doi:10.1016/S0016-7037(00)01283-8

Nonracemic isovaline in the Murchison meteorite: Chiral distribution and mineral association

SANDRA PIZZARELLO,[1,]* MICHAEL ZOLENSKY,[2] and KENDRA A. TURK[3]

[1]Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA
[2]NASA Johnson Space Center, Houston, TX 77058, USA
[3]NASA Ames Research Center, Moffet Field, CA 94035, USA

Abstract—The enantiomeric and carbon-isotopic composition of the amino acid isovaline have been analyzed in several samples of the Murchison meteorite and one sample of the Murray meteorite. L-Enantiomeric excesses of the amino acid were found to range from 0 to 15.2%, varying significantly both between meteorite stones and at short distances within a single stone. The upper limit of this range is the largest enantiomeric excess measured to date for a biologically rare meteoritic amino acid and raises doubts that circularly polarized light irradiation could have been the sole cause of amino acids chiral asymmetry in meteorites. Individual D- and L-isovaline $\delta^{13}C$ values ware found to be about +18‰, with no significant differences between the two enantiomers to suggest terrestrial contamination. The amino acid relative abundance also varied between samples, with isovaline/alanine ratios of 0.5 to 6.5. X-ray diffraction analyses of contiguous meteorite fragments suggest a possible correlation between isovaline and hydrous silicates abundances. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

The exclusive one-handedness of terrestrial amino acids and sugars is essential to the formation, structure, and function of biopolymers and is a defining molecular trait of terrestrial life. The unknown origin of this "homochirality" has been investigated for well over a century, since Pasteur first discovered it. The ensuing debate has paralleled in scope and rationale the more general studies about the origin of life: was biologic homochirality the product of prebiotic processes, or the result of selection brought about by life itself? Was it because of choice or chance? Was it at first broad-scaled, or was it of limited extent?

The finding of small but significant L-enantiomeric excesses (ee) in some amino acids of carbonaceous meteorites that are rare or unknown in the biosphere (Cronin and Pizzarello, 1997) appears to indicate that interstellar and planetary chemical evolution (i.e., purely physicochemical abiotic processes) could yield chiral asymmetry. It also suggests a possible prebiotic contribution to the origin of biologic homochirality by impact delivery of meteoritic material to the early Earth, i.e., if the organic compounds found in carbonaceous chondrites are representative of some fraction of the organic milieu present on the early Earth (Chyba and Sagan, 1992), the small meteoritic enantiomeric excesses could have provided a chiral bias sufficient for amplification that culminated in homochirality (Pizzarello and Cronin, 2000). The α-methyl-α-amino acids, which have shown significant enantiomeric excesses in meteorites, are known to resist racemization, and are helix formers when polymerized (Altman et al., 1988; Formaggio et al., 1995), seem particularly well suited for such a role in prebiotic chemistry.

It has been proposed that the optical activity of amino acids

in meteorites could be the result of asymmetric decomposition, brought about by ultraviolet circularly polarized light (UV CPL) irradiation of meteoritic organic compounds during their syntheses (Cronin and Pizzarello, 1997; Engel and Macko, 1997). The likelihood of this assumption was supported by theoretical and experimental work showing that UV CPL can produce enantiomeric excesses within the range so far observed in meteorite amino acids (Balavoine et al., 1974; Cronin and Pizzarello, 1997).

To further characterize enantiomeric excesses in meteorites, and to constrain the possible mechanism of their formation in prebiotic environments, we have assessed the extent of chiral asymmetry, relative distribution, and likely petrological association of meteoritic isovaline (2-amino-2-methylbutyric acid). This is one of the most abundant optically active amino acids in meteorites, where it is present with the largest L-excess (9%) (Pizzarello and Cronin, 2000). We have used several samples of the Murchison and Murray carbonaceous chondrites, both from interior and near-surface fragments, and from different curatorial facilities. To exclude the possibility of terrestrial contamination, the $\delta^{13}C$ of D- and L-isovaline enantiomers were measured individually by gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) in five representative samples of the two meteorites.

2. MATERIALS AND METHODS

2.1. Samples

Murchison analyses listed in Table 1 were obtained from powdered stones of 3 to 20 g weight, although the actual chiral analyses for some were performed with smaller portions of the powders. They are designated by their curatorial source: ASU indicates various specimens from the collections of the Arizona State University (Center for Meteorite Studies, ASU 828), and SMIT indicates specimen USNM 5341 obtained from the Smithsonian Institution. Sample ASU '70 was residual powder that had been stored below 0°C since the initial analyses of Kvenvolden et al. (1970). The I and E letters following these denom-

* Author to whom correspondence should be addressed (pizzar@asu.edu).

Table 1. L-Enantiomer excess and relative distribution of meteoritic isovaline from large (3–25 g) Murchison stones.

