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8. We have invented and examined a series of metal porphyrin catalysts that effect overall $4e^-$, $4H^+$ reduction of O_2 to 2 H_2O when adsorbed onto an EPG electrode (*9, 10*). Indirect evidence suggests that there is an essential association between the metal and an uncharacterized ligand derived from the EPG electrode (*11*). Hitherto, none of these oxygen electrode catalysts have contained an intramolecular axial ligand or an electroactive Cu ion. Furthermore, electrocatalytic $4e^-$ reduction of O_2 by these synthetic compounds has been limited to a pH below 3.5 and occurred at a limiting potential close to that connecting O_2 with H_2O_2 at those pH values.
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13. The previously reported compound **1** (*12*) has been characterized by elemental analysis, ^1H and ^{13}C nuclear magnetic resonace (NMR) spectroscopy, and mass spectrometry (MS). Complex **2** was prepared in two steps; both the metallated intermediate and **2** were shown to be homogeneous by TLC and were characterized by MS. Several examples of this capping reaction were reported in earlier work (*8*). The formation of **3** by a Michael addition and rotation has been modeled for the metal-free analog and characterized by TLC, MS, and ^1H NMR. Metallated complexes **3** and **4** were found to be homogeneous by TLC and have been characterized by MS. The quantitative titration of O_2, converting **4** to **5**, and the quantitative $4e^-$ reduction of **5** to **4** are described in the text, as is the characterization of the bridged peroxide **5**. Addition of more O_2 does not affect **5**, nor does the addition of more Cp_2Co affect **4**.
14. The technique of rotating ring-disk voltammetry permits the quantitative measurement of (unwanted) H_2O_2 production and allows discrimination between the formation of free H_2O_2 as an intermediate or merely as a minor side product. The ring-disk electrode assembly consists of a pyrolytic graphite disk inside a concentric Pt ring. The porphyrin to be tested as a reduction catalyst is applied to the graphite disk by irreversible adsorption. As the assembly is rotated, fresh O_2-saturated electrolyte is drawn vertically toward the disk surface and ejected radially across the disk and ring. The disk potential is controlled by a potentiostat, and the disk current-potential profile records the O_2 reduction process. At the same time, the ring is held at a potential where any H_2O_2 reaching it is rapidly oxidized to O_2. The ring current response thus monitors H_2O_2 production; and the ratio of disk to ring current, normalized for the collection efficiency, defines the relative contributions of the $4e^-$ and $2e^-$ reduction processes.
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16. Our preliminary cyclic voltammetric results with this Cu-Co–imidazole system in tetrahydrofuran under N_2 show two reversible redox couples: Cu(I)-(II) and Co(II)-(III) at a potential $E_{1/2}$ = 0.26 V and 0.6 V versus NHE, respectively. The presence of O_2 should shift both potentials to higher values. Our electrocatalytic reduction of O_2 begins at ~0.3 V versus NHE.

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Enantiomeric Excesses in Meteoritic Amino Acids

John R. Cronin and Sandra Pizzarello

Gas chromatographic–mass spectral analyses of the four stereoisomers of 2-amino-2,3-dimethylpentanoic acid (DL-α-methylisoleucine and DL-α-methylalloisoleucine) obtained from the Murchison meteorite show that the L enantiomer occurs in excess (7.0 and 9.1%, respectively) in both of the enantiomeric pairs. Similar results were obtained for two other α-methyl amino acids, isovaline and α-methylnorvaline, although the α hydrogen analogs of these amino acids, α-amino-*n*-butyric acid and norvaline, were found to be racemates. With the exception of α-amino-*n*-butyric acid, these amino acids are either unknown or of limited occurrence in the biosphere. Because carbonaceous chondrites formed 4.5 billion years ago, the results are indicative of an asymmetric influence on organic chemical evolution before the origin of life.

The origin of homochirality, that is, the almost exclusive one-handedness of the chiral molecules found in terrestrial organisms, is a key problem of the origin of life. Both biotic and abiotic theories of homochirality have been proposed (*1*). According to the former, life was initially based on achiral molecules or racemates, and the use of specific enantiomers came about through evolution. In the latter, a tendency toward homochirality is presumed to have been inherent in chemical evolution, and thus the asymmetry preceded the origin of life.

