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Research carried out during Year 3 is described in the attached manuscript draft which will be submitted for publication.

Chirality and mineral association of isovaline in the Murchison meteorite

Abstract

Chiral and carbon-isotopic analyses of isovaline have been carried out on numerous samples of the Murchison and one sample of the Murray carbonaceous chondrite. The isovaline was found to be heterogeneous with regard to enantiomeric excess (ee) both between samples and within a single Murchison sample. L-Excesses ranging from 0 to 15% were observed. The isovaline $\delta^{13}C$ was found to be about +18‰. No evidence was obtained suggesting terrestrial contamination in the more abundant L-enantiomer. A correlation was observed between isovaline (also α-aminoisobutyric acid) concentration and PCP content of five CM chondrites. It is suggested that isovaline, along with other meteoritic α-methyl amino acids with ee, are of presolar origin. The possible formation of ee in extraterrestrial amino acids by exposure to circularly polarized light or by magnetochiral photochemistry is discussed.

Key words: Murchison meteorite, Murray meteorite, amino acids, isovaline, chirality, carbon isotopes, PCP.

Introduction

We have found that isovaline (Iva, α-methyl-α-amino butanoic acid), along with four other α-methyl-α-amino acids, occurs in both the Murchison and Murray meteorites with a significant L-enantiomeric excess (Cronin and Pizzarello, 1997; Pizzarello and Cronin, 2000). These chirally asymmetric meteoritic amino acids may have implications for the origin of the homochirality of terrestrial life. If the organic compounds found in carbonaceous chondrites are representative of some fraction of the organic milieu present on the early earth, small enantiomeric excesses therein could have provided a chiral bias sufficient for amplification culminating in homochirality (Pizzarello and Cronin, 2000). α-Methyl-α-amino acids, which resist racemization and are avid helix-formers when polymerized, seem particularly well suited for such a role in prebiotic chemistry.

How meteoritic amino acids came to exist in this enantiomerically unbalanced condition is a question of considerable interest and one that has been posed in a more general context for a long time. Over 100 years ago, Pasteur came to realize that, just as life arises only from life, its chiral asymmetry results from the chiral asymmetry of each preceding generation. Following this line of thought, he wondered what "asymmetric forces" might have acted on organic matter at the time of the origin of life, broken its primordial symmetry, and given impetus to the development of homochirality (Pasteur, 1883).

The amino acids found in carbonaceous chondrites have general characteristics that clearly indicate their production by abiotic processes (Kvenvolden et al., 1970; Cronin and Chang, 1993). They are nearly racemic, structurally diverse, with all possible isomeric forms represented, and are found in amounts that decrease exponentially within homologous series. Furthermore, they are isotopically distinct from their terrestrial counterparts, being substantially enriched in the heavier stable isotopes of C, H, and N (Epstein et al., 1987; Engel et al., 1990; Pizzarello et al, 1991; Engel and Macko, 1997). The isotopic enrichment, particularly in deuterium, is suggestive of chemistry at very low temperature, e.g., the ion-molecule reactions that occur in cold interstellar clouds (Wannier, 1980; Penzias, 1980). Thus, it is possible that meteoritic amino acids are of presolar origin (Epstein et al., 1987).

It has been proposed that circularly polarized light (CPL), electromagnetic energy that is inherently asymmetric, can be generated within an interstellar cloud and interact with its organic compounds, thus giving rise to enantiomeric excesses in the chiral components (Rubenstein et al., 1983; Bonner and Rubenstein, 1987; Bailey et al, 1998). It was later suggested that such a process might account for the asymmetry of the meteoritic amino acids (Cronin and Pizzarello, 1997; Engel and Macko, 1997). In principle, CPL can effect an enantiomeric excess in an amino acid either through synthesis or by the asymmetric photolysis of its racemate. Although the former has not been demonstrated in the laboratory, Flores et al. (1977) produced enantiomeric excesses of about 2% in leucine by photolysis of its racemate with UV CPL. Nishino et al. (2001) extended this work and showed that the photolysis occurs only under acidic conditions and proceeds via a Norrish Type II mechanism to give glycine and hydrocarbons derived from the leucine side chain. Recently, Bonner and Beard (2000) have shown that elliptically polarized UV light (UV EPL) also effects the asymmetric photolysis of DL-leucine.