No.	Sample	L-ival ee% (n)	σ	ival/ala[a]	ival/aiba[a]
1	ASU'70 I	3.6 (7)	±0.3	2.0	0.31
2	ASU'70 E	3.0 (5)	±1.3	1.3	0.27
3	ASU I	6.0 (5)	±0.4	1.0	0.27
4	ASU I	5.2 (14)	±0.5	—	—
5	ASU I	15.2 (8)	±0.2	6.8	0.28
6	ASU E	12.6 (6)	±0.4	0.8	0.24
7	SMIT E	0.2 (6)	±0.3	0.3	0.15
8	SMIT E	3.4 (8)	±0.6	0.5	0.21
9	ASU av[b] I	10.6 (33)	±0.6	2.6	0.29
10	Standard 1[c]	−0.4 (8)	±0.6		
11	Standard 2	−1.0 (22)	±0.6		

[a] Abundances obtained by integration of GC-MS peaks.
[b] Average of data from Table 2.
[c] For correction of samples 1–3 and 7–8.

inations indicate interior (≥5 mm from the surface) and exterior fragments, respectively. The samples 1 to 5 listed in Table 2 are ~0.5-g contiguous fragments taken ~5 mm below the fusion crust from the face of a freshly broken ASU stone. Isotopic analyses were conducted for some of these samples (Table 3), chosen from those remaining in sufficient amount after chiral analyses to represent different enantiomeric distribution in the meteorite. The Murray meteorite isotopic values listed in Table 3 were obtained from new analyses of a portion of a large meteorite sample used for a previous study (Pizzarello and Cronin, 2000), and stored frozen since.

2.2. Sample Preparation

All samples were powdered in an agate mortar and the amino acids and other water-soluble compounds were extracted with 100°C water. The extracts of larger stones (Table 1) were concentrated by rotary evaporation, acidified, applied to a cation exchange column, and then eluted sequentially with water and 2 N NH₄OH. Various amounts of the basic eluates were set aside for total amino acid analyses and the remaining were dried, redissolved, and applied to a C18 semiprep reverse-phase column for the collection of fractions containing individual or sets of amino acids of equal carbon chain length. For 0.5-g samples (Table 2), one-tenth of the extracts were used for direct analyses and the remaining processed by reverse-phase chromatography without desalting. All reverse-phase eluted fractions were again desalted on a small ion-exchange column, and the NH₄OH eluates derivatized to give the amino acid N-trifluoroacetyl (TFA)-isopropyl esters for gas chromatography–mass spectrometry (GC-MS) analysis. Details of these preparative procedures are also provided in Pizzarello and Cronin (2000).

2.3. Molecular and Chiral Analyses

Enantiomeric analyses were carried out by GC-MS with a Hewlett-Packard (HP) 5580/HP 5970 or HP 5580A/HP5970B instruments and

Table 2. Spatial variation of L-isovaline enantiomer excesses (ee) within a Murchison stone.[a]

Sample no.	L-iva ee% (n)	σ	iva/ala	iva/aiba
1	15.0 (6)	±1.0	2.1	0.24
2	3.8 (8)	±0.6	0.5	0.20
3	14.6 (5)	±0.4	2.9	0.30
4	6.2 (8)	±0.5	0.5	0.31
5	13.2 (6)	±0.4	6.7	0.40
Standard	0.4 (8)	±0.6		

[a] From the ASU collection.

Table 3. δ^{13}C (‰) values[a] of meteoritic L- and D-isovaline.

Sample[b]	L-ival ee%	L-ival δ^{13}C	σ	D-ival δ^{13}C	σ
1. Murchison I	13.2	+18.0	0.3	+16.0	1.9
2. Murchison I	6.0	+17.8	1.9	+11.5	1.6
3. Murchison E	12.6	+21.9	1.2	+19.9	0.9
4. Murchison E	0	+17.5	—	+17.3	—
5. Murray I	6.0	+20.0	2.5	+18.8	1.7
6. Standard[c]		−28.0	0.9	−31.9	1.2

[a] Values ‰ (PDB) were obtained by GC-C-IRMS and corrected for derivatization and average standard fractionation (see Methods). Values are averages of three analyses, except for 4, which are the averages of two.
[b] Samples, top to bottom, are also described as sample 5 in Table 2, as samples 3, 6, and 7 in Table 1, and in Fig. 2.
[c] Combined DL peak: −30.5‰.

capillary column coated with a chiral β-hepta amylose phase (25 m × 0.25 mm, 0.7 μm thickness, Chirasil-Dex CB, Chrompack). The operating conditions were as follows: He gas flow, 1.0 mL/min; temperature program: 70°C, 5 min, 70 to 100°C at 2°/min, 100 to 200°C at 4°/min. Enantiomeric excesses (ee = L% − D%) are standard corrected mean values based on n integrated ion intensities, where n includes multiple specific ions selected from multiple runs. Significance of the difference between the sample and standard mean values was calculated by Student's t test of two independent means (Ipsen and Feigl, 1970). The elution times of the N-TFA-isopropyl esters of isovaline enantiomers on Chirasil-Dex CB were established to be L (S) > D (R) by the use of individual enantiomer standards (ACROS organics).

Before integration or isotopic analyses, the chromatographic purity of the enantiomeric derivatives was established by scanning and adding the fragmentation masses of all the spectra along each individual peak. The subsequent subtraction of one peak's total of added spectra from that of the other would clearly show the presence, if any, of interfering masses in the spectra of either enantiomer (Pizzarello and Cronin, 2000). GC-MS analyses also allowed an overview of the amino acids present in the fraction samples and any possible interferences with the targeted isovaline. The meteorite fraction containing isovaline was also found to contain the other five carbon α-amino acids valine and norvaline, plus some of the β- and γ- amino acid species. All are known (Cronin et al., 1985) and were identified with large chromatographic separation from isovaline.

