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10. Plate motions are specified by Euler (angular velocity) vectors giving either the relative motion between a plate pair or the absolute motion of an individual plate. These vectors can now be derived from space geodetic data and were previously derived from data recording plate motions averaged over the past few million years [C. Chase, *Geophys. J.* **29**, 117 (1972); J. Minster *et al.*, *ibid.* **36**, 541 (1974)]. ITRF-94, a reference frame for space geodetic data [C. Boucher, *IERS Technical Note 20* (Observatoire de Paris, Paris, 1996)], is designed to agree on average with the absolute plate motion model NNR NUVEL-1A, termed NNR-A. The latter is a revision of model NNR, derived by combining the assumption of no net torque on the lithosphere [D. Argus and R. Gordon, *Geophys. Res. Lett.* **18**, 2039 (1991)] with global relative plate motion model NUVEL-1 [C. DeMets *et al.*, *Geophys. J. Int.* **101**, 425 (1990)], reflecting a change in the magnetic anomaly time scale subsequent to the publication of NUVEL-1. NUVEL-1A and NNR-A predict plate motion directions identical to those for NUVEL-1 and NNR NUVEL-1, but 4% slower [C. DeMets *et al.*, *Geophys. Res. Lett.* **21**, 2191 (1994)]. Because rate data in the models come from ridges, the predicted rates across subduction zones are derived indirectly by the closure of plate circuits. Space geodetic velocities in ITRF-94 can be compared with plate motions predicted by NNR-A, and relative motions are typically compared with NUVEL-1A (*30*).
11. J. Robbins, D. Smith, and C. Ma [in *Space Geodesy and Geodynamics*, D. Smith and D. Turcotte, Eds. (American Geophysical Union, Washington, DC, 1993), pp. 21–36] noted the discrepancy at Easter Island between the motion estimated from SLR and that predicted by NUVEL-1A. However, data at one site provide only the two horizontal velocity components and are hence insufficient to define the three components of the Nazca plate's angular velocity vector, which requires horizontal velocity measurements at two sites (*30*).
12. Space geodetic data for plate motions over a few years generally agree surprisingly well with the predictions of global plate motion models derived by estimating plate motions over millions of years (*2, 11, 30*). However, changes in plate motions over the past 3 My have been suggested for other plate pairs both from GPS data (*30*) and magnetic anomalies [C. DeMets, *Geophys. Res. Lett.* **22**, 3545 (1995)]. Because our Nazca–South America Euler vector was derived from a short time series at only two sites, it is unclear whether importance should be ascribed to the discrepancy between it and the vector from NUVEL-1A. The discrepancy may reflect the limited data, NUVEL-1's derivation without direct data across the subduction zone, or a change in plate motions. Assessment of such possible changes should improve as additional space geodetic sites and longer time series become available.
13. For the permanent sites in South America, we used the data available since 1 August 1994: 3 years at KOUR and FORT, 2 at BRAZ, and 1.5 at LPGS. The resulting Euler vector in ITRF-94 has pole at 21.63°S, 154.22°W; magnitude of 0.134°/My; an error ellipse with major (σ_{max}) and minor (σ_{min}) axes 16.6° and 4.4°, respectively; a major axis oriented −78.5° [clockwise from north (cw from N)]; and a rotation rate uncertainty (σ_ω) of 0.012°/My. The Nazca plate data yield a Euler vector in ITRF-94 [pole at 34.32°N, 101.12°W; magnitude, 0.735°/My; σ_{max}, 3.62°; σ_{min}, 0.7°; azimuth, −4° (cw from N); and σ_ω, 0.03°/My] and hence a Nazca–South America relative Euler vector with pole at 40.58°N, 90.52°W, magnitude of 0.713°/My; and uncertainties σ_{max}, 4.4°; σ_{min}, 2.2°; azimuth, −7.4° (cw from N), and σ_ω, 0.03°/My.
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31. Supported by NASA's Geodynamics program and NSF's Small Grants for Exploratory Research program. We thank the Instituto Geografico Militar, Bolivia, the Instituto Geofisico del Peru, and University Navstar Consortium (especially J. Richardson, B. Baker, and K. Feaux) for invaluable assistance in GPS campaigns; J. Lee and V. Berhow for assistance with site selection; S. Wdowinski, R. Russo, C. DeMets, and R. McCaffrey for helpful discussions; and the international geodetic community for maintaining a permanent GPS network with publicly available data.

