The origin of organic matter in the Martian meteorite ALH84001

Luann Becker a,*, Brian Popp b, Terri Rust b, Jeffrey L. Bada c

a Hawaii Institute of Geophysics and Planetology, University of Hawaii at Manoa, Honolulu, HI 96822, USA
b School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Honolulu, HI 96822, USA
c Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA 92093-0212, USA

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Abstract

Stable carbon isotope measurements of the organic matter associated with the carbonate globules and the bulk matrix material in the ALH84001 Martian meteorite indicate that two distinct sources are present in the sample. The δ13C values for the organic matter associated with the carbonate globules averaged −26‰ and is attributed to terrestrial contamination. In contrast, the δ13C values for the organic matter associated with the bulk matrix material yielded a value of −15‰. The only common sources of carbon on the Earth that yield similar δ13C values, other then some diagenetically altered marine carbonates, are C4 plants. A δ13C value of −15‰, on the other hand, is consistent with a kerogen-like component, the most ubiquitous form of organic matter found in carbonaceous chondrites such as the Murchison meteorite. Examination of the carbonate globules and bulk matrix material using laser desorption mass spectrometry (LDMS) indicates the presence of a high molecular weight organic component which appears to be extraterrestrial in origin, possibly derived from the exogenous delivery of meteoritic or cometary debris to the surface of Mars.

Keywords: Mars; Alan Hills meteorites; exobiology; extraterrestrial geology; organic carbon; C-13/C-12

1. Previous studies of carbon isotopes and organic matter in ALH84001

The announcement by McKay et al. [1] that evidence of biological activity may be present in the Martian meteorite ALH84001, has resulted in a reassessment of how to search for life on Mars and elsewhere. In the case of the Mars meteorite report, all of the key pieces of evidence presented were identified in abundant, zoned domains of calcium–iron–magnesium carbonate [2]. Much of the controversy generated by ALH84001 centers around stable carbon isotopic studies of the carbonates and the associated organic matter. The δ13C values for the carbonate globules in ALH84001 range up to +42‰, well outside the δ13C range of terrestrial carbonates [2,3]. Shortly before the McKay et al. report, a single δ13C value of −22‰ was reported for the combustible carbon, which is apparently derived from organic matter associated with the carbonate globules, and is indistinguishable from terrestrial organic matter [4].

Recently, Jull et al. [5] carried out stepped combustion experiments on ALH84001 and measured δ13C values of −22 to −32‰ and a 14C content of...
up to 60% modern terrestrial carbon, consistent with a terrestrial origin for most of the organic material. The carbonate fractions of ALH84001 revealed $\delta^{13}C$ values of +32 to +40‰ and a low $^{14}C$ content, consistent with an extraterrestrial origin. In addition, a small amount (~50 ppm) of a carbonaceous component of unknown origin with a $\delta^{13}C$ value of −15‰ and a low $^{14}C$ activity, combusting in the temperature range of ~400–600°C, was found [5]. Based on these measurements, it was suggested that this component was either a residual carbonate phase or a more refractory ‘pre-terrestrial’ organic component.

The only organic compounds identified, thus far, in ALH84001, are trace quantities (ppm) of poly-cyclic aromatic hydrocarbons (PAHs) and amino acids [1,6]. The predominantly L-enantiomeric composition of the amino acids suggests they are mainly terrestrial contaminants probably derived from ice meltwater that had percolated through the meteorite. The source of the PAHs in this meteorite is much more difficult to ascertain because PAHs are ubiquitous in the universe and on Earth PAHs are the products of slow geochemical diagenetic reactions and the burning of biomass [7,8]. In fact, except for possibly obtaining stable carbon isotope compositions on these compounds, the origin of the PAHs cannot be determined [9].

Recently, Clemmett et al. [10] have argued that the PAHs detected in the ALH84001 carbonate globules could not be associated with terrestrial contamination based on their solubility in water. It is further suggested that PAHs do not have an affinity to absorb to carbonate material as was previously suggested by Becker et al. [11]. However, studies of PAHs in natural systems show that these compounds can be leached from organic matrixes into the aqueous phase [12]. In addition, the aqueous solubility of PAHs is also apparently enhanced in the presence of dissolved humic-like material [13]. Reports of PAHs in sediments and suspended matter in the aquatic environment indicate that these compounds bind to the surfaces of carbonate grains and are remarkably persistent [14]. Based on the previous stable carbon isotope and radiocarbon measurements [5], the bulk of the organic matter in the ALH84001 carbonates is a terrestrial component which could leach or absorb PAHs (e.g. humic-like material) into the meteorite. Thus, the notion that PAHs are somehow precluded from possible introduction into ALH84001 by ice meltwater percolating through the meteorite matrix and absorbing to the surfaces of mineral grains is simply not a tenable argument [10].

