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On the Selection of Biomolecular Chirality during Chemical Evolution

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ON THE SELECTION OF BIOMOLECULAR CHIRALITY DURING CHEMICAL EVOLUTION (*)

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Abstract. From the point of view of (a) chemical evolution and (b) exobiology (the origin of life in the universe), we discuss the possibility that the source of homochirality may be of extraterrestrial origin. The recent suggestions for testing this possibility in future planetary missions are discussed. In particular, we consider some factors that should be taken into consideration due to the possible presence (in the cell wall of some bacteria) of enantiomers of the opposite chirality to that found in proteins. We also discuss the implications of phase transitions of the type postulated by Salam in 1991 to occur in racemic mixtures of amino acids. Salam's contribution referred to the role of phase transitions in the induction of the observed homochirality of protein amino acids. This was assumed to occur in a racemic mixture that, as a consequence of the conjectured phase transition, turned homochiral beneath a certain critical temperature T_c . In the present review we discuss selected theoretical aspects of the question of homochirality. The relevance of starting a new generation of experiments is pointed out, as suggested by the present author in 1991. These experiments should test a form of condensed matter that has so far not been at the forefront of research from the point of view of the phase transitions. We discuss those aspects of the origin of homochirality which are still valid and require verification.

1. Introduction

1.1. CHEMICAL EVOLUTION AND THE ORIGIN AND EVOLUTION OF LIFE

The preliminary questions that are raised when we attempt to lay the scientific bases of the origin of life are: Where did the biomolecules come from?. Were they synthesized on Earth or, is there a need to study this problem in the context of exobiology (i.e., within a systematic search for life beyond the Earth)?

In order to gain some insights into these fundamental questions it is important to recognise molecular relics of earlier stages of chemical and biological evolution. This review is devoted to one of the most important relics amongst them, but we should be aware from the beginning about the broad spectrum of conditions in which biomolecules can present themselves in the universe.

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We have seen in the introductory lecture that all the basic building blocks of life can, in principle, be synthesized in the laboratory. The question of how such synthesis may have occurred in the early Solar System is not an idle one:

Firstly, four satellites with atmospheres resembling the Earth's paleoatmosphere exist in the Solar System. Io is the first (closest) of the Galilean satellites of Jupiter (which has altogether 16 satellites). Io has a thin atmosphere of sulphur dioxide.

The second Jovian moon, and the smallest of the Galilean satellites) Europa has some oxygen in its atmosphere (Hall *et al.*, 1995). Titan, perhaps the most intriguing component of the Solar System (cf. below), is a satellite of Saturn. It is surrounded by mainly molecular nitrogen atmosphere, but there is also a substantial component of methane.

Finally, the last satellite known to have an atmosphere is Triton, the largest of the eight known moons of Neptune. It has a tenuous atmosphere with surface pressure of 15 microbars, mainly of nitrogen but with a trace of methane. It is remarkable that one of the components of the model paleoatmospheres of the chemical evolution experiments (ammonia) does not seem to be present in appreciable quantities in any of the satellites that have an atmosphere.

Secondly, chemical evolution is turning into an important chapter of the space sciences. This development may be illustrated with the questions raised by current studies of Titan. In the atmosphere of this satellite, the largest of Saturn's 18 confirmed satellites (bigger than even Mercury), biopolymers may possibly arise in this planet-like satellite. Indeed, under the action of sunlight it is possible that there may be liquid bodies of mixtures of ethane or methane on its surface. The Cassini-Huygens mission, under preparation at present, will attempt to obtain more reliable information on Titan. It includes a spacecraft (Cassini, built by NASA) bearing the atmospheric probe Huygens (built by the European Space Agency). The mission is due for launch in October, 1997 (Raulin *et al.*, 1995).

1.2. CHEMICAL EVOLUTION IN THE EARLY EARTH ATMOSPHERE

Chemical evolution on Earth seems to have taken place from 4.6-3.9 thousand million years before the present (Gyr bp), a geologic time interval which is known as the Hadean subera within the Archean era. It should be noticed, however, that considering the impacts by large asteroids in the early Earth does not necessarily exclude the possibility that the period of chemical evolution may have been considerably shorter. Indeed, the Earth may have been continuously habitable by non-photosynthetic ecosystems from a very remote date, namely since approximately 4.44 Gyr bp (Sleep *et al.*, 1989). In subsequent suberas of the Archean (3.9-2.5 Gyr bp) life, as we know it, certainly was present. This is well represented by fossils of the domain Bacteria, which is particularly well documented by many species of the phylum Cyanobacteria (Schopf, 1993). Once again, it should be kept in mind that the content and the ratios of the two long-lived isotopes of reduced organic carbon in some of the earliest sediments (retrieved from the Isua peninsula, Greenland, some 3.8 Gyr bp), may convey a signal of biological carbon fixation (Schidlowski, 1995). This reinforces the expectation that chemical evolution may have occurred in a brief fraction of the Hadean subera, in spite of the considerable destructive potential of large asteroid impacts during the same geologic interval in all the terrestrial planets, as well as on the Moon.