3 October 1997; accepted 26 November 1997

A Search for Endogenous Amino Acids in Martian Meteorite ALH84001

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Trace amounts of glycine, serine, and alanine were detected in the carbonate component of the martian meteorite ALH84001 by high-performance liquid chromatography. The detected amino acids were not uniformly distributed in the carbonate component and ranged in concentration from 0.1 to 7 parts per million. Although the detected alanine consists primarily of the L enantiomer, low concentrations (<0.1 parts per million) of endogenous D-alanine may be present in the ALH84001 carbonates. The amino acids present in this sample of ALH84001 appear to be terrestrial in origin and similar to those in Allan Hills ice, although the possibility cannot be ruled out that minute amounts of some amino acids such as D-alanine are preserved in the meteorite.

The report by McKay *et al.* (*1*) that the martian meteorite ALH84001 contains evidence of biological processes on Mars remains controversial. Of central importance is whether ALH84001 contains endogenous organic compounds, and if so, whether these compounds are biological or abiotic in origin. The bulk meteorite is reported to contain 100 to 200 parts per million (ppm) of combustible carbon (*2*), supposedly derived from organic compounds. So far, however, the only specific compounds that have been reported are parts per million amounts of polycyclic aromatic hydrocarbons (PAHs) detected in the carbonate globule component of the meteorite (*1*). Another martian meteorite collected in the Antarc-

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tic, EETA79001, also contains combustible carbon (*3*), but analyses of the amino acids in this meteorite indicated that this organic carbon is terrestrial contamination derived from Antarctic ice meltwater (*4*). Because EETA79001 contains a similar suite of PAHs as ALH84001 (*5*), it is possible that the PAHs in ALH84001 are terrestrial contaminants as well.

In any investigation of organic compounds possibly derived from life on Mars, it is important to focus on compounds that play an essential role in biochemistry as we know it and that have properties such as chirality (handedness) which can be used to distinguish between biotic versus abiotic origins (*6*). Amino acids are one of the few compound classes that fulfill these requirements. Amino acids are the building blocks of proteins and enzymes that are integral components of terrestrial biology. In addition, only L amino acids (the L enantiomers) are incorporated into proteins during biosynthesis. The structural principles on which biomacromolecular activity is based suggest that any functional biochemistry must use a single enantiomer of any molecule that has a chiral carbon. Because there are no apparent biochemical reasons why L amino acids should be selected over D amino acids, it is generally assumed that life elsewhere could be based on either L or D amino acids, but not both (*6*). In contrast to the L amino acids associated with terrestrial biology, all known laboratory abiotic synthetic processes result in racemic mixtures of amino acids, and the amino acids in carbonaceous chondrites are nearly racemic when terrestrial contamination is absent (*7*). In contrast to amino acids, PAHs have no known role in biochemistry on Earth, although they can be produced from the combustion or long-term diagenesis of biologically derived organic compounds such as sterols and triterpenes (*8*). PAHs also appear to be widespread throughout the universe (*9*). The molecular architecture of PAHs, with the possible exception of their stable isotope composition, cannot be used to determine whether they are terrestrial or extraterrestrial in origin.

We investigated the abundances of amino acids, as well as their enantiomeric composition, in ALH84001 using high-performance liquid chromatography (HPLC) with fluorescent detection (*10*) carried out at the limits of sensitivity of the method (detection limit $\sim 10^{-15}$ mol). Three separate chunks of an ALH84001 sample (*11*) were crushed into a coarse powder that was split into two separate portions of 485 and 463 mg. These crushed samples were then carried through a procedure designed to investigate amino acids in the free and bound state in the carbonate components of the meteorite, as well as the total amino acids present in the noncarbonate fraction (*12*). As controls, 500 mg of crushed serpentine (a hydrated magnesium silicate) that had been heated at 500°C for 3 hours and 133 mg of a crushed sample of the Antarctic lunar meteorite MAC88105 (split 139, parent 2) were carried through the same processing procedure. To demonstrate that the processing procedure we used did recover amino acids from meteorites, we also investigated a 100-mg crushed portion of the Murchison carbonaceous chondrite using the same procedure.