An important consideration, however, is that only a small percentage (~1%) of the bulk organic matter in ALH84001 is in the form of PAHs or amino acids. Based on the amount of total combustible carbon measured in ALH84001 (~240 ppm) [4,5] there still remains a large fraction of organic matter that is not characterized by these two compound classes. While it may be difficult to obtain $\delta^{13}C$ measurements for individual compounds in ALH84001 at such low concentrations, it is possible to determine the isotopic composition of the bulk organic matter. Previous efforts to measure the carbon isotopic signature for the organic matter in ALH84001 involved stepped heating of the bulk rock [4,5]. This approach assumes that any combustible organic matter is present in carbonates and, thus, does not provide information about other mineral phases that may also contain organic matter. In this study, we have investigated the $^{13}C/^{12}C$ ratios in the organic matter isolated from the carbonate globules and the bulk matrix material. In addition, we re-examined the PAHs in ALH84001 using laser desorption mass spectrometry (LDMS) in order to determine the association between $\delta^{13}C$ values and PAH components.

2. Analytical methods

A 0.46 g portion of an ALH84001 sample (251; this is a fragment of the parent split 84001, 65) was carried through an acid dissolution procedure designed to separate organic matter complexed to the carbonate globules from the organic matter associated with the bulk matrix material. Carbon isotopic analyses were carried out for the acid-soluble (carbonate-rich) and bulk matrix fractions of organic matter of ALH84001 (Table 1). Two crushed samples of ALH84001 (extracts A, B) were weighed, placed in pre-combusted quartz tubes, and then reacted with 1 ml of 1 M HCl (overnight) to remove carbonate. A third bulk sample (C) previously reacted with 1 M HCl, was treated again with 6 M HCl, at 150°C for 3 h. After approximately 24 h, the acid soluble supernatant was transferred to separate
pre-combusted quartz tubes and re-weighed. The remaining bulk material was rinsed thoroughly with double distilled water to remove any residual acid.

For the isotopic analyses, the various residues were transferred to tubes and vacuum dried, cupric oxide added, flame sealed, and combusted at 780°C for at least 8 h followed by 1 h at 500°C before cooling the samples to room temperature. The combustion-released CO₂ was cryogenically purified and manometrically quantified within three days of combustion and stored in 6-mm flame-sealed pyrex collection tubes until analyzed on a Finnigan MAT252 isotope ratio-monitoring mass spectrometer [15]. Analytical uncertainty for all carbon isotopic analyses was better than 0.05%. Carbon isotopic compositions are reported in δ-notation relative to Pee Dee belemnite (PDB) and have been HCl/CuO-blank corrected (0.005 μmoles, and δ₀ = −27.61 ± 0.03‰, n = 3). In contrast to the measurable amounts of CO₂ found in the acid soluble and bulk residues, insufficient nitrogen (<0.05 μmol N₂) was recovered for nitrogen isotopic measurements.

Laser desorption mass spectrometry (LDMS) was used to characterize PAHs and kerogen-like material in the organic matter associated with the carbonate globules and the bulk matrix material in ALH84001 (for details on LDMS technique see Ref. [11]). Briefly, several pieces of the ALH84001 meteorite were examined under a light microscope to locate the carbonate globules. The carbonate-rich pieces were carefully separated from the non-carbonate or ‘bulk matrix’ (i.e., no carbonate globules present) pieces. Both the carbonate-rich and the non-carbonate pieces were crushed using a clean (annealed at 500°C) mortar and pestle. A portion of the carbonate-rich material was treated with 1 M HCl to remove organic matter associated with the acid soluble carbonate-rich component. The acid soluble supernatant was allowed to dry under vacuum and the remaining residual was placed on a stainless steel disc and transferred into a high vacuum chamber (≈ 2 × 10⁻⁷–2 × 10⁻⁸ torr). LDMS spectra were obtained using a KRATOS (linear) time-of-flight (TOF) instrument at the University of Hawaii. Neutral and ionized molecules were desorbed off the substrate using a pulsed 337-nm ultraviolet nitrogen laser at low fluences (10⁶ W/cm²). The remaining bulk rock material was also examined ‘directly’ for PAHs and kerogen-like material using the LDMS described above. In addition, a sample of the Murchison meteorite was treated with acid, extracted with an organic solvent (toluene) and was sublimed at 200, 400 and 600°C respectively (for more details on the extraction and sublimation procedure for Murchison, see Ref. [16]). The Murchison sublimates were examined directly using LDMS and the spectra were compared to those obtained for the ALH84001 1 M HCl and bulk matrix material (see Section 3).