2. The search for the origin of homochirality

2.1. IS THE ORIGIN OF HOMOCHIRALITY EXTRATERRESTRIAL?

The property of homochirality is particularly relevant in the identification of microorganisms for the *in situ* search for extraterrestrial homochirality (SETH), an

endeavour that is at the other extreme of complexity from the search for extraterrestrial intelligence (SETI) (Drake, 1996; Drake and Sobel, 1992).

This recent research proposal may eventually be implemented by means of an apparatus denominated the 'SETH cigar' (MacDermott and Tranter, 1995). The most useful physical techniques that may be used in this context are circular dichroism (CD) and optical rotatory dispersion (ORD, the functional relationship between the angle of rotation and the wavelength of the polarized light). Normally these techniques imply equipment that is too bulky. Both techniques, CD and ORD may allow the determination of the sign and magnitude of the optical rotation to be measured, as well as the identity of the putative homochiral molecule.

MacDermott and Tranter propose instead to miniaturize the equipment by just restricting the search to the optical rotation that would be produced by a chiral molecule. Their idea is based on the property of some crystals (dichroism) of being able to absorb selectively light vibrations in one plane, but allowing the vibrations at right angles to go through. Two polarized films at right angles are introduced in the presence of small electronic devices consisting of regions (p-n junctions) in which semiconductors are present on either side, so that their conductivity is due to the flow of electrons ('n-type') and mobile holes ('p-type'), respectively. This device is called a light-emitting diode.

In addition, a detector is used, which consists of a semiconductor diode that produces a significant photocurrent when illuminated (photodiode). With this arrangement no light should reach the detector unless the plane of polarization is rotated. In this manner racemic mixtures will not be capable of allowing light to reach the detector. Hence a signal in the detector is certain proof that the sample tested is homochiral.

Homochirality may be considered as a signature for life anywhere in the universe. Due to the progress in research and the availability of a whole series of forthcoming space missions (towards the end of this decade and the beginning of the next), the problem of chemical evolution has been virtually transferred from the laboratories of organic chemistry to the space sciences.

In this context we may recall the intriguing ideas of Bonner and Greenberg. These authors suggest, independently, that circularly polarized light from neutron stars on passing clouds of interstellar dust may selectively eliminate one or the other enantiomer in the dust mantle, if mirror image molecules are originally present (Bonner, 1991, Greenberg *et al.*, 1995).

Another possible astrophysical source of homochirality may be the supernovas, according to some recent work (Cline *et al.*, 1995). We may state in general that living systems translate their genes, following the rules of the genetic code, into proteins composed of relatively a small number of L-amino acids. The strength of this statement may be illustrated with the discovery that out of the 74 amino acids that were found in the Murchison meteorite (cf., Sec. 1.1), only 55 have been found in extraterrestrial samples and none of them has been shown conclusively to have a chiral bias (Oro *et al.*, 1990). These numbers give us considerable insights, when we recall that the protein monomers are chosen from a very restricted set of twenty amino acids.

2.2. IS OPTICAL-PURITY UNIVERSALLY VALID?

Homochirality is generally valid for all organisms, but some care must be taken with this concept when we consider the highest taxa:

2.2.1. Exceptionally, in the domain Bacteria (encompassing thermotogales, the flavobacteria and relatives, the cyanobacteria, the purple bacteria, the Gram-positive bacteria, and the green nonsulfur bacteria) cell walls may contain D-amino acids, as in the case of *Bacillus brevis* or *Lactobacillus arabinosus*. This has been reviewed some time ago (Ulbright, 1981). The main conclusion from our point of view is that some

D-amino acids, such as D-phenylalanine and D-glutamic acid may be present in bacterial permeable extracellular coat (wall), which is secreted by the protoplasm; the bacterial envelope may contain a layer of peptidoglycan (rigid components consisting of polysaccharide and polypeptide chains). The significant result is that in the peptidoglycan molecules we find the presence of D-phenylalanine and D-glutamic acid.

2.2.2. A related topic is the interaction of antibiotics with bacterial cell walls. This may serve to further illustrate the relevance of optical purity of living organisms. In fact, most antibiotics with D-amino acids are resistant to proteases (these are enzymes that may digest proteins by hydrolysis of peptide bonds) and peptidases (enzymes that are also able to hydrolyse peptides into components amino acids).