2.4. Isotopic Analyses

For GC-C-IRMS, GC conditions were the same as for GC-MS, the only difference being a He flow of 1.2 mL/min. A Finnigan high-temperature conversion interphase III, and Mat Delta⁺-XL IRMS were used. Oxidation was at 960°C with a ceramic oxidation reactor bearing NiO/CuO/Pt wires. Isotopically calibrated n-alkane standards (Chiron AS, Trondheim, Norway) were analyzed frequently throughout the analyses to confirm the efficiency of combustion catalysts in the oxidation reactor.

Data were analyzed with Finnigan ISODAT software. Standard CO₂ δ^{13}C was −41.72 (PDB)‰. The δ notation expresses the isotopic ratios as follows: $\delta‰ = (R_{sample} − R_{standard}/R_{standard}) \times 10^3$. For carbon R = ^{12}C/^{13}C and the standard for the analyses was PDB. δ^{13}C (PDB) of isopropanol was found to be −27.89‰, by elemental analyzer (EA)-IRMS, and that of trifluoroacetic anhydride (TFA) was −40.3‰, as determined by GC-C-IRMS of N-TFA ammonia. Individual mass balance equations for derivatization correction were therefore $\delta^{13}C_{ival}$ = $[\delta^{13}C_{der.ival} − 0.3 (−27.89) − 0.2 (−40.3)]/0.5$.

Standard D- and L-isovaline isotope values were determined with both racemic and individual enantiomer standards, the latter standards being injected either separately or combined. Small (~1 to 4‰) differences were found for the δ^{13}C values of the individual enantiomers when determined after chromatography of the combined standards. These are due mainly to the tailing of the peaks and increase upon decreasing baseline resolution, e.g., with samples that are too large.
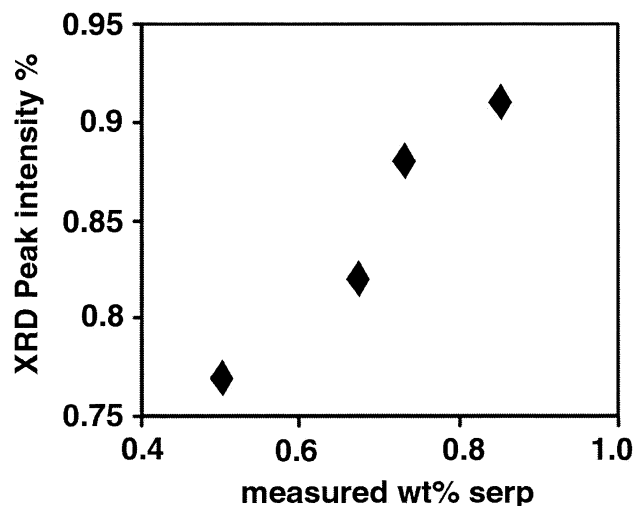
Fig. 1. Plot of measured relative peak intensities for XRD 7.2A peak for serpentine as compared with the 3.88 A peak for olivine, vs. serpentine (wt%) in five standard mixtures.

These differences were determined by using the ISODAT integration values of manually defined standard peaks and a curve-fitting software designed for the analysis of overlapping peaks (PeakFit version 4.06, SPSS; Goodman and Brenna, 1994). Results by the two methods were comparable and allowed the optimization of conditions. For meteorite analyses, runs that did not meet the baseline resolution criteria established by standard analyses were discarded. For analyses of samples showing acceptable GC baseline resolution, individual meteoritic L- and D-isovaline peaks were manually defined giving an equal time parameter to their integration, which was taken from the start of the L-peak to the start of the D-peak on the m/z 44 trace. Isotopic values were then corrected on the basis of the average difference recorded for the standards injected before and after meteorite samples analysis.

2.5. Petrographic Analyses

We prepared four standards with different mixtures of antigorite serpentine (the dominant mineral of fine grained matrix) and forsterite (an olivine and the dominant mineral of coarse-grained meteorite components). For each, we made high-precision X-ray diffraction (XRD) scans through the highest intensity diffraction peak for serpentine (d = ~7.2 A) and one diagnostic peak for forsterite (d = 3.88 A), to determine the relation of peak intensity to weight percentage of each of the two minerals in the mixture. Meteorite and standard samples were prepared by slurring the powder with alcohol on a glass slide, allowing the samples to dry in air, and analyzed under identical conditions. XRD scans were collected on a Scintag XDS2000 diffractometer that used Cu-Kα radiation at 45 kV and 40 mA. Data were acquired by spinning the samples while running from 10° to 15° and 30° to 40° 2-θ at a scan rate of 0.25°/min with a 0.02° step. Errors for this procedure are estimated at 10% (Fig. 1).

2.6. Standards and Blank

A procedural blank and a DL-isovaline standard were carried through the entire meteorite sample procedure. The DL-isovaline standard (Aldrich, recrystallized) δ13C was −28.35‰ (EA); carbon fractionation at derivatization was found to be −2.2‰.

3. RESULTS AND DISCUSSION

Figure 2 displays an example of the chromatographic resolution that was obtained for meteoritic isovaline after the preparative procedures described above. As the figure shows, these resulted in a clear analytical separation of the amino acid

enantiomers that allowed detailed chiral and isotopic analyses unhindered by interference. The results of Murchison isovaline molecular and enantiomeric analyses are summarized in Tables 1 and 2 that list, respectively, data sets obtained from larger meteorite stones of various provenience and from smaller fragments taken contiguously from a single stone (~1 cm center to center). Values are given for L-isovaline (ival) enantiomeric excess percentage and for the abundance ratios of the amino acid relative to alanine (ala, 2-amino propanoic acid) and to α-aminoisobutyric acid (aiba), i.e., the achiral lower homologue of isovaline within the group of α-branched amino acids.