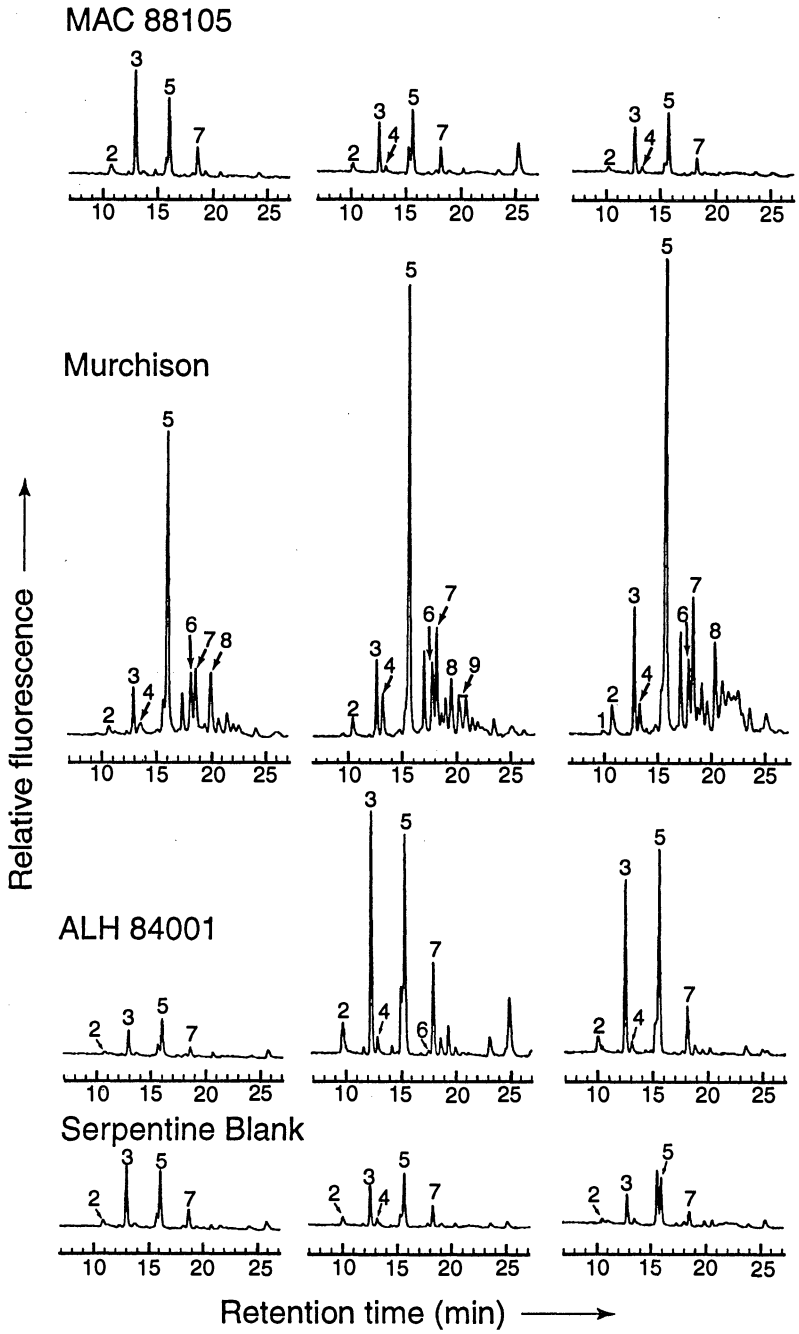

Fig. 1. The 7- to 27-min region (no peaks were observed outside this time period) of the HPLC chromatograms. OPA/NAC derivatization of amino acids in the 1 M HCl–soluble, unhydrolyzed fraction (extract A, left), the HCl-soluble, HCl-hydrolyzed fraction (extract B, middle), and the 1 M HCl–insoluble, HCl-hydrolyzed (extract C, right) from the Antarctic lunar meteorite MAC88105, the Murchison meteorite, the martian meteorite ALH84001, and the serpentine blank. Peaks were identified by comparison of the retention times with those of an amino acid standard run at the same time (representative chromatograms of standards are available on request). The peak identifications are as follows: 1, D-aspartic acid; 2, L-aspartic acid; 3, DL-serine; 4, DL-glutamic acid; 5, glycine; 6, D-alanine; 7, L-alanine; 8, AIB; and 9, DL-isovaline.