Meteorites, specifically the carbonaceous chondrites, carry a record of the organic chemical evolution of the early solar system (*2*). It is reasonable to suppose that if some asymmetric process influenced the formation or degradation of organic compounds in the parent molecular cloud, the solar nebula, or the prebiotic solar system, then enantiomeric excesses would have resulted and might still be observable in the organic compounds of carbonaceous chondrites. Evidence for such an effect has been sought in the form of net optical rotation by meteorite extracts (*3*), as well as by directly measuring enantiomer ratios of specific chiral compounds (*4–6*). The results have been either negative or unconvincing, the latter largely because of the suspicion of terrestrial contamination when small excesses of the L enantiomers have been reported in meteoritic amino acids that are also common in the biosphere (*7*). Collectively, these results have given rise to the widely held view that the chiral compounds of meteorites occur as racemic mixtures. In contrast, we report here the detection of enantiomeric excesses in four amino acids indigenous to the Murchison meteorite.

We initially targeted for study 2-amino-2,3-dimethylpentanoic acid (2-a-2,3-dmpa), an amino acid with two chiral centers and, consequently, four stereoisomers (8) (Fig. 1). This amino acid meets two important criteria: (i) It is present in the Murchison meteorite (9) but has not been reported to occur in terrestrial matter, and (ii) its two chiral centers are resistant to epimerization because one (C-2) lacks a hydrogen atom and the other (C-3) has a methine hydrogen atom of low acidity. Consequently, it is likely that the chiral centers retained their original configurations through the aqueous and mild thermal processing experienced by the meteorite parent body (*10*) and that the original enantiomer ratios have not been compromised by contamination.

We synthesized 2-a-2,3-dmpa in the laboratory as a mixture of the four stereoisomers (9) and analyzed them individually by gas chromatography–mass spectrometry (GC-MS) of their *N*-fluoroacyl isopropyl esters on Chirasil-L-Val and Chirasil-D-Val capillary columns. The four stereoisomers are well resolved on both phases (Fig. 2), although this requires the use of *N*-pentafluoropropionyl (PFP) isopropyl esters with the L phase and *N*-trifluoroacetyl (TFA) isopropyl esters with the D phase. The two diastereomeric pairs were separated on Chirasil-L-Val but overlap

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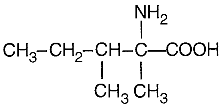
on Chirasil-D-Val. The absolute configuration of the stereoisomer giving rise to each chromatographic peak was unambiguously determined (*11*).

We extracted the amino acids with water from powdered samples of the Murchison meteorite. Extracts from two samples were prepared, and one was subjected to acid hydrolysis (6 N HCl, 110°C, 24 hours). The samples were each concentrated and applied to a cation exchange column (AG-50W, H^+), and after elution of the acidic and neutral components with water, the amino acids were obtained by elution with 2 M NH_4OH (*12*). We then obtained a fraction containing the four 2-a-2,3-dmpa stereoisomers by chromatography on a C_{18} reverse-phase column (Supelcosil LC-18) using a procedure that achieves group separation of amino acids by carbon number and separates most of the isomeric C_7 α-amino acids from each other (*9*). The eluate was collected in fractions, and those containing 2-a-2,3-dmpa were combined, readsorbed on AG-50W, and eluted as before to remove buffer ions. This preparation was dried, derivatized, and analyzed by GC-MS as described for the standard.



$$CH_3{-}CH_2{-}\underset{CH_3}{\underset{|}{CH}}{-}\overset{NH_2}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}COOH$$

Fig. 1. Structure of 2-a-2,3-dmpa. This amino acid has two chiral centers and, consequently, four stereoisomers: the D and L forms of α-methylisoleucine and α-methylalloisoleucine.

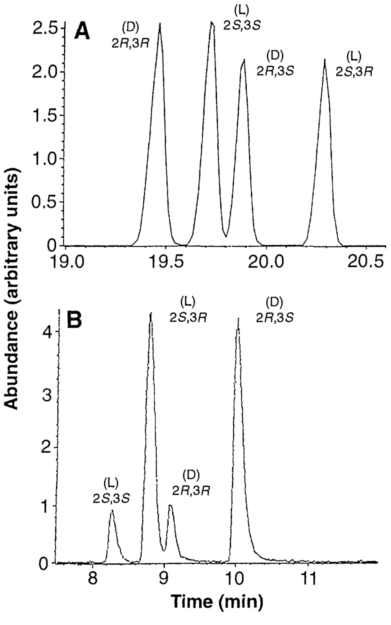


Fig. 2. (**A**) Single-ion chromatogram (*m/z* = 246, M-87) of synthesized 2-a-2,3-dmpa stereoisomers run as *N*-PFP isopropyl esters on Chirasil-L-Val. (**B**) Single-ion chromatogram (*m/z* = 196, M-87) of synthesized 2-a-2,3-dmpa stereoisomers run as *N*-TFA isopropyl esters on Chirasil-D-Val. This standard was recrystallized more extensively than that used in (A) and consequently was depleted in the 2*S*,3*S* and 2*R*,3*R* diastereomers.