As the data show, the magnitude of L-isovaline enantiomeric excesses was found to differ greatly between small and larger meteorite stones alike and to vary from 0 to 15.2%. The range of this variability is much larger than previously established by Pizzarello and Cronin (2000) and its upper limit of L-ee = 15.2% extends well beyond the theoretical boundaries set for amino acid decomposition by UV CPL. This irradiation is chiral electromagnetic energy that is inherently asymmetric and can affect a chiral amino acid either through synthesis or by asymmetric photolysis of its racemate. Although the former has not been demonstrated in the laboratory, enantiomeric excesses of up to 2.5% have been produced by UV CPL photolysis of racemic leucine (Flores et al., 1977; Nishino et al., 2002). The differential photolysis by UV CPL has its basis on the unequal absorption by the two enantiomers of a chiral molecule for this irradiation. It is expressed by the anisotropy factor **g**, given by the ratio between the difference in UV CPL absorption by the two enantiomers (expressed by their extinction coefficients) and the average total absorption, i.e., the larger this difference and the **g** for a molecule, the larger will be the difference in the extent of photolysis between the two enantiomers and the resulting ee. The **g** is a strict physical parameter that dictates the extent of enantiomeric excesses achieved by a given chiral molecule with the duration of the reaction and before both enantiomers are completely decomposed. For amino acids the **g** is quite low, ~0.02 (Balavoine et al., 1974; Nishino et al., 2002), and restricts the possible enantiomeric excesses by UV CPL to a maximum of ~10%, a value obtained only with 99,99% decomposition and at the acidic pH of 1 (Nishino et al., 2002). From this perspective, the L-excesses measured for meteoritic isovaline would seem to refute the suggestion that UV CPL was the sole causation of its asymmetry.

Could isovaline enantiomeric differences between meteorite samples be the result of varying degrees of terrestrial contamination? Besides surface samples, interiors of meteorites can also acquire microbial contamination (Oro' and Tornabene, 1965; Steele et al., 1999) and isovaline is not unknown in the biosphere where it occurs in fungal peptides in the D-configuration (http//w.w.w.cryst.bbk.ac.uk/peptaibol/welcome.html). This is the opposite configuration from that of common protein amino acids and, were isovaline a contaminant in the meteorite, it would be expected to both reduce the L-ee and lower the isotopic values of the D-enantiomer of the indigenous amino acid (Engel et al., 1990). The isotopic analyses of meteoritic isovaline (Fig. 3), and the δ13C values listed in Table 3, do not support this latter possibility.

It can be seen from the data that the isovaline carbon from four Murchison samples and one Murray sample is isotopically heavy, as expected (Engel et al., 1990; Pizzarello et al., 1991),
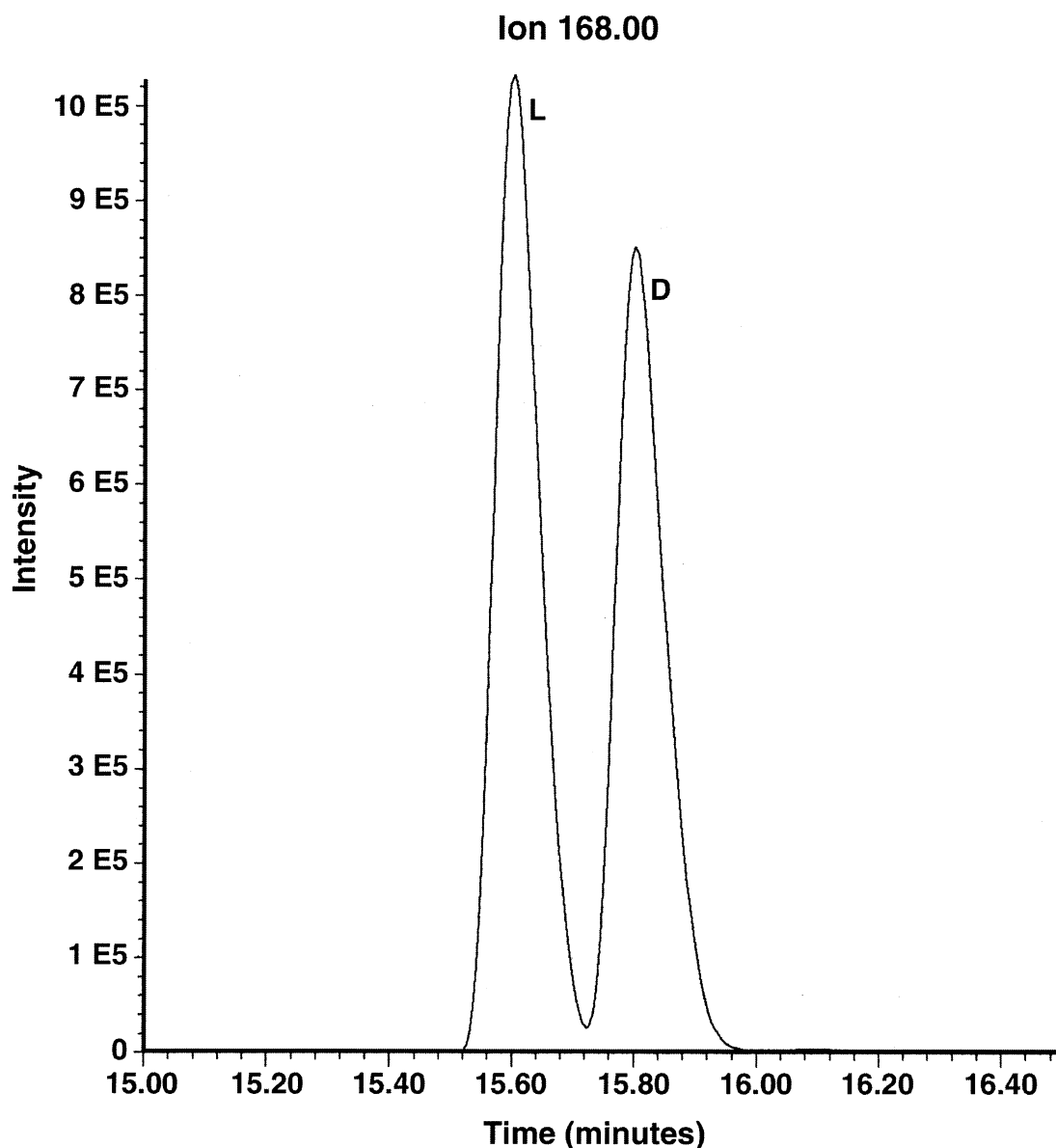
Ion 168.00