Because the extinction coefficients of the leucine enantiomers for UV CPL (or EPL) are not very different ($g \cong 0.02$)[1], both enantiomers are subject to photolysis, and substantial enantiomeric excesses are achieved only as the reaction approaches completion. For example, Flores et al. (1977) required 59% and 75% overall decomposition of leucine to achieve 1.98% and 2.50% enantiomeric excess, respectively. From the theoretical treatment of Balavoine et al. (1974) it is seen that a practical limit for ee of about 9% is reached for a fixed population of aliphatic amino acid molecules subjected to irradiation with UV CPL. (For $g \cong 0.02$: ee = 9.2% at 99.99% decomposition.) It seems likely that in any natural setting UV CPL irradiation would occur under conditions inferior to the optimized conditions used in laboratory studies and, consequently, that ee values smaller than maximal, perhaps much smaller, would be observed if asymmetric photolysis of a racemate were the operative mechanism. From this perspective, the L-excesses measured for isovaline in both the Murchison (ee = 6.0%) and Murray (ee = 8.4%) meteorites seem rather large.

The finding of enantiomeric excesses in meteoritic amino acids has been validated in part by the fact that the amino acids showing L-excesses are either unknown or are relatively rare on the Earth and thus are likely to be uncontaminated. In the case of isovaline, terrestrial occurrence is rare but not unknown; consequently, the probability that its enantiomeric ratio in meteorites has been altered by contamination is not zero. In this study, we have carried out both enantiomeric and carbon-isotopic analyses of isovaline from several different Murchison samples and from a sample of the Murray meteorite in order to assess the possibility that contamination has affected its enantiomeric ratio.

Materials and methods

Samples. Murchison analyses are designated either A (various specimens acquired from the collections of the Arizona State University (ASU) Center for Meteorite Studies (ASU 828)) or S (a specimen acquired from the Smithsonian Institution (USNM 5341)). Sample A1 was residual powder from enantiomeric analyses reported earlier (Cronin and Pizzarello, 1997); Sample A2-1 through 5 were approximately 0.5 gm contiguous chips taken about 5 mm below the fusion crust from the face of a freshly broken stone; Sample A3 was residual powder which had been stored below 0° C since the initial analyses of Kvenvolden et al., 1970); Sample A4 was acquired by NASA-Ames Research Center; Sample A5 was a powder prepared at NASA-Ames from pieces of various ASU samples; Sample S1 and S2 were acquired by NASA-Ames.

Sample preparation. Samples not received as powders were crushed and powdered in an agate mortar. The amino acids and other water-soluble compounds were extracted with 100° water. The extract was separated from the insoluble powder by centrifugation, concentrated by rotary evaporation, acidified, and applied to a cation exchange column, which was then eluted sequentially with water and 2N NH_4OH. The NH_4OH eluate was dried, redissolved, applied to a reverse-phase column, and the isovaline fraction collected. After desalting on a small ion-exchange column, N-trifluoroacetyl (TFA)-isopropyl esters of isovaline samples and standards along with a norleucine internal standard were prepared for GC-MS analysis. Details of these preparative procedures are given in Pizzarello and Cronin (2000).

Enantiomeric analysis. Enantiomeric analyses were carried out by GC-MS using either a Hewlett-Packard HP 5580/HP 5970 or HP 5580A/HP5970B instrument equipped with a 25m x 0.25mm capillary column coated with a chiral β-hepta amylose phase of 0.7mm thickness (Chirasil-Dex CB, Chrompack). The operating conditions were: He gas flow, 1.2 ml/min; temperature program: 70°C, 5 min, 70°-100°C at 2°/min 100°-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 using Student's t test of two independent means (Ipsen and Feigl, 1970). The relative retention times of the N-TFA-isopropyl esters of isovaline enantiomers on Chirasil-Dex CB were established to be L (*S*) < D (*R*) using a standard of *S*-isovaline prepared according to the method of Berkowitz and Smith (1995).