The GC-MS results obtained for the meteoritic 2-a-2,3-dmpa on both Chirasil-L-Val– and Chirasil-D-Val–coated columns (Fig. 3) show that the intensities of the peaks corresponding to the L enantiomers of both diastereomers [that is, (2*S*,3*S*)- and (2*S*,3*R*)-2-a-2,3-dmpa], are greater than those of the D enantiomers. Similar chromatograms were obtained with all of the major characteristic fragment ions: M-87, M-98, M-116, and M-200 for TFA and M-250 for PFP. We calculated mean L-enantiomer percentages and standard deviations (1σ) on the basis of the integrated peak areas (Table 1). The significance of the difference between the means of the meteorite and standard L-enantiomer percents was evaluated with the use of Student's *t* test for independent means (*13*). In each case, the meteorite's value was found to be significantly greater than that of the standard. The deviations from 50% L enantiomer observed for the standard were assumed to represent systematic error, and the means of the meteorite analyses were corrected accordingly. The averaged values for the corrected L-enantiomeric excesses are 7.0 ± 0.8 (2*S*,3*S*) and 9.1 ± 1.1 (2*S*,3*R*).

Several possible sources of error must be ruled out before the observed L enantiomeric excesses can be attributed to indigenous 2-a-2,3-dmpa. First, the possibility that some unanticipated asymmetric effect could have caused a partial loss of the D enantiomers during extraction or isolation was ruled out by a control experiment in which a racemic 2-a-2,3-dmpa standard solution was added back to the pre-extracted Murchison powder, dried, extracted, and analyzed as before. The results (Table 1) do not show significant enantiomeric excesses. The possibility that a bias in favor of the L enantiomers is inherent in the analytical method is eliminated by these results. The fact that 2-a-2,3-dmpa standards run concurrently with the meteorite analyses consistently gave results within 1% of the expected racemic condition validates the GC-MS analysis.

Contamination of the 2-a-2,3-dmpa by a terrestrial source of the L enantiomers seems improbable. A search of *Chemical Abstracts* failed to produce a report of the natural occurrence of 2-a-2,3-dmpa other than that in the Murchison meteorite (*9*). Moreover, the occurrence of both an L amino acid and the L enantiomer of its diastereomer would be unprecedented. For example, α-epimerization of L-isoleucine during protein diagenesis gives rise to D-alloisoleucine, but L-alloisoleucine has only been found in trace amounts, in million-year-old fossil shells (*14*).

The most likely possibility for analytical artifact is the persistent coelution of other compounds with the two L enantiomers of 2-a-2,3-dmpa. Organic compounds isolated from carbonaceous chondrites comprise mixtures of total structural diversity: for example, all 14 of the β-, γ-, and δ-amino alkanoic acids through C_5 (*15*) and all 33 of the α-ami-