Fig. 2. GC-MS analysis of a derivatized (N-TFA, O-isopropyl) Murray isovaline sample with 6% L-ee, m/z 168 single ion trace.

and that the D-enantiomer is only slightly lighter than the L-enantiomer. Considering that $\Delta\delta^{13}C$ value is $\leq$2‰ in four of the five samples and that the σ values are of comparable magnitude, the significance of these differences is doubtful. Certainly there is no isotopic basis for believing the L-excess to be a result of contamination. In the case of sample 2, for which the $\Delta\delta^{13}C$ is relatively large, the possibility of terrestrial contamination in the D-enantiomer appears possible, in which case the measured L-enantiomeric excess is a minimal value. Also, there is no reason to suspect that any unknown procedural interference would have altered the isotopic comparison of the D-, L-isovaline GC-C-IRMS peaks. Although some factors (e.g., kinetic effects resulting from uneven performance of injection or combustion interface; see Meier-Augenstein, 1997, for a review) could influence the absolute accuracy of the isotopic values and increase the variability of repeat data, they would leave unchanged the relative isotopic values of the two enantiomers, at least when analyzed contemporaneously.

The apparent indigenous nature of large enantiomeric excesses for isovaline in both the Murchison and Murray meteorites, and the inadequacy of the UV CPL photolysis model for the generation of amino acids asymmetry, requires us to look to other possible processes for their production. In this context, it is worth considering the relative abundance ratios of the amino acids listed in Tables 1 and 2. The data show that the ratios of α-methyl amino acids to α-H amino acids (of which the ival/ala ratio is representative) vary significantly even within small distances of the same stone, whereas the distribution of α-methyl amino acids to each other (ival/aiba) remain nearly constant. Another interesting notation from theses molecular
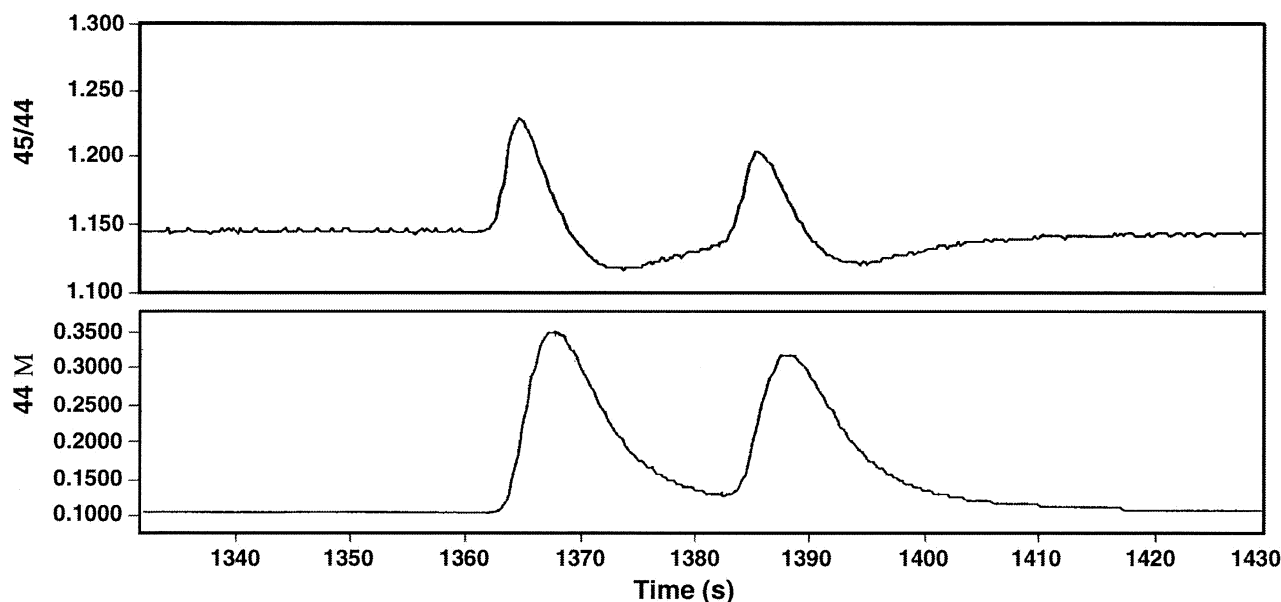
Fig. 3. m/z 44 (bottom) and 45/44 (top) traces of a GC-C-IRMS analysis of Murray L- and D-isovaline enantiomers. Analysis was preceded by HPLC separation to give a sample contained only five-carbon amino acids.

analyses, which is not reported in Table 2 and was obtained by the quantitative estimate of absolute amino acid amounts in the small contiguous samples, was that it is the distribution of α-amino isobutyric and isovaline that vary between samples, whereas that of alanine remain fairly stable.