3. Results

The δ¹³C values for the organic matter released by dissolving the carbonates in 1 M HCl, were −25‰ and −27‰ respectively (Table 1). These values are similar to previous measurements reported for ALH84001 organic matter (−22‰ to −33‰) [4,5] and are indistinguishable from terrestrial organic material [17]. The remaining bulk matrix sample (previously extracted with 1 M HCl) yielded a δ¹³C value of −7.9‰. We attribute this δ¹³C value to a residual acid-insoluble carbonate phase. In order to eliminate the residual carbonate component, a separate bulk matrix sample previously reacted with 1 M HCl, was treated again with 6 M HCl for 3 h at 150°C. Examination of the acid-treated bulk material using X-ray diffraction (XRD) indicated that no residual carbonate material was present. This sample yielded a δ¹³C value of −15‰, a 10‰ difference in comparison to the organic matter associated with the carbonates. A δ¹³C value of −15‰ is unusual with respect to terrestrial sources with only some diagenetically altered carbonates and C₄ plants having a similar value [18]. A δ¹³C of −15‰ on the other hand, is consistent with a ‘kerogen-like’ component present in carbonaceous chondrites. For example, studies of the kerogen-like material in the Murchison meteorite have yielded an average δ¹³C value of −15.8 ± 1.4‰ [19]. Thus, it would appear that the organic matter associated with the ALH84001 bulk matrix is best explained as extraterrestrial in origin, possibly derived from meteoritic or cometary debris exogenously delivered to the surface of Mars.

Separate samples of the crushed ALH84001 material were carried through the same extraction pro-
Fig. 1. The PAHs detected in the ALH84001 organic matter associated with the carbonate globules (top spectrum) and the bulk matrix material (lower spectrum) analyzed using LDMS [10]. Principal peaks at \( m/z = 178, 202, 252, 276, 278 \) and \( 300 \) atomic mass units (amu) were assigned to phenanthrene (C\(_{14}\)H\(_{10}\)), pyrene (C\(_{16}\)H\(_{10}\)), chrysene (C\(_{18}\)H\(_{12}\)), perylene or benzopyrene (C\(_{20}\)H\(_{12}\)), benzoperylene or anthanthrene (C\(_{22}\)H\(_{12}\)), anthanthracene (C\(_{22}\)H\(_{14}\)) and coronene (C\(_{24}\)H\(_{12}\)). A high-mass envelope is also evident in these spectra which is consistent with the presence of a kerogen-like component. The interpretation of a kerogen-like component in these spectra also agrees with the stable carbon isotope value (\( \\delta^{13}C \sim -15\%_C \)) which is similar to values reported for the kerogen-like material in the Murchison meteorite [12].
Table 1
Carbon isotope results for organic matter of ALH84001 Martian meteorite

<table>
<thead>
<tr>
<th></th>
<th>CO₂ (μmol)</th>
<th>Organic mat. (ppm)</th>
<th>δ¹³C‰</th>
<th>δ¹³C‰ (blk. cor.)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid soluble, 5.7 mg</td>
<td>0.621</td>
<td>~1300</td>
<td>−24.95</td>
<td>−24.68</td>
</tr>
<tr>
<td>Bulk residual, 150 mg</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Sample B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid soluble, 6.2 mg</td>
<td>0.587</td>
<td>~1100</td>
<td>−25.29</td>
<td>−25.04</td>
</tr>
<tr>
<td>Bulk residual, 152 mg</td>
<td>0.466</td>
<td>37.1</td>
<td>−10.28</td>
<td>−7.86</td>
</tr>
<tr>
<td>Sample C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid soluble, 9.4 mg</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Bulk residual, 484 mg</td>
<td>0.484</td>
<td>13.0</td>
<td>−16.54</td>
<td>−15.07</td>
</tr>
</tbody>
</table>

Data for the organic material (ppm) were obtained for the total organic carbon associated with the carbonate component (~2%). Previous measurements of the organic carbon in ALH84001 have all been reported relative to the whole rock [4–6]. Based on this study the bulk of the organic carbon resides in the acid soluble carbonate-rich phase.