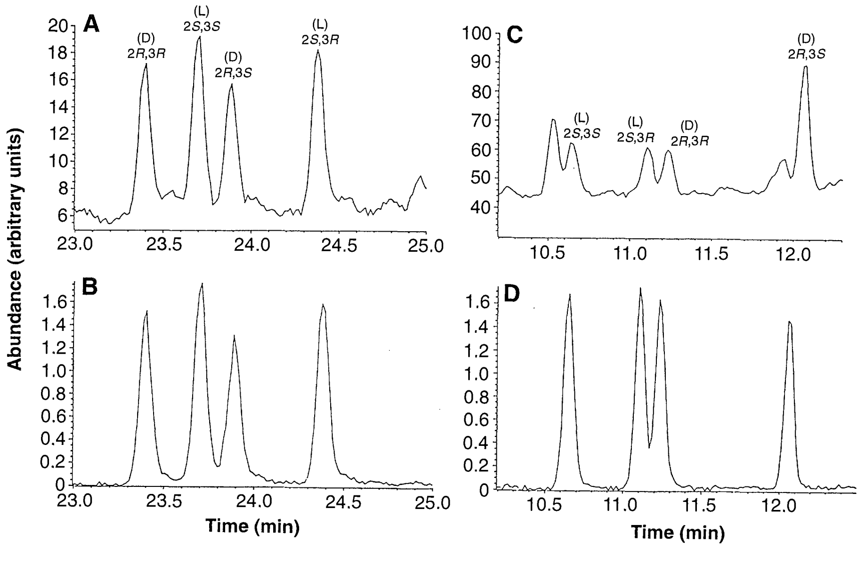


Fig. 3. (**A**) Total-ion chromatogram of 2-a-2,3-dmpa stereoisomers from the Murchison meteorite run as *N*-PFP isopropyl esters on Chirasil-L-Val. (**B**) Single-ion chromatogram (*m/z* = 246, M-87) of that in (A). (**C**) Total-ion chromatogram of 2-a-2,3-dmpa stereoisomers from the Murchison meteorite run as *N*-TFA isopropyl esters on Chirasil-D-Val. The 2*R*,3*S* stereoisomer coelutes with an unknown substance (base peak *m/z* = 204). (**D**) Single-ion chromatogram (*m/z* = 196, M-87) of that in (C).

no alkanoic acids through C_7 (9) are present in the Murchison meteorite. Such structural diversity makes coelution a significant possibility that must be rigorously excluded; however, the range of potential interfering substances can be narrowed to (i) those compounds that elute with 2-a-2,3-dmpa from both the ion exchange and reverse-phase chromatographic steps used before GC-MS analysis and (ii) those that contribute to the four major mass spectral fragment ions used for calculation of the L enantiomer excesses. We considered the most likely possibilities to be other C_7 amino acid isomers, such as (i) another open-chain C_7 α-amino acid (16, including diastereomeric forms), (ii) an *N*-methyl C_6 α-amino acid, (iii) an amino position isomer, that is, one of the C_7 β- through ζ-amino acids (90, including diastereomeric forms), and (iv) a nonisomeric C_5- or C_6-ring–containing C_7 amino acid.

Coelution of another open-chain C_7 α-amino acid was ruled out on the basis of the C_{18} reverse-phase chromatographic step used in obtaining 2-a-2,3-dmpa for analysis. All of the other open-chain C_7 α-amino acids were shown to be separated from 2-a-2,3-dmpa by this procedure. The C_7 α-amino acids eluting from the C_{18} column immediately before and after 2-a-2,3-dmpa were shown to be separated from its four stereoisomers by Chirasil-Val GC, thus assuring that imperfect fraction collection would not add coeluting isomers.

Sarcosine (*N*-methyl glycine) and *N*-methyl alanine have been found in Murchison extracts (*5*), and the presence of higher *N*-methyl amino acids is expected. Mass spectra of *N*-TFA-*N*-methyl amino acid esters show a characteristic fragment ion at mass-charge ratio $m/z = 110$ (*16*), and we have observed the corresponding ion ($m/z = 160$) in mass spectra of the corresponding *N*-PFP derivatives. The presence of both ions in the respective mass spectra of a fluoroacylated *N*-methyl C_6 amino acid ester was confirmed with *N*-methyl leucine. Fragment ion searches at these mass numbers across the 2-a-2,3-dmpa L-enantiomer peaks were negative.

Having excluded the open-chain C_7 and *N*-methyl C_6 α-amino isomers of 2-a-2,3-dmpa as interferences, it is necessary to consider the numerous C_7 amino-position isomers. Although standards of these amino acids are not available, an earlier systematic study of the mass spectral fragmentation of the C_5 β-, γ-, and δ-amino acids (*17*) provides a basis for predicting the major mass spectral fragment ions of the C_7 β- through ζ-amino acids. A search for these fragment ions gave negative results.

Finally, the structurally similar cyclic amino acids must be considered as possible contaminants. The mass spectra of *N*-TFA proline esters are relatively simple and are dominated by the cyclic iminium ion resulting from loss of the esterified carboxyl group (*18*). The molecular ion and the fragment ion resulting from loss of the trifluoroacetyl group are also apparent. The corresponding ions (M-87, M^+, and M-97 or M-147 for PFP derivatives) for *N*-TFA isopropyl esters of cyclic C_7 amino acids (ethyl or dimethyl five- or methyl six-membered rings) have masses different from those we used to calculate peak areas and are, in any case, absent from the mass spectra of the meteoritic 2-a-2,3-dmpa stereoisomers.

