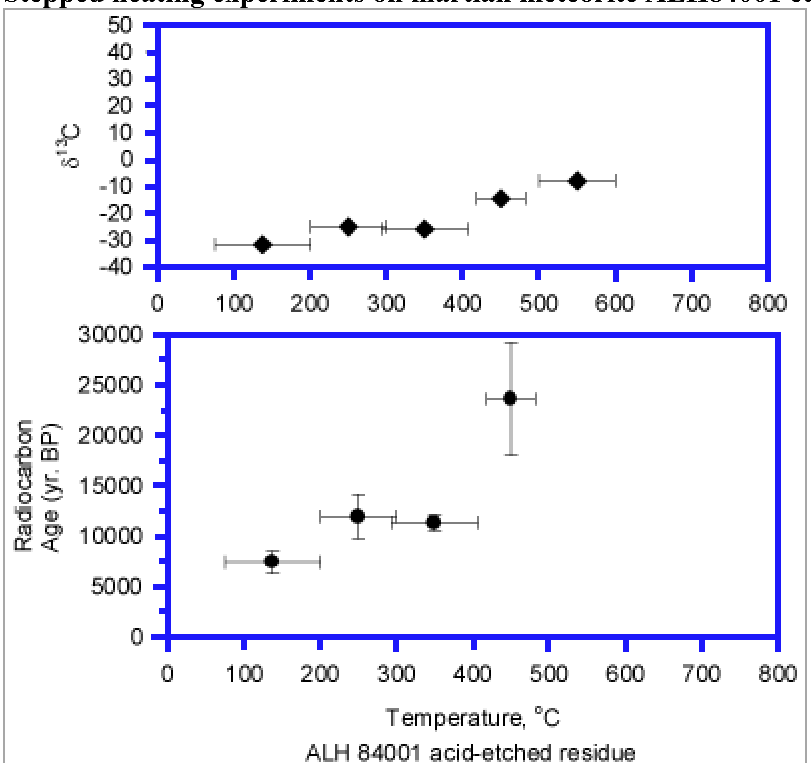
The intermediate temperature (~400-600°C) fractions correspond to combustion of the carbonate minerals. The data show that the carbonate fraction of ALH84001 has higher ^{13}C coupled with a high apparent age (hence low in ^{14}C). This is consistent with an extraterrestrial origin for the carbonate, in accord with observations of the occurrence of the carbonate minerals in ALH84001. In contrast, data for EET79001 reveal that the carbonate mineral component of that rock has exchanged with terrestrial carbon dioxide to some extent, because we observe ^{14}C in these fractions. EET79001 appears to be more contaminated with terrestrial carbon than is ALH84001.

The large difference in both ^{14}C and ^{13}C measurements of organic and carbonate fractions of ALH84001 indicates that it is extremely unlikely that they could have formed from a common source of carbon. If we only had the ^{13}C data, we might suspect strong fractionations of the carbon isotopes might have occurred, for example between methane and carbon dioxide. But these occur only under certain conditions, and we might be tempted to say these conditions existed sometime during the history of ALH84001. However, this would require that the ^{14}C concentration be the same in both phases, which they are clearly not. Thus, our ^{14}C "label" is very important.

Our ^{14}C data tell us if these phases have some terrestrial contaminants that were either of biological origin or at some time in equilibrium with the Earth's atmosphere. Radiocarbon measurements reveal that the carbonate CO_2 is low in ^{14}C. The fraction 500-600^oC appears to be the purest carbonate release, with the fraction of modern carbon being <0.04. This also supports the preterrestrial nature of these ALH carbonates.

In order to more completely understand what's going on, we performed a combustion on a sample of ALH84001 that had been etched with phosphoric acid to remove any carbonates. The carbon dioxide released by acid etching gave 337 ppm carbon as carbonate, with ^{13}C of +37.10±0.01‰. This is very similar to the 367 ppm carbon released in the previous stepped combustion of ALH84001 between 430 and 600 ^oC. So, this confirms that our temperature fractions give similar amounts of carbonate in 430-600 ^oC. These new results are shown in the graph below.

Stepped heating experiments on martian meteorite ALH84001 etched with phosphoric acid



(adapted from Jull et al., 1998, Science, v.279, p. 366-369.)

The results confirm the general trend already observed, that the organic material combusting between 75-400^oC is isotopically light, with ^{13}C of -31.9 to -25‰, and the fraction of modern carbon in these different steps is 23-40% modern (equivalent to 7,400 to 11,900 years old.) Above 400^oC, our study indicates that the ^{13}C-enriched carbonate is removed by acid etching; ^{13}C values of -14.7 and -8.1‰ and low ^{14}C suggest the possible presence of another component. This small component seems to us to be indigenous carbon-bearing material other than carbonates. Its higher temperature of combustion rules out most organic compounds. We think this could be a more durable material, with high molecular weight or perhaps some residual carbonate which didn't dissolve in the acid.

Significance for Fossils-in-ALH84001 Hypothesis

The organic material in ALH84001 can be identified by its combustion behavior, and contains several discrete components. We do not assert we have completely separated all these components. We identified low-temperature (<400^{o}C) combustible material (probably organic phases) which appears to be the result of two or more contamination events at about 13,000 years ago, which introduced carbon with ^{13}C about -25‰; a recent event of ^{13}C about -34‰; and presumably other intermediate events are possible. We can also identify a more resistant phase, ~47ppm C, which combusts between 400-500^{o}C and is characterized by ^{13}C of -14.7‰ and low ^{14}C. This phase must be indigenous to the meteorite and hence presumably, Mars. This mysterious phase represents a little less than ~20% of the carbon-bearing material in this meteorite, but it is not certain it is an organic compound. Hence, we say that at least 80% of the organic material of ALH84001 is of terrestrial origin.

What are the implications for the data reported by David McKay and his colleagues? They studied only organic compounds in the form of polycyclic aromatic hydrocarbons (PAH) in ALH 84001. This material represents less than 1% of organic material in this meteorite. The small size of this fraction precludes ^{14}C measurements, even by our sensitive techniques. Our results suggest that most of the organic material in ALH84001 is terrestrial contamination. We cannot rule out some indigenous organic material being present, but our data point out the importance of fully understanding how much contamination has occurred in all the martian meteorites.

Many tests are planned by us and others. We hope that chemical separations of different organic compounds will tell us more about their origins.

Additional Resources

Jull, A. J. T., C. Courtney, D. A. Jeffrey and J. W. Beck, 1998, Isotopic evidence for a terrestrial source of organic compounds found in martian meteorites Allan Hills 84001 and Elephant Moraine 79001. *Science***, v. 279**, p. 366-369.

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NSF-University of Arizona Accelerator Mass Spectrometer Facility.

Taylor, G. J., "Life on Mars -- The Debate Continues." *PSR Discoveries*. **March 1997**. <http://www.psrd.hawaii.edu/Mar97/LifeonMarsUpdate.html>

Taylor G. J., "Not Quite a Meeting of the Minds." *PSR Discoveries*. **March 1997**. <http://www.psrd.hawaii.edu/Mar97/LPSCreport.html>