The HPLC chromatogram obtained for MAC88105 (Fig. 1) shows that the peak areas are close to those in the serpentine blank, but trace amounts of glycine (~0.1 ppm), DL-serine (~0.2 ppm), and L-alanine (~0.1 ppm) were detected in the 1 M HCl–soluble, unhydrolyzed fraction (extract A, which accounts for ~20% of the total weight of the sample). No detectable amino acids (<10 to 20 ppb) above blank levels were found in the other MAC88105 extracts. The amino acids in the 1 M HCl–soluble, unhydrolyzed fraction of MAC88105 are terrestrial contaminants because only L-alanine was detected and because lunar soils have been found to contain <10 ppb of glycine along with lesser amounts of aspartic and glutamic acids, serine, and alanine (*13*). The Murchison sample yielded amino acids in each of the three extracts (Fig. 1). The predominant amino acids were found to be aspartic and glutamic acids, glycine, alanine, α-aminoisobutyric acid (AIB), and isovaline, which is consistent with the major amino acids previously detected in Murchison (*14*). The combined amount of the major detected amino acids in all three fractions was ~10 ppm, which is about half of what we found when we processed our Murchison sample using the standard 100°C water extraction method (*7*, *14*). This suggests that some of the Murchison amino acids were destroyed by the acid extraction procedure. The D/L ratios for alanine and isovaline in our Murchison extracts were found to be close to the racemic value of 1.0 (after correction with a racemic standard), which is consistent with the D/L ratios for these amino acids reported in uncontaminated samples of Murchison (*7*). However, the D/L aspartic acid ratio is significantly less than 1, which indicates that terrestrial contamination has affected some of the amino acids in this Murchison sample.

Analyses of ALH84001 (Fig. 1 and Table 1) reveal that there are essentially no amino acids detectable above blank levels in the 1 M HCl–soluble, unhydrolyzed fraction (extract A), which indicates that there are no free amino acids present in this sample. However, there are parts per million amounts of amino acids in the 1 M HCl–soluble, hydrolyzed fraction (extract B), although the two separate samples gave different values, suggesting that the amino acids in this component are not homogeneously distributed. This variability in amino acid distribution is consistent with the heterogeneous chemical and isotopic compositions previously reported in the ALH84001 carbonates (*15*). The HCl-soluble, hydrolyzed component should represent bound amino acids present in the carbonates in the meteorite, although some other mineral phases such as apatite could have also dissolved during the 1 M HCl treatment. Trace (parts per billion) levels of amino acids were also detected in the 1 M HCl–insoluble, hydrolyzed component (extract C), but these amino acids may still have been derived from carbonates that did not totally dissolve during the 1 M HCl, room-temperature digestion. The detected amino acids consist primarily of glycine, serine, and alanine, with traces of aspartic and glutamic acids. Some other minor peaks that are not present in the serpentine blank are present in the chromatograms of ALH84001. One of these peaks, which is also present in MAC88105 extract B, has a retention time (~25 min) similar to methylamine (Fig. 1). However, when the extracts were spiked with a methylamine standard, separate peaks were observed, which indicates that this peak is not methylamine. No AIB above blank levels was found in any extract from ALH84001 (Table 1). For aspartic acid, only the L enantiomer was detected, although any trace amounts of D-aspartic acid that might be present would have been below the detection limit. For alanine, trace amounts of D-alanine appear to be present in the 1 M HCl–soluble and –insoluble hydrolyzed extracts, especially in the sample with the lower overall amino acid content (for example, sample 2). The calculated D/L alanine ratios are in the range ~0.05 to ~0.4. However, because the small peaks with a retention time characteristic of D-alanine could be chromatography artifacts, these D/L alanine values must be considered uncertain and are upper limits (*16*). The D-alanine content of the bulk meteorite (amount in extracts B and C divided by the amount of meteorite analyzed) is estimated to be <0.01 ppm.