Isotopic analysis. Gas chromatographic conditions were as described above. The output of the gas chromatograph (GC) (HP 6890) proceeded through a 0.32 x 30mm deactivated silica column into a Cu-Ni-Pt alumina oxidation reactor maintained at 950°C and then into a Thermoquest Finnigan Delta Plus isotope-ratio mass spectrometer (IRMS) consisting of three Faraday cups (m/z 44, 45, 46) for measurement of CO_2. Data were analyzed using Finnigan ISODAT software. Isotopic ratios were calibrated against a CO_2 reference standard of known composition (-41.72‰) and are presented as $\delta^{13}C$

values relative to PDB. The $\delta^{13}C$ of isopropanol (-27.89‰) was established by elemental analyzer (EA)-IRMS. The EA was a Carlo Erba 1108 in the C, N mode with He as carrier gas. The $\delta^{13}C$ value of trifluoroacetic anhydride (-40.3 ‰) was obtained by GC-C-IRMS of N-trifluoracetamide. The individual mass balance equation for correction of isovaline for the contribution of carbon contributed by derivatization was therefore: $\delta^{13}C_{\mathrm{ival}} = [\delta^{13}C_{\mathrm{ival\ deriv.}} - 0.3\,(-27.89) - 0.2\,(-40.3)]\,/\,0.5$

Amino acid analysis. The data of figure 1 were obtained by ion exchange chromatography with two-temperature o-phthalaldehyde detection (Cronin et al., 1978)

Results and discussion

Relation to previous work. Some of the isovaline enantiomeric excesses shown in Tables 1 and 3 differ greatly from the earlier results of Kvenvolden et al. (1970). More to the point, reanalysis of the same Murchison powder used in their pioneering work (Sample A3, Table 1) gave L-ee values of 3.6% and 2.6% for exterior and interior samples, respectively. These values are perhaps near the precision limit of the method used in the earlier work. It should be remembered that it was carried out, not with the goal of establishing the exact enantiomeric ratio of the amino acids, but rather to evaluate the possibility that amino acids are indigenous to the meteorite and are products of abiotic chemistry. Consequently, the results of our reanalysis are not in serious disagreement with the earlier conclusion that amino acids occur in Murchison with "almost equally abundant enantiomers." A more serious disagreement is with the more precise work of Pollock et al. (1975), who found Murchison isovaline to be exactly racemic. This analysis was intended to accurately determine the isovaline enantiomer ratio; however the fractionated sample used still retained numerous other components and the analysis did not include mass spectral assessment of the purity of the enantiomer peaks. Therefore, it cannot be considered definitive. Sample heterogeneity with respect to ee, which is discussed below, may also be a factor in our failure to replicate that finding.

Contamination and isovaline enantiomeric excesses. The data presented in Tables 1 and 3 show a surprising range of ee values for the various samples analyzed, i.e., from essentially zero (racemic) to an L-excess of 15.2%, values substantially less and much greater, respectively, than those observed by us heretofore (Cronin and Pizzarello, 1997; Pizzarello and Cronin, 2000). In order to assess the possibility that varying degrees of terrestrial contamination were responsible for these differences, analyses were carried out on samples of the Murchison meteorite taken from near the surface (exterior) as well as from below the contamination zone (interior). The results are given in Table. 1. It is commonly observed that surficial samples of meteorites are contaminated with terrestrial matter and samples taken from the interior less so or not at all (Harada and Hare, 1980). Consequently, if contaminant isovaline were contributing to the enantiomeric excess, larger ee values would be expected for the exterior samples. In the two cases where a direct comparison can be made, samples A2 and A3, this is not observed, rather a larger L-ee was found in the interior sample of both.

This argument against contamination is based on the assumption that terrestrial isovaline, like most biological amino acids, is of the L-configuration; however, this assumption may not be valid. The most extensive and potentially pervasive known terrestrial occurrence of isovaline is in a large family of fungal peptides, the peptaibols (Whitmore et al., 2000), where it is found as the D-enantiomer (Brückner et al., (1980).[2] Unless special precautions are taken in meteorite curation, some contamination of surfaces and fissures with airborne fungal spores is unavoidable, and fungal growth has been documented in at least one Murchison specimen (Steele et al., 1999). If fungal peptaibols contribute isovaline to meteorite samples, it would have the D-configuration and tend to diminish any inherent L-enantiomer excess. On the other hand, cleavage of peptide bonds with release of free D-isovaline from peptaibols seems unlikely under the extraction conditions used in this work. Since the peptaibols are believed to be made by non-ribosomal peptide synthesis, it is also possible that free L- and/or D-isovaline are produced by fungi as precursors of the peptide-bound D-enantiomer (Turner, 2001).

