Bioastronomy 2002: Life Among the Stars
IAU Symposium, Vol. 213, 2004
R.P.Norris and F.H.Stootman (eds.)

Extraterrestrial Chirality

Jeremy Bailey

Anglo-Australian Observatory, PO Box 296, Epping, NSW 1710

Abstract.
The homochirality of biological molecules — the almost exclusive use of L-amino acids and D-sugars — is a fundamental property of life, but its origin poses a problem. Recent work has shown an excess of the L enantiomer in amino acids in the Murchison and Murray meteorites, supporting the model, first proposed by Rubenstein et al. (1983) of an extraterrestrial origin for homochirality. This paper discusses the evidence for extraterrestrial chiral asymmetry, the processes which could have led to such asymmetry, and the possible relevance for the origin of biological homochirality on Earth.

1. Introduction

The discovery of the chirality of molecules was made more than 150 years ago by Louis Pasteur. In 1848 Pasteur found that sodium ammonium paratartrate formed crystals of two types with structures which were mirror images of each other. Pasteur correctly interpreted these crystal structures as representing an underlying asymmetry in the molecules which could exist in either left handed or right handed forms (enantiomers). Pasteur's further investigations revealed that such molecular asymmetry was found only in the products of living organisms. He speculated that understanding the origin of asymmetry might provide a key to the nature of life, and that it might reflect some cosmic asymmetric force (Haldane 1960).

The modern interpretation of chirality is that it usually arises as a result of the tetravalent nature of carbon. This leads to chiral asymmetry in cases where four different groups attach to a carbon atom. Thus many organic molecules are chiral, and when produced in living organisms are invariably found in homochiral form (molecules of only one handedness) whereas the same compounds, if synthesized in the laboratory from achiral precursors, would be made in the racemic form (an equal mixture of left and right handed molecules). Specifically the amino acids which are the building blocks of proteins are found only in the L-configuration whereas sugars (including the ribose and deoxyribose components of RNA and DNA) are found only in the D-configuration.

In general chemical processes only produce homochiral products starting from other homochiral molecules. Thus there is a problem of explaining how homochirality originated. The difficulty of finding any process that could have operated on the early Earth, has led to the suggestion of an extraterrestrial origin for homochirality through the action of circularly polarized light (Rubenstein et al. 1983; Bonner 1991). Support for this idea has come from the finding of an excess of the L-enantiomer in some amino acids in the Murchison meteorite.

2. Evidence for Extraterrestrial Chirality

The principle evidence supporting an extraterrestrial origin for biomolecular homochirality comes from the observation of excesses of L-amino acids in the Murchison and Murray meteorites. There have been a number of reports of an excess of the L-form of common protein amino acids such as alanine in the Murchison meteorite (Engel & Nagy 1982; Engel, Macko, & Silfer 1990; Engel & Macko 1997).

Cronin & Pizzarello (1997) have studied a number of the α-methyl amino acids which are present in the Murchison Meteorite. This series of amino acids has a methyl group in place of the hydrogen attached to the α-carbon atom. They are of interest for two reasons. Firstly they are rare or unknown in the terrestrial biosphere, while being relatively common in the Murchison meteorite. Secondly the lack of a hydrogen on the chiral centre carbon atom makes them highly resistant to racemization (Bada 1991) and thus likely to preserve any enantiomeric excess for long periods. Cronin & Pizzarello (1997) found excesses of the L enantiomer ranging from 2 to 9% in a number of these amino acids. They have also found similar but slightly smaller excesses in the same amino acids in the Murray meteorite (Pizzarello & Cronin 2000). More recently Pizzarello (2002) has reported that the enantiomeric excess of isovaline (the commonest of the chiral α-methyl amino acids) varies between different samples and different locations within the Murchison meteorite with values ranging from 0-15%.