The suite of amino acids (for example, glycine, serine, and L-alanine) detected in ALH84001 is, in general, similar to those detected in another Antarctic martian meteorite, EETA79001, and is also similar to the amino acid distribution in Allan Hills ice (Table 1). Although the absolute concentrations are different in ALH84001, EETA79001, and Allan Hills ice, the relative amino acid compositions are about the same. The hydrolyzed carbonate fraction (extract B) of ALH84001 sample 2 and the hydrolyzed carbonate component of EETA79001 have similar amino acid contents, whereas amino acids in the hydrolyzed carbonate fraction of ALH84001 sample 1 are more abundant. In the case of EETA79001, the amino acids were suggested to be derived from ice meltwater that percolated through the meteorite sometime during its residence in Antarctic ice (*4*). Alteration of the trace elemental compositions of several Antarctic eucrite meteorites (including several from the Allan Hills region) has also been attributed to a similar ice meltwater weathering process (*17*). Exposure to meltwater could take place either at the ice surface (*18*) or near the ice-bedrock interface where meltwater in some

Table 1. Summary of the average blank-corrected amino acid concentrations in the various extracts of two samples (listed as no. 1 and no. 2) of ALH84001, in the carbonate and bulk matrix of EETA79001 (*4*), and in Allan Hills ice (*4*). The results obtained for serpentine carried through the same procedures were used to make blank corrections for ALH84001. Peaks corresponding to the retention times of aspartic and glutamic acids were also observed in some of the ALH84001 extracts, but these were too small in comparison with the blanks for accurate quantitation. All analyses used derivatization times of 1 min except where indicated (*10*). Extract A: 1 M HCl–soluble, unhydrolyzed. Extract B: 1 M HCl–soluble, HCl hydrolyzed. Extract C: 1 M HCl–insoluble, HCl hydrolyzed. The uncertainties of the measurements are about ±0.02 ppm for ALH84001 extracts A and B; ±1 ppb for ALH84001 extract C; ±5 ppb for the EETA79001 carbonate fraction and bulk matrix; and ±0.001 ppb for the Allan Hills ice.

Sample (size)	DL-Serine	Glycine	D-Alanine	L-Alanine	AIB
			ALH84001		
Extract A					
No. 1 (2.4 mg)	<0.2 ppm	<0.1 ppm	<0.2 ppm	<0.2 ppm	<0.2 ppm*
No. 2 (3.6 mg)	<0.2 ppm	<0.1 ppm	<0.2 ppm	0.2 ppm	<0.5 ppm
Extract B					
No. 1 (7.0 mg)	7.1 ppm	4.8 ppm	<0.1 ppm	2.1 ppm	<0.1 ppm*
No. 2 (8.9 mg)	0.2 ppm	0.7 ppm	0.06 ppm	0.14 ppm	<0.2 ppm
Extract C					
No. 1 (484 mg)	14 ppb	50 ppb	<1 ppb	10 ppb	<1 ppb*
No. 2 (461 mg)	49 ppb	35 ppb	4 ppb	12 ppb	<4 ppb
			EETA79001		
Carbonate fraction†	198 ppb	170 ppb	10 ppb	214 ppb	<1 ppb
Bulk matrix‡	173 ppb	54 ppb	23 ppb	94 ppb	<1 ppb
			Allan Hills ice		
Residue§	0.26 ppb	0.26 ppb	0.012 ppb	0.096 ppb	<0.002 ppb

*Derivatization for 15 min. †HCl-soluble, HCl-hydrolyzed extract. ‡Lithology A, HCl hydrolyzed. §Residue remaining after meltwater evaporation: HCl hydrolyzed.

cases is extensive enough to form large subsurface lakes (*19*). The input from melting ice of nutrients, organic compounds, and viable organisms into meltwater pools or puddles may give rise to a range of diverse biological activities (*19*), which could play a role in the contamination of meteorites with terrestrial organic components.

The exact mechanism of terrestrial amino acid incorporation and retention by the meteorites is not known. We have found that in experiments where a sample of an amino acid standard was repeatedly passed through a small column containing $CaCO_3$ (1-μm grains), ~50% by weight of the amino acids originally present in solution were adsorbed by the carbonate after only 10 passes (this is equivalent to a water/mineral ratio of 14). Once adsorbed to the carbonate, the amino acids could only be liberated by dissolution and hydrolysis in 6 M HCl, a procedure similar to the one we used to obtain extract B from ALH84001. In similar experiments with magnetite, pyrite, carbonate grains, quartz, plagioclase, apatite serpentine, a mixture of clay minerals, and humic acid, amino acids were scavenged to a lesser extent. Thus, the periodic exposure of the meteorites to ice meltwater could result in the irreversible uptake of amino acids mainly by the carbonate mineral components. This contamination model is consistent with the distribution of amino acids we have found in the carbonate versus noncarbonate components of EETA79001 and ALH84001 (Table 1). Because the carbonate fractions of ALH84001 samples 1 and 2 contain different amounts of amino acid contamination, some carbonate components have apparently been more affected than others. This varying amount of contamination may be related to carbonate globule size and the extent of microfracturing (*20*).