Contamination of indigenous isovaline by terrestrial isovaline would, in addition to altering the enantiomeric ratio, decrease its isotope ratio because terrestrial amino acids are isotopically lighter than those of CM chondrites (Engel et al., 1990; Engel and Macko, 1997). In order to determine whether or not this is the case, we carried out carbon-isotopic measurements of the isovaline enantiomers by GC-C-IRMS and the results are shown in Table 2. The data have been corrected for the enantiomeric difference observed with standard isovaline assumed to be enantiomerically isobaric. It can be seen from these data that (1) the isovaline carbon from four Murchison samples and a Murray sample is isotopically heavy as expected and (2) the D-enantiomer is apparently lighter than the L-enantiomer, although considering that $\Delta\delta^{13}C$ value is ≤ 2 ‰ in four of the five samples and the σ values are of comparable magnitude, the significance of these differences is doubtful. Thus there is no isotopic basis for believing the L-excess to be a result of contamination. In the case of sample A1, for which the $\Delta\delta^{13}C$ value 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.

Intra sample variation of the isovaline ee. The great variation in the enantiomeric excesses observed in isovaline from different Murchison samples prompted us to investigate the variation within an individual stone. For this analysis approximately 0.5 gm contiguous chips were taken from a freshly exposed surface of a single stone. The results are given in Table 3. Again, variation of L-ee values over a wide range (3.8% to 15.0%) was observed.

Isovaline ee and amino acid composition. In an attempt to better understand the variation observed in isovaline ee values, isovaline/alanine (Iva/Ala) and isovaline/α-aminoisobutyric acid (Iva/Aib) ratios are given in Tables 1 and 3 as an index of differences in overall amino acid composition among the samples. We have previously noted interesting variations in the amino acid composition of different Murchison stones (Cronin and Pizzarello, 1983). The ratios of the α-methyl amino acids to α-H amino acids, e.g., Iva/Ala, have been seen to vary considerably among Murchison samples, although the ratios of the amounts of individual α-methyl amino acids to each other, e.g., Iva/Aib, and of α-hydrogen amino acids to each other remain nearly constant. Thus the α-methyl amino acids appear to comprise a set that is separate in some way from the α-hydrogen amino acids and subject to independent quantitative variation

It can be seen in Tables 1 and 3 that, as expected, the Iva/Aib ratios show little variation among samples, while the D-Iva/D-Ala are quite variable, even among samples from the same stone (Table 3). (The D-enantiomers were used for this comparison rather than total amounts because D-alanine is expected to be entirely indigenous.) In the data of Table 3 there is a correlation between a high content of α-methyl amino acids (high D-Iva/D-Ala) and the magnitude of the enantiomeric excess; however, this is not clearly seen in the data of Table 1.

The independent variation of these two general types of amino acid (α-methyl and α-hydrogen) suggests their association with different matrix phases. If so, their quantitative variation could reflect differences in the mixing ratio of these phases in the meteorite volume sampled. We have previously suggested an association of the amino acids of CM chondrites with so-called PCP [3] based on a correlation of the amount of this material and the total amino acid content of five CM chondrites (Cronin, 1989). In figure 1 we attempt to illustrate how the α-methyl and α-hydrogen amino acid suites correlate with the PCP content of these CM chondrites. The amino acid data are from analyses of the Murchison (1969), Bells (1961), Murray (1950), Santa Cruz (1939), and Crescent (1936) meteorites, the five most recent CM chondrite falls, and the PCP volumes are calculated from the data of McSween (1979, 1987). In figure 1a the correlation between the Iva/Ala ratio and PCP content of these meteorites can be seen. In figure 1b the meteoritic concentrations of Iva, Ala, and Aib (the most abundant α-methyl amino acid in CM chondrites), are plotted vs. PCP volume. From these data it is clear that the increase in the Iva/Ala ratio is dominated by the increase in Iva, the α-methyl amino acid, rather than by a systematic decrease in Ala. Both Iva and Aib increase sharply with increasing PCP content suggesting that, as we have previously noted, the α-methyl amino acids behave as a distinct group in this regard. The observation of this heterogeneity in 0.5g samples suggests that the associated mineral phase may have dimensions of the order of a mm or so.