We sought evidence for coeluting compounds in both the raw GC-MS data and in difference spectra obtained by subtracting the summed mass spectra of the D-enantiomer peaks from those of the L-enantiomer peaks, an operation that would enrich the resulting difference mass spectra in contributions from any compounds coeluting with the L enantiomers. On the basis of these analyses, we conclude that the L enantiomeric excesses observed in both diastereomeric pairs of 2-a-2,3-dmpa are characteristic of this amino acid as it occurs in the Murchison meteorite.

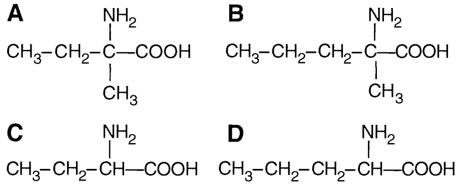
Enantiomeric analyses were extended to four additional amino acids (Fig. 4 and Table 2). The α-methyl amino acids isovaline and α-methylnorvaline showed significant L enantiomer excesses. Contamination again seems unlikely because α-methylnorvaline is unknown in the biosphere and isovaline has a restricted distribution (*19*). Careful searches were made for possible coeluting amino acids,

Table 1. The L (2*S*) enantiomeric excesses (ee) determined for 2-a-2,3-dmpa extracted from the Murchison meteorite. The corrected enantiomeric excesses were calculated as (|L − D|)/(L + D) × 100 = |%L − %D|. Analysis 1: Acid-hydrolyzed meteorite extract; *N*-PFP-^{i}Pr esters (^{i}Pr, isopropyl) run on Chirasil-L-Val. Analysis 2: Unhydrolyzed meteorite extract; *N*-PFP-^{i}Pr esters run on Chirasil-L-Val. Analysis 3: Unhydrolyzed meteorite extract; *N*-TFA-^{i}Pr esters run on Chirasil-D-Val. Analyses 4 and 5 represent the results of control experiments in which the unresolved 2-a-2,3-dmpa standard was added back to the previously extracted Murchison powder and then extracted and analyzed exactly as had been done with the indigenous amino acids. Confidence is based on Student's *t* test (*13*). Not sig., not significant.

Analysis	Sample				Standard				Confidence	Corr. ee (%)
	L (%)	σ	*n*	ee (%)	L (%)	σ	*n*	ee (%)		
				L (2S,3S) entantiomers						
1	52.5	1.9	3	5.0	48.8	1.9	14	−2.4	>95%	7.6
2	52.6	0.5	5	5.2	48.8	1.9	14	−2.4	>99%	7.6
3	51.7	0.4	10	3.4	49.0	1.3	13	−2.0	>99.9%	5.8
4	50.1	0.7	7	0.2	50.6	0.5	18	1.2	Not sig.	−1.0
5	50.3	0.7	16	0.6	50.6	0.5	18	1.2	Not sig.	−0.6
				L (2S,3R) enantiomers						
1	53.9	0.8	3	7.8	50.1	0.8	18	0.2	>99.9%	7.6
2	54.7	0.6	5	9.4	50.1	0.8	18	0.2	>99.9%	9.2
3	54.2	0.4	10	8.4	48.9	1.1	16	−2.2	>99.9%	10.4
4	49.7	0.9	7	−0.6	49.8	0.9	18	−0.4	Not sig.	−0.2
5	49.7	0.9	16	−0.6	49.8	0.9	18	−0.4	Not sig.	−0.2

Table 2. The L (2*S*) enantiomeric excesses determined for α-amino acids extracted from the Murchison meteorite. The corrected enantiomeric excesses were calculated as in Table 1. All analyses were carried out on C_{18} reverse-phase fractions obtained after cation exchange fractionation of the unhydrolyzed meteorite extract; *N*-TFA-^{i}Pr esters were run on Chirasil-L-Val. Confidence is based on Student's *t* test (*13*). Not sig., not significant.