To what extent this ice meltwater contamination process would affect other trace organic components such as PAHs is unknown. However, radiocarbon measurements (*21*) of EETA79001 and ALH84001 indicate that the bulk organic carbon, of which amino acids and PAHs contribute only a few percent or less, is terrestrial in origin. These radiocarbon studies coupled with the amino acid results presented here indicate that major and minor organic constituents in these martian meteorites are contaminants.

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7. In 1970 the Murchison meteorite was reported to contain endogenous amino acids based on the observation that amino acids having a chiral C were racemic (D/L ratio = 1.0) within the limits of the measurements [K. Kvenvolden *et al.*, *Nature* **228**, 923 (1970); K. Kvenvolden, J. G. Lawless, C. Ponnamperuma, *Proc. Natl. Acad. Sci. U.S.A.* **68**, 486 (1971); G. E. Pollack, C. Cheng, K. A. Kvenvolden, *Geochim. Cosmochim. Acta* **39**, 1571 (1975)]. Subsequent analyses of Murchison indicated that some protein amino acids showed an apparent enrichment in the L enantiomers, but this was considered to be the result of terrestrial contamination rather than from some sort of abiotic enantiomeric resolution or enrichment process [M. H. Engel and B. Nagy, *Nature* **296**, 837 (1982); J. L. Bada *et al.*, *ibid.* **301**, 494 (1983)]. Recently, J. R. Cronin and S. Pizzarello [*Science* **275**, 951 (1997)] found small L enantiomeric excesses (5 to 10%) in Murchison nonprotein amino acids not associated with terrestrial biochemistry. In general, whether the exclusive use of L amino acids in terrestrial biology was preordained or simply a matter of chance selection is still a matter of debate.
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10. In the analytical method used, amino acids were derivatized by OPA/NAC (*o*-phthaldialdehyde/*N*-acetyl L-cysteine, both obtained from Fisher). The derivatives were separated by reversed-phase HPLC with fluorescence detection and identified by comparison of retention times with standards [M. Zhao and J. L. Bada, *Nature* **339**, 463 (1989); *J. Chromatogr.* **A690**, 55 (1995); G. D. McDonald and J. L. Bada, *Geochim. Cosmochim. Acta* **59**, 1179 (1995); K. L. F. Brinton and J. L. Bada, *ibid.* **60**, 349 (1996); K. L. F. Brinton *et al.*, *Origins Life Evol. Biosphere*, in press]. The reaction of α-dialkyl amino acids such as α-aminoisobutyric acid (AIB) with the OPA/NAC reagent requires longer to reach completion. Thus, we carried out derivatizations for 1 and 15 min to provide an additional way to confirm the presence of these amino acids.
11. The pieces were from split 251, parent 65 (for the sampling diagram, see http://www-curator.jsc.nasa.gov/curator/antmet/marsmets/SampleSummary.htm). These pieces were selected by the meteorite curator at the Johnson Space Center (M. Lindstrom) for this study because they were enriched in carbonate globules. Before analysis, we inspected each piece with a microscope and found that they contained numerous pale amber colored, dark rimmed globules similar in appearance to the photograph of ALH84001 carbonate concretions published by J. W. Valley *et al.* [*Science* **275**, 1633 (1997)]. The combined weights of the 1 M HCl–soluble residues [extracts A and B described in (*12*)] indicate that carbonates make up about 1 to 2% by weight of the bulk meteorite in our ALH84001 sample, which is in agreement with the carbonate amounts reported by others [for example, see D. W. Mittlefehldt, *Meteoritics* **29**, 214 (1994), and A. H. Treiman, *ibid.* **30**, 294 (1995)].