Considerable variations in the relative composition of amino acids from different Murchison stones (Cronin and Pizzarello, 1983), and in particular the independent behavior of the α-branched amino acids (Pizzarello and Cronin, 2000), were noted before. This study appears to confirm the suggestion that α-methyl amino acids comprise a separate subset of meteoritic compounds that differs from other amino acids both quantitatively and in their degree of asymmetry. This apparently independent variation of asymmetry carrying α-methyl amino acids cannot be explained in simple terms of varying reactivity or conditions during their formation.

The distinguishing features observed to date for this subgroup of α-amino acids are those of being less prone than α-H amino acids to form derivatives, i.e., they are mainly extracted as "free" amino acids (Cronin and Pizzarello, 1983) and of displaying L-enantiomeric excesses. These differences could still be explained within a common pathway of formation for the two sets of α-amino acids (a-H and α-alkyl) by the reactive hindrance of the alkyl substituent toward formation of α-alkyl amino acid derivatives and the resistance to racemization of α-amino acids lacking an α-hydrogen during water processes (Pollock et al., 1975). However, a similar search for intrinsic properties of α-alkyl amino acids that could account for their varying relative abundance does not offer a likely explanation. For example, if the differences ival/ala ratios between samples were due to a lower stability of the α-H amino acids, and their decomposition or formation of derivatives upon parent body water alteration, it would be hard to explain the cases we observed where α-alkyl amino acids are very low against a constant suite of α-H species. A varying stability of α-methyl

amino acids, on the other hand, could account for their abundance but not enantiomeric variability because they do not racemize. (Also, were this the case, it seems that their abundance would have a negative relation to parent body water processes instead of a positive one; *vide infra*.)

Ultimately, we have to consider the implication of distinct synthetic pathways for the two subgroups of meteoritic α-amino acid or of their possible association with different matrix phases. Were these phases identified, they might also shed light on the locale or locales where meteoritic amino acids symmetry breaking took place. In broader terms, this possibility was investigated by Cronin (1989) who was able to show a relation between the total amino acid content of five different CM chondrites and their content of hydrous "poorly characterized phases" (PCP), as determined by McSween (1987) on the basis of mass-balance calculations. When the amino acid abundance values used by Cronin were plotted again in terms of individual amino acid content, a linear correlation was found only between PCP and isovaline abundance (i.e., no correlation was seen between alanine and PCP distribution; Cronin, personal communication).

Given the large heterogeneity we have observed between meteorite samples in this study, it is possible that the accuracy of the above correlation could have been compromised by differences between the various stones that were utilized for amino acid and PCP analyses. Therefore, we have undertaken a petrological survey of the very meteorite samples for which amino acid content was known (Table 2), and obtained X-ray diffraction spectra (XRDS) of their entire powders. To acquire a quantitative profile that could be related to amino acid abundances, we analyzed the powders in reference to standards simplified to represent the main features of Murchison mineralogy. Standards contained variable amounts of the hydrous silicate serpentine and the anhydrous silicate forsterite that are the dominant minerals in the carbonaceous chondrites fine
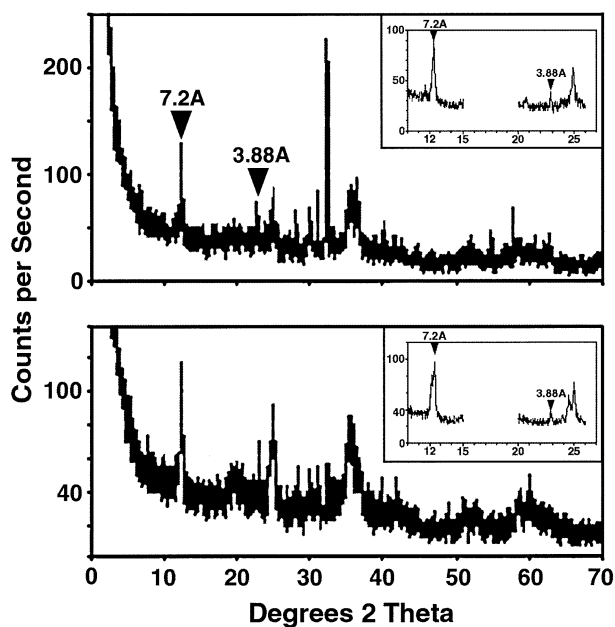
Fig. 4. X-ray diffraction scans collected for the entire powders of samples 2 (top) and 5 (bottom), see Tables 2 and 4. Inserts for each show more detailed scans through the diagnostic peaks at 7.2 and 3.88 A, which were collected at a slower scan rate to provide a better measure of background peaks and used for the mineralogical determination.
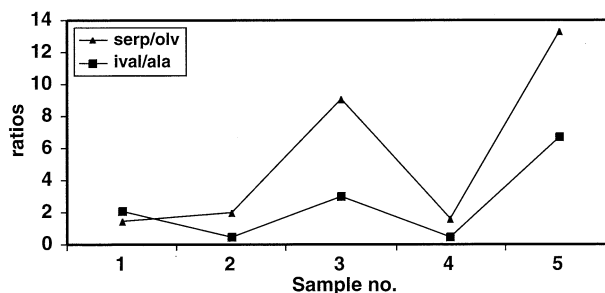

Fig. 5. Amino acid and silicate relative abundances within a Murchison fragment. isovaline/alanine are as in Table 2, and serpentine/olivine are relative to standards (Table 4 and Fig. 1). $\sigma = \pm 0.5$.