2.1. Contamination

It is important to exclude the possibility of contamination by terrestrial biological material as an explanation for the excess of L-amino acids in meteorites. It is well established that such contamination can easily occur (Steele, Toporski & McKay 2001) and indeed the original reason for looking at enantiomer ratios in Murchison was to exclude contamination since abiotic amino acids would normally be expected to be racemic. However, with the increasing evidence for intrinsic L-excesses in the extraterrestrial amino acids we need other ways to exclude contamination. The following arguments support an extraterrestrial origin for the amino acids showing the L-excesses.

- L-excesses are found in α-methyl amino acids which are rare or unknown in the terrestrial biosphere, whereas no excess is found in the corresponding α-hydrogen amino acids (Cronin & Pizzarello 1997; Pizzarello & Cronin 2000).

- Stable isotope ratios of carbon and nitrogen are consistent with extraterrestrial values rather than with the terrestrial biosphere (Engel & Macko 1997; Pizzarello 2002).

- Cronin & Pizzarello (1997) investigated 2-amino-2,3-dimethylpentanoic acid which has two chiral centers and thus four stereoisomers. They found

L-excesses for both of the enatiomer pairs, whereas biological production would be expected to form only one of the four stereoisomers.

These results would seem to rule out the possibility of the L excesses being the result of terrestrial contamination. Thus we appear to be seeing the result of an abiotic asymmetric process which had already occurred by the time of the formation of the meteorite 4.5 billion years ago.

However, there remains a difference between the results reported by Engel & Macko (1997) who find enantiomeric excesses in α-hydrogen amino acids (e.g., common protein amino acids such as alanine) and those by Pizzarello & Cronin (2000) who find excesses only in the α-methyl amino acids and not in their α-hydrogen analogues. Pizzarello & Cronin (1998) have suggested that the results of Engel & Macko (1997) may be innacurate as a result of insufficient chromatographic resolution.

3. The Origin of Extraterrestrial Chirality

The mechanism which has been most discussed for the origin of the enantiomeric excesses is the action of circularly polarized light (CPL). Ultraviolet CPL can discrimate between the enantiomers of amino acids through the process of asymmetric photolysis. Under CPL the two enantiomers are destroyed at slightly different rates leaving a slight excess of one enatiomer. This process has been demonstrated in a number of experiments (e.g., Flores, Bonner, & Massey 1977). However, the difference between the rates is small for amino acids so it is difficult to obtain enantiomeric excesses of more than a few per cent in this way.

For this process to operate in space we require that either amino acids, or some chiral precursor of the amino acids are present in interstellar material, and that there is a source of UV CPL. Attempts to detect gas-phase glycine in molecular clouds by means of its radio rotational lines have so far been unsuccessful (Snyder et al. 1983; Combes et al. 1996). However, several recent experiments show that amino acids or amino acid precursors can be formed by UV irradiation of simulated interstellar ice mixtures (Bernstein et al. 2002; Munoz Caro et al. 2002; Kobayashi et al. 2002). This suggests that the failure to detect glycine in the gas phase may be due to the fact that amino acids are present predominantly in the icy grain mantles, or may mean that amino acid precursors are present in the interstellar medium, with the amino acids themselves only being formed later by hydrolysis in the meteorite parent bodies.

Synchrotron radiation from neutron stars in supernova remnants was originally suggested as a source of UVCPL (Rubenstein et al. 1983; Bonner & Rubenstein 1987; Bonner 1991; Greenberg et al. 1994). However, very few supernova remnants show any optical synchrotron radiation, and in those that do (the very youngest remnants) no significant circular polarization is observed (Bailey 2001).

Substantial circular polarization has been measured in Infrared observations of high-mass star formation regions — 17% in Orion OMC-1 (Bailey et al. 1998; Chrysostomou et al. 2000) and 23% in NGC6334V (Ménard et al. 2000). The high polarization is attributed to scattering from aligned dust grains. The high dust obscuration to these massive star formation regions means that observations are only possible in the IR. However, calculations of the scattering of light from aligned grains with standard compositions and size distributions show that substantial circular polarization could still be produced at the UV wavelength required for asymmetric photolysis of amino acids (Bailey et al. 1998; Gledhill & McCall 2000).