One can only speculate as to the meaning of an association of the α-methyl amino acids and their enantiomeric excesses with the PCP phase of carbonaceous chondrites. The deuterium enrichments of chondritic amino acids, which suggest low-temperature interstellar chemistry, the lack of a plausible theory by which to explain the de novo formation of amino acids with enantiomeric excesses in the wet, dark interior of a chondritic parent-body, and the potential of photochemical theories to explain the origin of ee in organic compounds in presolar environments (see below) combine to suggest an interstellar origin for these compounds. If this is so, PCP may represent only partially altered interstellar grain matter which still retains much of its original organic content.

Origin of enantiomeric excesses. The apparent lack of a contribution from contamination and the finding of ee values up to 15% exacerbates the problem of accounting for the high ee values of meteoritic isovaline noted previously. Photosynthesis driven by UV CPL is limited to ee values governed by the *g*-value, i.e., approximately 1% and, as discussed previously, preferential photolysis of a racemate by UV CPL seems unlikely to have reached such values if conceived of in terms of the laboratory model, i.e., a single exposure of a fixed population of molecules to UV CPL. However, two possibilities mentioned by Balavoine et al. (1974) seem worth considering in this context. If a mechanism existed whereby the residual fraction of photolyzed amino acids could be accumulated from a large volume and experience a second exposure to UV CPL, this time starting with the small ee achieved previously, a further enhancement in ee could be attained, although again at the expense of the total amount of amino acid surviving. Such a process of accumulation and re-exposure might be envisioned occurring as an interstellar cloud collapses in the process of nebula formation. The second possibility is the secondary formation of amino acids by an asymmetric catalyst. In this case one must imagine the formation of an asymmetric catalyst by the preferential photolysis of a racemic compound (perhaps having a higher *g*-value than that of the aliphatic amino acids and thus achieving greater chiral purity in the process) and this enantiomerically enriched catalyst then acting to promote the formation of amino acids with substantial enantiomeric excesses. A third possibility, magnetochiral photochemistry. i.e., photochemistry with unpolarized light in a magnetic field, has recently been suggested as a possible chiral influence on the organic chemistry of the interstellar medium (Rikken and Raupbach, 2000). In this case, ee is dependent on the magnetic field strength and, presumably, rather large ee values could be obtained.

Conclusions

1. The magnitude of isovaline L-enantiomeric excess varies between and within samples of the Murchison meteorite, ranging from 0 (racemic) to 15%.

2. The average $\delta^{13}C$ value of Murchison isovaline is about +18‰ and the D- and L-enantiomers are not significantly different with respect to carbon isotope ratio.

3. Enantiomeric excess (ee) values determined for interior and exterior samples, along with carbon isotopic measurements, give no indication of a contamination contribution to the ee values determined for Murchison isovaline.

4. Isovaline and other α-methyl amino acids appear to be associated with PCP, i.e., serpentine/tochilinite aggregates, in the Murchison matrix.

5. The enantiomeric excesses observed in the Murchison α-methyl amino acids seem to be best explained by the operation of chiral photochemical processes in the presolar environment.

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Footnotes

1. The anisotropy factor, $g = \Delta\varepsilon/\varepsilon$, where $\Delta\varepsilon = \varepsilon_{LCPL} - \varepsilon_{RCPL}$, and $\varepsilon = 1/2\ (\varepsilon_{LCPL} + \varepsilon_{RCPL})$ = molar extinction coefficient of the racemate.

2. Isovaline has been reported in terrestrial sediments (Zhou and Bada, 1989; Mita and Shimoyama, 1998) where it is racemic and would not affect the enantiomer ratio significantly even in the unlikely event of meteoritic contamination.