Amino acid	Sample				Standard				Confidence	Corr. ee (%)
	L (%)	σ	*n*	ee (%)	L (%)	σ	*n*	ee (%)		
Isovaline	54.6	0.6	8	9.2	50.4	0.6	15	0.8	>99.9%	8.4
α-Methylnorvaline	51.4	0.4	10	2.8	50.0	0.2	10	0	>99.9%	2.8
α-Amino-*n*-butyric acid	50.4	0.2	3	0.8	50.2	0.2	12	0.4	Not sig.	0.4
Norvaline	50.2	0	3	0.4	50.0	0.2	10	0	Not sig.	0.4



$$CH_3{-}CH_2{-}\overset{NH_2}{\underset{CH_3}{C}}{-}COOH$$

$$CH_3{-}CH_2{-}CH_2{-}\overset{NH_2}{\underset{CH_3}{C}}{-}COOH$$

$$CH_3{-}CH_2{-}\overset{NH_2}{CH}{-}COOH$$

$$CH_3{-}CH_2{-}CH_2{-}\overset{NH_2}{CH}{-}COOH$$

Fig. 4. Four additional amino acids analyzed (Table 2): (**A**) isovaline, (**B**) α-methylnorvaline, (**C**) α-amino-*n*-butyric acid, and (**D**) norvaline. Isovaline and α-methylnorvaline showed enantiometric excesses.

as was done with 2-a-2,3-dmpa. The L excess found for isovaline differs from an earlier finding that this amino acid is racemic in the Murchison meteorite (*6, 20*); however, the previous work was carried out on a complex fraction containing at least 60 components, and the analysis was done by GC using a flame ionization detector, that is, without mass spectral control on the composition of the chromatographic peaks. The unmethylated analogs of these amino acids, that is, α-amino-*n*-butyric acid and norvaline, were found to be racemic. We did not examine the unmethylated analogs of 2-a-2,3-dmpa (isoleucine and alloisoleucine) because of the ubiquitous occurrence of L-isoleucine (2*S*,3*S*) and the possible occurrence of its epimerization product, D-alloisoleucine (2*R*,3*S*). The apparent excesses of these stereoisomers observed in an earlier analysis of the Murchison C_6 α-amino acids were attributed to contamination (*12*).

In view of the resistance of α-methyl amino acids to racemization (*6, 20*), the observed enantiomeric excesses likely represent the original state of these amino acids, whereas the more easily racemized α-H amino acids could have initially existed in nonracemic proportions and racemized during aqueous alteration of the carbonaceous chondrite parent body. On the other hand, it is possible that these two classes of amino acids represent the products of separate formation processes, differing in exposure to the asymmetric influence and, possibly, differing in time or place. This view is supported by two observations suggesting that the α-methyl amino acids are associated with a distinct meteorite phase: (i) they vary as a group in their concentrations relative to the α-H amino acids among different specimens of the Murchison meteorite (*21*), and (ii) they appear to be preferentially released from meteorite powders by mild extraction conditions.

Numerous mechanisms have been proposed for the abiotic generation of molecular asymmetry and have been critically reviewed (*1*). Of these, a hypothesis put forward by Bonner and Rubenstein (*22*) seems particularly relevant to the generation of enantiomeric excesses in meteoritic organic compounds. They proposed that large regions in interstellar molecular clouds could be exposed to a flux of circularly polarized light (CPL) of a specific handedness produced as synchrotron radiation by neutron stars. The complex organic mantles of interstellar grains thus could be exposed to ultraviolet CPL, resulting in asymmetric photosynthesis or degradation, that is, asymmetric photolysis of racemic constituents. Greenberg (*23*) considers the probability of an effective cloud-star encounter of this type to be at least 0.1 with respect to galactic clouds and has proposed that comets preserve enantiomeric excesses in their organic matter as a consequence of such an encounter by the presolar cloud. Enantiomeric excesses of the same order of magnitude as those reported here have been produced experimentally in racemic leucine exposed to ultraviolet CPL (*24*).

The production of enantiomeric excesses in amino acids by CPL according to (*22*) is not easily reconciled with the current formation hypothesis for meteoritic amino acids. A two-stage process has been proposed to account for the formation of the α-amino isomers (*25*). Deuterium (D) enrichments in the amino acids suggest that they are related to interstellar molecules (*26*), and their coexistence with a suite of α-hydroxy acids, corresponding in structure to the α-amino acids, suggests a Strecker synthesis of both sets of compounds (*27*). Because the organic-rich carbonaceous chondrites have, without exception, experienced aqueous processing, the two-step formation hypothesis proposes (i) incorporation of D-rich precursors (aldehydes, ketones, HCN, and ammonia) formed in the presolar molecular cloud into an asteroidal parent body and (ii) Strecker synthesis of α-amino acids during aqueous processing of the parent body.