However, there are difficulties in getting a geometry in a young stellar object such that large circular polarization would be seen by the dust grains (Lucas 2002), and even with 100% circular polarization it is hard to explain the levels of enantiomeric excess seen. This suggests that direct asymmetric photolysis of amino acids, as studied experimentally, is not sufficient to explain the meteorite asymmetries. Alternative possbilities are that the circular polarized light operates on some other molecule with larger circular dichroism, that is either a precursor or a catalyst in the reactions which subsequently make the amino acids, or that some photochemical process other than photolysis is involved.

4. Extraterrestrial Chirality and the Origin of Life

Finally we address the question of whether the chiral asymmetry present in early solar system material, as indicated by the Murchison and Murray results, could have played a role in the origin of biological homochirality.

There are a number of issues here. Firstly it is not clear how typical Murchison is of the material that might have been present in the early solar system. The recently studied Tagish Lake meteorite for example, showed a very different mix of organic material with few amino acids (Pizzarello et al. 2001). Comets should provide a better example of primordial solar system material, and space missions such as Rosetta will be able to study cometary material and even undertake chiral analysis (using the COSAC instrument, Thiemann & Meierhenrich 2001) to search for enantiomeric excesses similar to those seen in Murchison.

The material must then be delivered to Earth during the heavy bombardment phase. The Murchison meteorite shows that small bodies can reach the surface of Earth with their organic material intact as can interplanetary dust particles, but the amount of organic material reaching Earth in this way would be small. Much more organic material would reach the surface if impacts of large asteroids and comets can also contribute and there is increasing evidence that this is the case. Zhao and Bada (1989) have reported extraterrestrial amino acids at the K/T boundary, and extraterrestrial fullerenes have been reported at the K/T (Becker, Poreda, & Bunch 2000) and Sudbury (Becker, Poreda, & Bada 1996) impacts. Theoretical (Pierazzo & Chyba 1999) and experimental (Blank et al. 2001) studies of impact processes also suggest that survival of organics is possible in at least some cases.

Once the organic material reaches the surface of the Earth and gets into the oceans the α-hydrogen amino acids will begin to racemize on timescales which are short compared with their destruction timescales of $\sim 10^7$ years (Bada & Miller 1987). However, the α-methyl amino acids do not racemize significantly within their lifetimes (Bada 1991). Since these amino acids are relatively abundant in Murchison and have been shown to show enatiomeric excesses, these amino acids are likely to be the main carriers of chiral asymmetry in prebiotic material.

https://doi.org/10.1017/S0074180900193143 Published online by Cambridge University Press

The currently favoured idea for the origin of life is that the DNA-RNA-protein basis for life, was preceeded by an "RNA-World" phase in which RNA provided both the genetic material and the catalysts. This RNA-World may itself have been preceeded by a "pre-RNA-World" the nature of which is still uncertain. In this model protein synthesis is invented by the RNA-World, and it is not clear if proteins or peptides had any role in life before this stage. However, homochirality is required for an RNA-World to operate, and therefore may have originated before proteins were used by life. How, then could amino acid enantiomeric excesses have influenced the chiral development of life? A possible clue is provided by the results of Shibata et al. (1998). Their experiments show autocatalytic amplification of enantiomeric excess in which a chiral initiator with a small enantiomeric excess (as little as 0.1%) causes the system to develop a large enantiomeric excess (up to ~80%). The process worked with a range of different initiator compounds including amino acids. If some early stage in the origin of life had similar properties then an extraterrestrial compound with a small enantiomeric excess could act as the initiator. This need not be a compound that is currently associated with life. The α-methyl amino acids would be promising candidates.

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