

THE CHIRAL AMINES OF THE MURCHISON METEORITE: A PRELIMINARY CHARACTERIZATION. S. Pizzarello, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287. *pizzar@asu.edu*

L-enantiomeric excesses have been determined for some amino acids of the Murchison and Murray meteorites [1-4]. The finding has taken a particular significance in view of the homochiral distribution of biochemical molecules and the possible contribution of asymmetry-carrying organics to the early Earth by meteorite and cometary delivery. So far, evidence of non-racemic compounds in meteorites has been limited to a series of α -substituted amino acids, of which isovaline (2-amino 2-methyl butanoic acid) is the first homologue. This amino acid has been found in Murchison with varying L-enantiomeric excesses of up to 15% [5], the largest value determined to date.

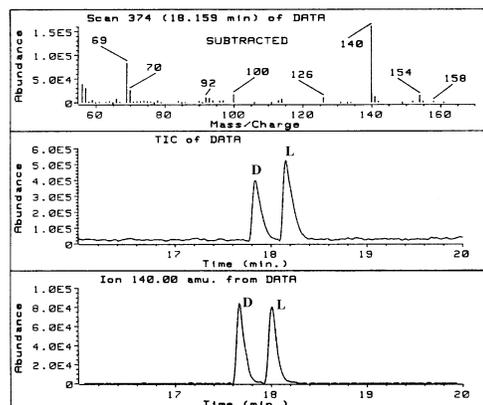
Amines are an abundant group of water-soluble organics in CM chondrites where they are found as a series of alkyl compounds of one to at least five-carbon chain length. Meteoritic amines show isotopic enrichments in deuterium, ^{13}C , and ^{15}N which are comparable to those displayed by amino acids with $\delta^{15}\text{N}$ values, in particular, that are very similar in both classes of compounds (+90 to +94%) [6]. In view of these similarities it has been proposed that at least a fraction of meteoritic amines could have derived from amino acids *via* decarboxylation, which is a common pathway of thermal decomposition for α -amino acids. The molecular distribution of Murchison amines would be compatible with this proposal, since sixteen of the twenty amines identified in the meteorite could have derived from known Murchison α -amino acids.

We report here an investigation of the chiral distribution of Murchison amines, obtained from a 20 g stone of the meteorite (Center for Meteorite Studies, Arizona State University). Amines were collected from the water extracts as volatile bases (at pH \sim 12) by cryogenic transfer and subsequently separated by HPLC (BIORAD, Aminex HPX-72-O column) into fractions of individual or small groups of compounds of similar carbon chain length. Amines were again recovered from these samples by cryogenic transfer and then dried as hydrochloride salts. Chiral analyses were performed by Gas Chromatography-Mass Spectrometry (GC-MS) of the amine volatile N-trifluoro acetyl (TFA) or N-pentafluoro propionyl PFP) derivatives [6], using a fused silica column coated with a cyclodextrine bonded phase (CHROMPACK, CP-Chirasil-Dex CP, 25m x 0.25mm, 0.25 μm df).

The identification of individual Murchison amines was achieved by comparison of their mass spectra and

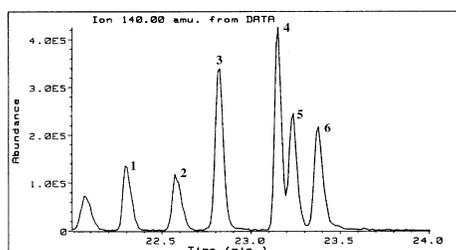
chromatographic retention times with those of derivatized standards. This is a common compound recognition process which became particularly important for amines since these compounds share very low ionization energy and a simple α -cleavage fragmentation which is not always accompanied by M^+ , $\text{M}-1^+$, or other diagnostic low abundance ions (e.g. all α -H, and α -methyl compounds have base peaks at m/z 126 and 140, respectively). Also the GC phase employed is unpredictable as to the order of elution of the two enantiomers of a chiral compound, whose identification always requires confirmation with individual enantiomer standards. Being chiral amines less numerous than amino acids, of the twenty four alkyl amines with one- to five-carbon chain that can be derivatized with TFA (i.e. excluding the N-disubstituted species) only five have one chiral center. These amines are: *sec*-butyl; 1-, and 2-methyl butyl; 1, 2-dimethyl propyl; and N-methyl *sec*-butyl.

A positive L-enantiomeric excess has been determined for Murchison *sec*-butyl amine that has the value of 17.8%, with a $\sigma=0.8$ for six data. Figure 1 shows the mass spectrum of the meteoritic amine (top) and its chromatographic separation (center) compared with that of a standard.



No other chiral identification could be established with certainty for the remaining amines isolated from the Murchison extract. An example of these findings is given in Figure 2, that shows the GC resolution of three meteorite amines, by m/z 140 single ion. 1, 2-dimethyl propyl amine enantiomers (peaks 1,2) show a small enantiomeric excess of peak 1 over peak 2 (of \sim 1.5%) that cannot be characterized for lack of single enantiomer standards and an unknown six-carbon amine (3, 4) similarly cannot be identified for lack of standards,

while showing one of the enantiomers with an approximate excess of 1.7%. The remaining peaks (5, 6) represent 1-methyl butyl amine enantiomers that appear to be racemic.



The results of the Murchison *sec*-butyl amine analysis represent the first finding of L-enantiomeric excesses in meteorites outside the α -amino acid subgroup. *Sec*-butyl (1-methyl propyl) amine is also a α -substituted compound and has the same carbon-nitrogen molecular structure as the amino acid isovaline, from which it derives upon decarboxylation. The value of the amine L-excess is also comparable to those shown by isovaline in Murchison and this correspondence of chiral data appears to support the suggestion of a secondary, thermal production of the amine from the amino acid

It has been proposed that the optical activity observed in some meteoritic amino acids could be the result of UV Circularly Polarized Light (CPL) irradiation of the compounds during their syntheses, accompanied by the asymmetric decomposition of amino acid racemic mixtures. The likelihood of this assumption was supported by the fact that the enantiomeric excesses initially observed in meteoritic amino acids were within the range predicted for the UVCPL chiral effect [2]. UV CPL is asymmetric radiation that can photolyze the enantiomers of a chiral compound with different rates and produce, with time of irradiation, enantiomeric excesses. However, the extent of these excesses will vary with the degree of anisotropy of absorption for a chiral molecule and it can be shown [7] that alkyl amino acids have a maximum attainable enantiomeric excess of about 9% upon UV CPL induced decomposition.

The UV CPL photolysis model, therefore, appears inadequate to explain the new chiral data established for *sec*-butyl amine, as well as those previously determined for isovaline, and requires us to look to other possible processes for their formation. A possibility mentioned by Balavoine et al. [7] seem particularly worth considering in this context as it could be applied to interstellar as well as nebular and planetary processes. It is the secondary formation of amino acids, and therefore their derivatives, by an asymmetric catalyst. In this case one must imagine the formation of such catalyst by the preferential photolysis of a racemic compound having a

larger difference between the extinction coefficients of its enantiomers than those of aliphatic amino acids and thus able to achieve greater chiral purity in the process. This enantiomerically enriched catalyst could then act to promote the formation of amino acids with substantial enantiomeric excesses.

As for L-enantiomeric excesses in other soluble organics extracted from a meteorite of fairly long terrestrial exposure, the possibility of contamination needs to be addressed for these data also. Similarly to isovaline [5], *sec*-butyl amine has a limited distribution in the biosphere, where it is found as an agricultural fungicide [8]. This would make a terrestrial contamination by the L-enantiomer of the amine very unlikely although not impossible, given the volatility of the compound.

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