3. The matrix of carbonaceous chondrites is composed of fine-grained hydrous silicates (serpentines) and complex Fe-Ni-S-O-bearing phases, the so-called "poorly characterized phases" (PCP) now known to be composed of cronstedtite, tochilinite, magnetite, troilite, pentlandite, calcite, and carbonaceous matter. PCP is now sometimes referred to as tochilinite/serpentine aggregates.

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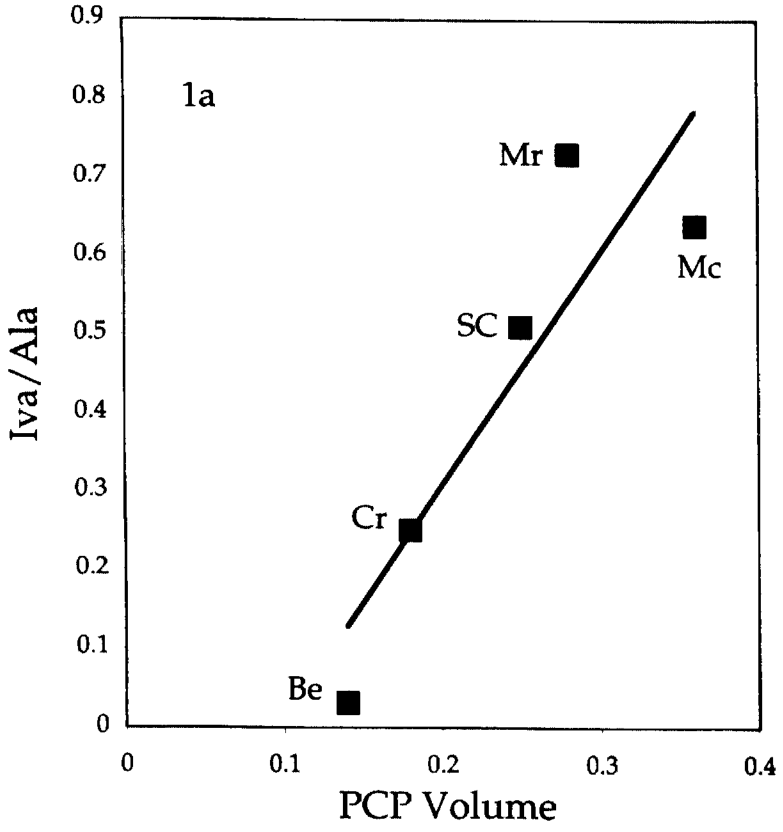
Figure legend

Fig. 1 (a) Plot of Iva/Ala ratio vs CM chondrite volume fraction PCP. Iva/Ala was determined by ion exchange amino acid analysis and meteorite volume fraction PCP was calculated from the data of McSween (1979; 1987) as described in Cronin and Pizzarello (1983). (b) Plot of CM chondrite concentrations of Iva ▲, Aib ■, and Ala O, vs. PCP volume as in (a). Meteorite abbreviations: Bells, Be; Crescent, Cr; Murchison, Mr; Murray, Mu; Santa Cruz, SC. The Murchison data points represent amino acid analyses of two samples obtained, respectively, from the collections of Arizona State University and the Smithsonian Institution.