* nd = no data, sample not available for isotope analyses. * blk. cor. = blank corrected.

In order to assess the stability of the PAHs and kerogen-like material observed in ALH84001, we sublimed an extract of the Murchison meteorite at 200, 450 and 600°C (Fig. 2a–c). The Murchison spectra is characterized by a marked shift from predominantly lower molecular weight compounds (PAHs) at 200°C, to a more prominent higher molecular weight envelope (kerogen-like material) at 600°C. Thus, the presence of a high mass envelope in ALH84001 may be attributed to the stability of these compounds even after being subjected to rather high shock pressures and temperatures (>45–50 GPa; ~1200°C) upon ejection from the surface of Mars [21]. The PAHs, on the other hand, appear to be much less stable with increasing temperature, and it is possible that these compounds would not have survived the impact event. These impact-generated high temperatures and shock pressures may also explain the lack of ‘intact’ more fragile organic compounds, (carboxylic acids, amino acids, amines etc.) in ALH84001, which are abundant in the Murchison meteorite [19].

4. Discussion

The isotope and organic analyses carried out, thus far, on ALH84001 and in Antarctic blue ice are...
Table 2
Summary of the isotope and organic analyses in Allan Hills ice and the ALH84001 Martian meteorite

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Total organic C (ppm)</th>
<th>$^{13}\text{C}_a$ $^{13}\text{C}_b$</th>
<th>$^{13}\text{C}_c$</th>
<th>Percent modern $^{13}\text{C}$</th>
<th>Amino acids (ppm)</th>
<th>Polycyclic aromatic hydrocarbon (ppm)</th>
<th>Kerogen-like material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antarctic Allan Hills blue ice</td>
<td>~0.200 to 0.300</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>~0.001</td>
<td>≤0.001</td>
<td>nd</td>
</tr>
<tr>
<td>[23]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALH84001 bulk rock</td>
<td>~240 ppm</td>
<td>°C $^{13}\text{C}$ ppm 30 °C $^{13}\text{C}$ ppm 101 °C $^{13}\text{C}$ ppm 112 °C $^{13}\text{C}$ ppm 178 °C $^{13}\text{C}$ ppm 235 °C $^{13}\text{C}$ ppm 335 °C $^{13}\text{C}$ ppm 365 °C $^{13}\text{C}$ ppm 395 °C $^{13}\text{C}$ ppm 425 °C $^{13}\text{C}$ ppm 455 °C $^{13}\text{C}$ ppm 485 °C $^{13}\text{C}$ ppm 515 °C $^{13}\text{C}$ ppm 545 °C $^{13}\text{C}$ ppm 575 °C $^{13}\text{C}$ ppm 605 °C $^{13}\text{C}$ ppm 635 °C $^{13}\text{C}$ ppm 665 °C $^{13}\text{C}$ ppm 695 °C $^{13}\text{C}$ ppm 725 °C $^{13}\text{C}$ ppm 755 °C $^{13}\text{C}$ ppm 785 °C $^{13}\text{C}$ ppm 815 °C $^{13}\text{C}$ ppm 845 °C $^{13}\text{C}$ ppm 875 °C $^{13}\text{C}$ ppm 905 °C $^{13}\text{C}$ ppm 935 °C $^{13}\text{C}$ ppm 965 °C $^{13}\text{C}$ ppm 995 °C $^{13}\text{C}$ ppm</td>
<td>40 to 60</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>[4,5]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALH84001 carbonates (1 M HCl)</td>
<td>~1000 ppm</td>
<td>nd</td>
<td>nd</td>
<td>~26%</td>
<td>0.1 to 7</td>
<td>~0.1 to 1</td>
<td>nd</td>
</tr>
<tr>
<td>[this study]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALH84001 bulk matrix</td>
<td>~12 ppm</td>
<td>nd</td>
<td>nd</td>
<td>~15%</td>
<td>~0.300</td>
<td>~0.1 to 1</td>
<td>nd</td>
</tr>
<tr>
<td>[this study]</td>
<td></td>
<td></td>
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<td></td>
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</table>

The data in this table are taken from [4–6,23] and this study. Although the kerogen-like component associated with the carbonates was not completely separated, 47 ppm of an organic component with a $^{13}\text{C}$ of −15% was released using H$_3$PO$_4$ acid treatment [5]. The detected amino acids in both ALH84001 and the Antarctic ice consist only of the L-enantiomers, indicating that they are terrestrial in origin, and are apparently not of great age (racemization should generate some D-amino acids over periods millions of years even at Antarctic temperatures, [23]). The sources of the organic components in the Antarctic ice are not known. In the case of total organic carbon in Greenland ice, a single $^{13}\text{C}$ (~21%) measurement (J.L. Bada, unpublished result) suggests a marine origin for the bulk organic carbon.