In this case, if exposure to asymmetric CPL was limited to the presolar molecular cloud, only the precursor ketone (3-methyl-2-pentanone), which carried the chiral carbon atom destined to become C-3 of 2-a-2,3-dmpa, would have been directly affected. Upon conversion of this partially homochiral ketone to 2-a-2,3-dmpa by the nonstereospecific Strecker synthesis, a D enantiomer excess would be observed in one diastereomeric pair and an L enantiomer excess in the other (*28*). The observation of an L excess in both diastereomeric pairs eliminates this possibility.

The finding of L enantiomer excesses in both stereoisomers of 2-a-2,3-dmpa indicates that the complete molecule experienced the asymmetric effect; however, in the context of the two-step formation hypothesis, this restraint would require that exposure to CPL occurred in the early solar system after amino acid synthesis in the parent body had been completed. This course of events seems unlikely because shielding of the Strecker products by the parent body or within the parent-body regolith would block or substantially diminish the CPL.

Accepting the Bonner-Rubenstein hypothesis (*22*), we would conclude that the two-stage interstellar–parent body hypothesis is not applicable to the nonracemic amino acids and propose that formation of these amino acids occurred entirely in the interstellar medium. This explanation would be consistent with the possible separate origin for the α-methyl amino acids mentioned above. If, on the other hand, all of the meteorite amino acids were formed in the interstellar medium, enantiomeric excesses might be expected in a broader range of compounds in comets than in carbonaceous chondrites, because comets probably have not experienced aqueous processing, with the attendant possibility of racemization, to the same extent as have the carbonaceous chondrites. There is suggestive, although not conclusive, evidence for the interstellar gas-phase occurrence of glycine (*29*). Little is known of the nature of organic compounds in the solids and ices of interstellar grains, but future organic analyses of comets promise to be of great interest in this regard. If comets contain organic compounds at a level of structural complexity similar to the carbonaceous chondrites, then assessment of optical rotation or enantiomeric ratios should be a high-priority goal (*30*).

The finding of enantiomeric excesses in amino acids indigenous to the Murchison meteorite constitutes the first natural evidence for the operation of an abiotic process for enantiomeric enrichment. The observations suggest that organic matter of extraterrestrial origin could have played an essential role in the origin of terrestrial life as provider of the initial enantiomeric excesses from which homochirality developed. Although the excesses observed are modest, plausible mechanisms have been proposed by which such excesses might have been amplified prebiotically, for example, polymerization accompanied by formation of chiral secondary structure (*31*).

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11. The assignment of absolute configurations to the individual chromatographic peaks was made as fol-

lows. On Chirasil-Val columns, the amino acid enantiomer having the same α-carbon configuration as the Val moiety of the chromatographic phase typically has the longer retention time of the pair [E. Bayer, *Z. Naturforsch. B* **38**, 1281 (1983)]. This expectation was verified for the 2-a-2,3-dmpa stereoisomers by preparing the *N*-chloroacetyl derivatives of a synthetic standard containing all four stereoisomers and partially digesting this standard with hog kidney acylase I, which specifically hydrolyzes the amide linkages of L enantiomers [C. G. Baker, S. J. Fu, S. M. Birnbaum, H. A. Sober, J. P. Greenstein, *J. Am. Chem. Soc.* **74**, 4701 (1952)]. One of the resulting free L amino acids and the four residual unhydrolyzed *N*-chloroacetyl stereoisomers were isolated from the reaction mixture, the latter was acid hydrolyzed, and both preparations rechromatographed on the Chirasil-L-Val and Chirasil-D-Val phases after appropriate derivatization. The expected behavior was observed, that is, two diminished peaks (L) from the residual chloroacetylated stereoisomers corresponding in retention times to those expected for the L enantiomers and a corresponding match of the isolated free amino acid (L) with the expected L-enantiomer retention time of the (2*S*,3*S*-2*R*,3*R*) pair. The (2*S*,3*S*-2*R*,3*R*) and (2*S*,3*R*-2*R*,3*S*) diastereomer pairs of 2-a-2,3-dmpa were identified from the chemical shifts of their α-methyl groups observed in proton nuclear magnetic resonance (NMR) spectra of the methyl esters ($CDCl_3$) and comparison with literature values for the corresponding (2*S*,3*S*)- and (2*R*,3*S*)-2-a-2,3-dmpa methyl esters [U. Schöllkopf, R. Tölle, E. Egert, M. Nieger, *Liebigs Ann. Chem.* **1987**, 399 (1987)]. The diastereomer pairs were present in the standard in different amounts and thus, the GC-MS chromatograms and the NMR spectrum could be correlated.