4. CONCLUSIONS

It seems unlikely that ee values as high as those determined for the amino acid isovaline in this study could have been reached by UV CPL photolysis alone, i.e., by a single exposure of meteoritic amino acids to UV CPL. Balavoine et al. (1974) discussed the possibility that recurrent photolytic processes by UV CPL could produce substantial asymmetry in organic compounds. This repeated exposure can be envisioned during interstellar cloud collapse (Cronin and Reisse, 2003) and would give larger enantiomeric excesses, albeit with loss of total compound, both in organics with low anisotropy, as the amino acids, and in those with larger anisotropy, which could then act as catalysts for the secondary propagation of optical activity. Although these irradiation processes remain possible as a sole, or partial, sources of asymmetry for amino acids in meteorites, the correlation shown in some Murchison fragments between asymmetry-carrying isovaline and hydrous silicates appears also to suggest that the formation of meteoritic amino acid L-excesses may have been secondary to their interaction with the lithic environment. Were this the case, it would shift the burden of asymmetry to meteoritic minerals and the possibility that, at some point in their cosmic history, they could have acquired asymmetry of chiral centers or entire assemblages.

A locale associated with water processes for the causation or amplification of enantiomeric excesses in Murchison and Murray amino acids would concur with our present understanding of the formation of these meteoritic compounds. On the basis of their overall molecular and isotopic distribution, it is postulated that most organic compounds in carbonaceous chondrites formed during a period of parent body water alteration by the reactions of volatile, low-molecular-weight interstellar precursors (see Cronin and Chang, 1993, for a review). More pointedly for amino acids and hydroxy acids, a Strecker-like synthesis from aldehydes and ketones, HCN, water, and ammonia has been proposed (Peltzer and Bada, 1978). The possibility that this reaction could, in fact, represent a pathway of formation for amino acids in meteorites appears confirmed by the finding in Murchison of imino acids, compounds also predicted by the Strecker synthesis (Lerner, personal communication; Pizzarello and Cooper, 2001).

So far, however, no hypotheses has sufficiently addressed the differences in molecular, chiral, and isotopic (Pizzarello et al., unpublished results) distribution of meteoritic α-alkyl-amino acids in the context of their formation that may have been, at

grained matrix and the olivines of coarse grained components, respectively. The accuracy of these standard analyses is shown in Figure 1 (see Materials and Methods, in which details of meteorite and standard analyses can also be found), and representative XRDS of two meteorite powders are shown in Figure 4.

The total and relative amounts of serpentine and olivine obtained by XRDS of the five Murchison samples are listed in Table 4 and their mass abundance ratios are plotted with the corresponding ival/ala ratios in Figure 5. Although the data points for the analyses are limited to five, a good relation is shown between isovaline and serpentine distribution in these Murchison powders, which agrees with the correlation observed by Cronin between isovaline and PCP content in five carbonaceous chondrites.

Table 4. Spatial variation of Serpentine and Olivine abundance[a] within a Murchison stone.

Sample[b]	Serpentine	Olivine	serp/oliv + serp[c]	serp/oliv[d]
1	3191	1520	0.64	1.5
2	1283	424	0.75	2.0
3	1982	126	0.94	9.1
4	1971	889	0.69	1.6
5	1788	84	0.96	13.3

[a] As total count of X-ray photons.
[b] As in Table 2.
[c] From raw intensities.
[d] Mass ratios.

least in part, unique in including chiral selection. It should be noted that Tables 1 and 2 show only a partial correlation between a high content of α-methyl amino acids (i.e., high ival/ala) and the magnitude of their enantiomeric excess. This may indicate that additional processes of formation may have been at work for these amino acids as well, besides the one(s) that lead to symmetry braking. Although the molecular data presented here add to past and recent reports of large distribution variability in meteoritic organic suites (Cronin, 1989; Pizzarello et al., 2001), the observation of variable extent of enantiomeric excesses in Murchison isovaline is new. This variability, together with the partial correlation in ival abundance and ee noted above, point to complex, possibly multiple, synthetic processes for meteoritic amino acids for which we cannot as yet account and which will require further extensive detailed investigation.

The expanded range of L-excesses recorded for isovaline in several meteorite samples allows renewed speculation about the possible contribution of meteoritic amino acids to the origin of terrestrial homochirality as well as speculation on the likelihood that molecular asymmetry held an astrobiological significance for the origin of life elsewhere. As noted before (Pizzarello and Cronin, 2000), the α-methyl amino acids, although not common in the extant biosphere, would have been well suited to provide the early Earth with both enantiomeric excesses and means for their amplification by subsequent chemical evolution. These amino acids, by not being amenable to racemization and having helix-inducing and stabilizing effects, could retain initial enantiomeric excesses in aqueous environment and effectively amplify even modest enantiomeric excesses by the formation of secondary structures (Brack and Spach, 1981) or by intervening as asymmetric catalysts in prebiotic processes.