* Step heating H$_3$PO$_4$ acid etch.  
* Step heating bulk rock.  
* Conventional this study.  
* Treated with 1 M HCl, some heavy carbonates may be present.  
* Treated with 6 M HCl, stable isotope analyses is consistent with kerogen-like component.
summarized in Table 2. The $\delta^{13}C$ isotope values of $-22\permil$ to $-32\permil$ ([4,5] and this study) and the radiocarbon measurements [5], coupled with predominately L-amino acids [6], suggests that the organic matter associated with the carbonate globules is terrestrial in origin, likely introduced by ice meltwater percolating through the meteorite [6,11,22,23]. In contrast, the $\delta^{13}C$ isotope value of $-15\permil$ measured in separate samples of ALH84001 ([5], and this study), coupled with the presence of a kerogen-like component in our mass spectra (Fig. 1), appears to be best explained as a pre-terrestrial component. These results, thus, provide the first definitive evidence that there was some sort of organic material present on
Mars when ALH84001 was ejected from the surface. It's interesting to note that the extraterrestrial kerogen-like component in ALH84001, detected using LDMS, could only be confirmed by measuring the stable isotopes outside of the carbonate mineral phase (e.g. the 6 M HCl bulk extract which contains no carbonate).

An important question that remains, however, is whether this indigenous organic matter detected in ALH84001 was formed as a result of biogenic or abiogenic processes and whether it was synthesized on the surface of Mars or was exogenously delivered to the planet. Recent measurements of the oxygen isotopes in ALH84001 carbonate-rich material revealed a $\Delta^{17}O$ anomaly which can only be explained by a highly oxidized surface at the time that the ALH84001 carbonates formed [24]. The presence of highly oxidizing surface conditions was also used to explain the lack of organic compounds detected during the Viking missions [25]. These new findings suggest similar conditions may have existed early on in the development of the Martian atmosphere. If this was indeed the case, then the organic matter found in ALH84001 could not have formed on the surface of the planet because the conditions would have been unfavorable for the prebiotic synthesis and the subsequent accumulation of organic compounds.

While the oxidizing conditions are problematic for the synthesis of organic matter on Mars, they do not eliminate entirely the possibility of exogenous delivery of organics to the surface. Mars has a lower surface gravity than Earth, giving rise to a lower atmospheric entry velocity for debris infalling to the surface of the planet [26]. The mass of meteoritic debris expected to survive Martian atmospheric entry without melting has been estimated to be $8.6 \times 10^6$ kg/yr [26,27]. Because Mars is a less tectonically active planet in comparison to the Earth, the long term accumulation of exogenous organic compounds may have been a potentially important source of abiotic organic matter on Mars. Organic compounds contained within exogenous debris could have been protected from oxidation, especially once this material was incorporated into rocks and sediments. Thus, exogenous delivery may have played an important role in the origins of life by seeding planets such as Mars and the early Earth with organic molecules.

If the organic matter associated with the ALH84001 bulk matrix material is indeed a kerogen-like component, similar to the Murchison meteorite, then an abiogenic, exogenous origin is favored. An interesting caveat concerning the chemistry of carbonaceous chondrites is that, despite the variety of organic components and hydrous minerals available, the level of complexity and limited suite of compounds detected fall short of assimilating life as we know it. The presence of simple organic molecules (amino acids, purines and pyrimidines) like those observed in the Murchison meteorite [12], in combination with aqueous conditions which may have characterized early Mars, could ultimately have resulted in the formation of more complex organics and perhaps life itself. Future missions to Mars will provide the opportunity to assess the chemistry of the Martian crust and select samples needed to properly evaluate this compelling question. Hence, while the ‘life’ signs in ALH84001 appear to be all but erased by their lengthy stay in the Antarctic ice, the key aspects of understanding the origins of life on the Earth and perhaps other planets may still be preserved in rocks and sediments on Mars.

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