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28. This result is analogous to the α-epimerization of L-isoleucine (2*S*,3*S*), which gives D-alloisoleucine (2*R*,3*S*); however, in the case of a Strecker synthesis, the 2*S*-2*R* equilibrium is achieved by formation of the chiral center rather than by inversion of the configuration at an existing chiral center. As envisioned here, the C-3 of 2-a-2,3-dmpa would not necessarily have been homochiral as in the case of biological isoleucine, but might have had only a modest enantiomeric excess. Consequently, excesses of the D and L enantiomers of the respective diastereomers would also have been small.
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32. We thank C. Moore of the Arizona State University Center for Meteorite Studies for a sample of the Murchison meteorite; M. Madison for calculation of the isomer numbers using the program ASSEMBLE [B. D. Christie and M. E. Munk, *Anal. Chim. Acta* **200**, 347 (1987)]; R. Nieman for help in obtaining and interpreting NMR spectra; J. Bada, K. Kvenvolden, and an anonymous reviewer for constructive reviews of the manuscript; and the NASA Exobiology Program for research support (NAGW-1899).

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Atomistic Simulation of Shock Wave–Induced Melting in Argon

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A three-dimensional molecular dynamics simulation of shock wave loading was undertaken to investigate the Hugoniot equation of state at the transition of argon from solid to liquid. The simulated data agree with shock wave and static high-pressure experimental data. The melting transition in this simulation occurs without overshooting the argon melting temperature. There are two discontinuities that may bracket a mixed-phase region of solid and liquid along the simulated argon Hugoniot. This is an intrinsic feature of the Hugoniot crossing the argon melting curve and does not require the addition of any solid-solid phase transition.

Shock wave experiments are particularly well suited for molecular dynamic (MD) simulations because in such experiments sample sizes are small and time scales are short (*1*). Few studies have been devoted to the simulation of shock wave–induced phase transitions (*2*), and none of them were done in three dimensions. I have simulated the shock wave–induced melting transition for Ar, an element for which many physical parameters are well known and for which I have simulated the melting curve (*3*), which agrees with experimental data (*4*). Argon transforms to liquid directly from the face-centered-cubic (fcc) phase without any high-pressure and high-temperature solid-solid phase transformations (*5*).

The initial configuration for the simulation consisted of Ar atoms in an fcc lattice with n by n by m unit cells translated in x, y, and z directions, respectively, with n varying from 5 to 10 and m varying from 60 to 120 in different simulations. The minimum number of atoms was 6000, and the maximum was 48,000. Calculations with different numbers of atoms showed that 6000 atoms is sufficient to obtain reliable results. Periodic boundary conditions were applied in the x and y directions. An Ar-Ar interaction was described in terms of the Buckingham potential (*3*, *6*, *7*). The shock wave was generated through the motion of a piston in the $-z$ direction with a given velocity (U_p). The interaction of the Ar atom with the piston was calculated on the assumption that a piston is a solid homogeneous Ar crystal. On the side of the sample opposite the piston (at $z = 0$) Ar atoms interacted with the elastic wall. The time step for solving equations of motion was 4 fs, and the number of time steps varied from 3000 to 6000. I cross-checked all calculations, using simulations with various time, time step, length of sample, cutoff radius of interaction, cross-sectional area, number of atoms, and initial conditions.

The propagation of the shock wave front was observed in snapshots of the structure (a supplementary figure is available to online subscribers at http://www.sciencemag.org), allowing rather precise (error less than 1%) measurement of the shock wave velocity (U_s). To measure the sound velocity V_s in the shock-compressed part of the sample, I stopped the piston at some time step (usually time step 1000) and measured the velocity of the rarefaction wave. Pressure profiles were used to determine U_s and V_s (*8*). Volume (V), pressure (P), and temperature (T) were monitored as a function of z. I also calculated P and V from U_p-U_s data using two of the Rankine-Hugoniot (RH) relations:

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