1a
Iva/Ala
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
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0.2
0.3
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PCP Volume
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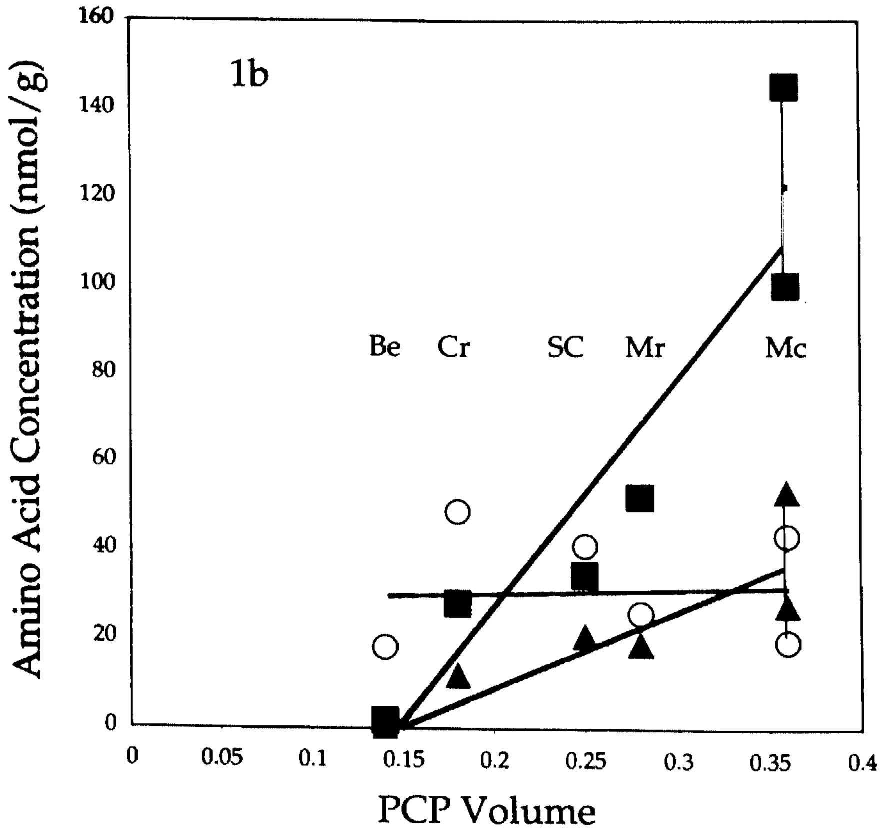
1b
Amino Acid Concentration (nmol/g)
160
140
120
100
80
60
40
20
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
PCP Volume
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Table 1. Variation of isovaline L-enantiomer excess among Murchison stones.

Sample	Location	Iva/Aib	D-Iva	L-Iva	n	σ	L-ee	Corrected
			D-Ala	(%)			(%)	L-ee (%)
A1	interior	----	----	52.4	14	0.5	4.8	5.2
A2	interior	0.28	6.8	57.4	8	0.2	14.8	15.2
A2	exterior	0.24	0.8	56.1	6	0.4	12.2	12.6
Standard	----	----	----	49.8	8	0.6	-0.4	0
A3	interior	0.31	2.0	51.3	5	0.3	2.6	3.6
A3	exterior	0.27	1.3	50.8	7	1.3	1.6	2.6
A4	interior	0.27	1.0	52.5	5	0.4	5.0	6.0
A5	?			52.8	5	1.0	5.6	6.6
S1	exterior	0.15	0.3	49.6	6	0.3	-0.8	0.2
S2	exterior	0.21	0.5	51.2	8	0.6	2.4	3.4
Standard	----	----	----	49.5	22	0.6	-1.0	0

Table 2. $\delta^{13}C$ (‰) values for meteoritic L- and D-isovaline.

Sample	Location	L-Ival	σ	D-Ival	σ
A2-6	interior	+18.0	0.3	+16.0	1.9
A1	interior	+17.8	1.9	+11.5	1.6
A2	exterior	+21.9	1.2	+19.9	0.9
S	exterior	+17.5	---	+17.3	---
Murray	interior	+20.0	2.5	+18.8	1.7
average	----	+19.0	1.9	+16.7	3.3
Standard	----	-28.0	0.9	-31.9	1.2

Table 3. Spatial variation of isovaline L-enantiomer excess within a Murchison stone.

Sample	Location	Iva/Aib	D-Iva	L-Iva	n	σ	L-ee	Corrected
			D-Ala	(%)			(%)	L-ee (%)
A2-1	interior	0.24	2.1	57.3	6	1.0	14.6	15.0
A2-2	"	0.20	0.5	51.7	8	0.6	3.4	3.8
A2-3	"	0.30	2.9	57.1	5	0.4	14.2	14.6
A2-4	"	0.31	0.6	52.9	8	0.5	5.8	6.2
A2-5	"	0.40	6.7	56.4	6	0.4	12.8	13.2
Standard	----	----	----	49.8	8	0.6	-0.4	0