12. All glassware and tools used were annealed overnight at 500°C. The vial received from the Antarctic Meteorite Laboratory curator containing the allocated sample of ALH84001 (consisting of nine separate chunks) was opened in a positive pressure (1-μm filtered air) clean room. Individual fragments were crushed in a mortar and pestle, and the crushed material was split into two samples and transferred into preweighed test tubes and weighed again. To remove surface contaminants, we rinsed the samples with double-distilled H_2O at room temperature. The H_2O was removed (analyses indicated that there were no significant amino acid levels above blanks), then 1 ml of 1 M HCl (double distilled) was added and the sample left at room temperature overnight. The next day, the sample was centrifuged, and one-third of the 1 M HCl supernatant was placed in a tube, dried under vacuum, weighed, and desalted with Bio-Rad AG50W-X8 cation exchange resin before amino acid analysis to determine free amino acids (this is extract A). The remaining two-thirds of the supernatant was placed in another tube, dried under vacuum, weighed, and then subjected to vapor-phase HCl hydrolysis at 150°C for 3 hours [A. Tsugita *et al.*, *J. Biochem.* **102**, 1593 (1987); R. G. Keil and D. L. Kirchman, *Mar. Chem.* **33**, 243 (1991)]. The sample was then dried under vacuum and desalted for amino acid analysis to determine bound amino acids (this is extract B). The undissolved residue from the 1 M HCl extraction was dried, weighed again, and subjected to vapor-phase HCl hydrolysis as described above. After removal of HCl under vacuum, the sample was extracted with 1 ml of water, and both supernatant and residue were dried and weighed. The water extract was then desalted and analyzed to determine amino acids not associated with carbonate in the original sample (this is extract C). All the final desalted residues from each of the extracts were suspended in 50 μl and analyzed by the HPLC OPA/NAC method described in (*10*). A diagram of the processing procedure will be provided on request.
13. K. L. F. Brinton and J. L. Bada, *Geochim. Cosmochim. Acta* **60**, 349 (1996). The D/L ratios of aspartic acid and alanine indicate that even in pristine lunar soils, some of the detected amino acids are terrestrial contaminants. In addition, the detected endogenous amino acids in lunar soils are apparently not actually present in the soil itself, but are generated from a soil component (HCN?) during sample processing.
14. K. Kvenvolden *et al.*, *Nature* **228**, 923 (1970); K. Kvenvolden, J. G. Lawless, C. Ponnamperuma, *Proc. Natl. Acad. Sci. U.S.A.* **68**, 486 (1971); J. R. Cronin and S. Pizzarello, *Adv. Space Res.* **3**, 5 (1983).
15. For example, see E. R. D. Scott, A. Yamaguchi, A. N. Krot, *Nature* **387**, 377 (1997) and references therein.
16. Because the total amount of D-alanine detected in the extracts was only around 10^{-12} mol or less, we were unable to confirm peak identification using HPLC and mass spectrometry.
17. D. W. Mittlefehldt and M. M. Linstrom, *Geochim. Cosmochim. Acta* **55**, 77 (1991).
18. E. K. Gibson Jr. and F. F. Andrawes, *Proc. Lunar Planet. Sci. Conf.* **12** 1223 (1980).
19. G. K. A. Oswald and G. de Q. Robin, *Nature* **245**, 251 (1973); J. C. Ellis Evans and D. Wynn-Williams, *ibid.* **381**, 644 (1996); A. P. Kapitsa *et al.*, *ibid.*, p. 684.
20. Radiocarbon and stable C isotopic measurements have shown that ALH84001 carbonates, especially those in the size range <250 μm, have experienced various amounts of terrestrial alteration [A. J. T. Jull, C. J. Eastoe, S. Cloudt, *J. Geophys. Res.* **102**, 1663 (1997)].
21. A. J. T. Jull *et al.*, *Science* **279**, 366 (1997).

22. We thank the Meteorite Steering Group in association with NSF, NASA, and the Smithsonian Institution, as well as the meteorite curator M. Lindstrom at the NASA Johnson Space Center, for providing the samples. We thank K. Kvenvolden and H. Craig for providing the Murchison and Allan Hills ice samples, K. Brinton for helpful discussions, and J. Higbee for encouragement. Collection of the Allan Hills ice samples was supported by NSF Polar Programs grant DPP91-18494 to H. Craig. Supported by grants from the NASA Ancient Martian Meteorite Research Program and the NASA Specialized Center for Research and Training in Exobiology at University of California at San Diego.

30 September 1997; accepted 15 December 1997