Associate editor: G. D. Cody

REFERENCES

Altman E., Altman K. H., Nebel K., and Mutter M. (1988) Conformational studies on host–guest peptides containing chiral α-methyl-α-amino acids. *Int. J. Protein. Res.* **32,** 344.

Balavoine G., Moradpour A., and Kagan H. B. (1974) Preparation of chiral compounds with high optical purity by irradiation with circularly polarized light, a model reaction for the prebiotic generation of optical activity. *J. Am. Chem. Soc.* **96,** 5152–5158.

Brack A. and Spach G. (1981) Enantiomer enrichment in early peptides. *Origins Life* **11,** 135.

Chyba C. F. and Sagan C. (1992) Endogenous production, exogenous delivery, and impact-shock synthesis of organic molecules: An inventory for the origins of life. *Nature* **355,** 125–132.

Cronin J. R. (1989) Origin of organic compounds in carbonaceous chondrites. *Adv. Space Res.* **9,** 259–264.

Cronin J. R. and Pizzarello S. (1983) Amino acids in meteorites. *Adv. Space Res.* **3,** 5–18.

Cronin J. R., Pizzarello S., and Yuen G. U. (1985) Amino acids of the Murchison meteorite: II Five carbon acyclic primary β-, γ-, and δ-amino alkanoic acids. *Geochim. Cosmochim. Acta* **49,** 2259–2265.

Cronin J. R. and Chang S. (1993) Organic matter in meteorites: Molecular and isotopic analyses of the Murchison meteorite. In *The Chemistry of Life's Origins* (eds. J. M. Greenberg, et al.), pp. 209–258. Kluwer.

Cronin J. R. and Pizzarello S. (1997) Enantiomeric Excesses in Meteoritic Amino Acids. *Science* **275,** 951–935.

Cronin J. R. and Reisse J. (2002) Chirality and the origin of Homochirality. In *The Footsteps of Life* (eds. M. Gargaud et al.). Presses Universitaires de Bordeaux, Pessac. In press.

Engel M. H., Macko S. A., and Silfer J. A. (1990) Carbon isotope composition of individual amino acids in the Murchison meteorite. *Nature* **348,** 47.

Engel M. H. and Macko S. A. (1997) Isoptopic evidence for extraterrestrial nonracemic amino acids in the Murchison meteorite. *Nature* **389,** 265.

Flores J. J., Bonner W. A., and Massey G. A. (1977) Asymmetric photolysis of (R,S)-leucine with circularly polarized light. *J. Am. Chem. Soc.* **99,** 3622–3625.

Formaggio F., Crisma M., Bonora G. M., Pantano M., Valle G., Toniolo C., Aubry A., Bayeul D., and Kamphuis J. (1995) R-isovaline homopeptides adopt the left-handed 3_{10}-helical structure. *Peptide Res.* **8,** 6–14.

Goodman K. J. and Brenna J. T. (1994) Curve fitting for restoration of accuracy for overlapping peaks in gas chromatography/combustion isotope ratio mass spectrometry. *Anal. Chem.* **66,** 1294–1301.

Ipsen J. and Feigl P. (1970) *Barcroft's Introduction to Biostatistics.* 2nd ed. Harper and Row.

McSween H. Y. Jr. (1987) Aqueous alteration in carbonaceous chondrites: Mass balance constraints on matrix mineralogy. *Geochim. Cosmochim. Acta* **51,** 2469–2477.

Meier-Augenstein W. (1997) The chromatographic side of isotope ratio mass spectrometry—Pitfalls and answers. *LC-GC* **15,** 244–253.

Nishino H., Kosaka A., Hembury G. A., Matsushima K., and Inoue Y. (2002) The pH dependence of the anisotropy factors of essential amino acids. *J. Chem. Soc. Perkin Trans. 2* **3,** 582–590.

Oro' J. and Tornabene T. (1965) Bacterial contamination of some carbonaceous meteorites. *Science* **150,** 1046–1048.

Peltzer E. T. and Bada J. L. (1978) α-Hydroxycarboxylic acids in the Murchison meteorite. *Nature* **272,** 443–444.

Pizzarello S., Krishnamurthy R. V., Epstein S., and Cronin J. R. (1991) Isotopic analyses of amino acids from the Murchison meteorite. *Geochim. Cosmochim. Acta* **55,** 905–910.

Pizzarello S. and Cronin J. R. (2000) Non racemic amino acids in the Murchison and Murray meteorites. *Geochim. Cosmochim. Acta* **64,** 329–338.

Pizzarello S., Cooper G. W. (2001) Molecular and chiral analyses of some protein amino acid derivatives in the Murchison and Murray meteorites. *Meteorit. Planet. Sci.* 897–909.

Pizzarello S., Huang Y., Becker L., Poreda R. J., Nieman R. A., Cooper G., and Williams M. (2001) The organic content of the Tagish Lake Meteorite. *Science* **293,** 2236–2239.

Pollock G. E., Chang S.-N., Cronin S. E., and Kwenvolden K. A. (1975) Stereoisomers of isovaline in the Murchison meteorite. *Geochim. Cosmochim, Acta* **39,** 1571–1573.

Steele A., Westall F., Goddard D. T., Stapleton D., Toporski J. K. W., and McKay D. S. (1999) Imaging of the biological contamination of meteorites: A practical assessment. *Lunar Planet. Sci.* **30,** 1321.