2.2.3. A second exception concerns another one of the three highest taxa, the domain Archaea encompassing the kingdoms Crenarchaeota (which, for instance, includes the genus *Pyrodictium* and the genus *Thermoproteus*) and Euryarchaeota (for instance, the extreme halophiles and archaeobacteria capable of producing methane as a byproduct of the reduction of carbon dioxide). Organisms in this domain contain L-glycerol in their membrane phospholipids, instead of the standard D-glycerol, as we mentioned above, which is characteristic of the phospholipids of the cellular membranes of the other two domains, Eukarya (the animals, the ciliates, the green plants, the fungi, the flagellates and the microsporidia) and Bacteria.

2.3. DEVIATION FROM HOMOCHIRALITY AND THE SETH CIGAR

Such deviations from homochirality of the biomolecules (cf., 2.2.1) should not deter the development of the equipment currently being designed for testing homochirality in extraterrestrial environments for several reasons, prominent amongst which we may point out:

2.3.1. A large fraction of the mass of a cell is embodied in proteins and not in the cell envelope. We expect the design of the SETH cigar to be able to account for samples which are predominantly homochiral, such as the putative bacterial fossils that may be eventually encountered in a terrestrial planet (for instance, Mars) a possibility that has so far not been ruled out (cf., Table 1).

TABLE 1: Approximate chemical composition of a bacterial cell (Alberts *et al.*, 1989).

| <i>Cellular components</i> | <i>Percent of total cell weight</i> |
|--|-------------------------------------|
| Water | 70 |
| Inorganic ions | 1 |
| Sugars and precursors | 1 |
| Amino acids and precursors | 0.4 |
| Nucleotides and precursors | 0.4 |
| Fatty acids and precursors | 1 |
| Other small molecules | 0.2 |
| Biomolecules (proteins, nucleic acids and polysaccharides) | 26 |

2.3.2. Estimates of the abundance of some of the homochiral biomolecules invariably give a large value to the enantiomer favoured by living organisms. For instance, the D:L ratio for glucose on Earth is of the order of $10^{15} : 1$ (Lederberg, 1965).

2.3.3. The design of equipment to test homochirality has also to take into consideration the related problem of racemisation of amino acid residues of proteins that are not subject to turnover. A simple example taken from the Domain Eukaryota may serve to illustrate this point. Dentine is the main constituent of teeth, lying between enamel and pulp cavity. It is mesodermal in origin and similar in composition to bone (yet, it may contain 70% inorganic material). The degree of aspartic acid racemisation in dentine may be considered a measure of aging, as by the age of 60 about 6% of the aspartic acid residues will have racemised in humans (Helfman and Bada, 1976).

2.3.4. We agree with MacDermott (1996) that the occurrence of homochirality of different handedness in different Solar System planets would rule out current ideas of the electroweak interaction being the source of homochirality. This verification is sufficiently important to merit the expense of carrying out the experiment *in situ*. Yet, the detection of the same handedness of putative extraterrestrial microfossils with the handedness of the Earth biota would not be a test of the current theories, as we have to recall that bacterial life arose very early on Earth, possibly towards the end of the late heavy bombardment period, in which significant exchange of material should have occurred, prior to the end of the Hadean subera (earlier than about 3.8 Gyr bp). Comparative planetology demonstrates this possibility (Murray *et al.*, 1981) with the combined testimony of the surfaces of the terrestrial planets.

2.4. HOMOCHIRALITY AND THE ELECTROWEAK INTERACTION

The search for the origin of homochirality from the point of view of the effects of the weak interactions started in the 1950s. This has led to the proposal of various mechanisms that have been postulated in order to account for homochirality. Amongst them we should recall the differential decomposition and resolution of enantiomers under beta-irradiation (the Vester-Ulbricht hypothesis).

The experimental confirmation of this theoretical conjecture has been much discussed over the last three decades (Garay, 1993). More ingenious mechanisms have been recently postulated, such as the possible relevance of molecular decay in the origin of homochirality (Li, 1994).

In the standard model of Glashow, Salam and Weinberg, the electroweak interactions arise by the exchange of photons, massive charged W^{+-} and neutral Z^0 bosons of spin 1 between quarks (u,d,s,c,b,t) and leptons (electron, muon, the tau particle and three types, or 'flavours', of neutrinos). Within the framework of this model, a substantial body of previous work has suggested the parity-violating electroweak neutral current (mediated by the Z^0 boson) as the main physical force inducing the observed homochirality (Keszthelyi, 1995). Neutral current weak interactions are predicted to induce small energy differences, equal in magnitude but opposite in sign between the enantiomers. Such a 'parity-violating energy difference' between the enantiomers (twice the small induced energy difference in each enantiomer) may induce energy shifts to both enantiomers, which in spite of being small effects they are, nevertheless, subject to calculation as well as to the eventual effect of amplification mechanisms (MacDermott, 1995). We shall return to this topic more fully in Sec. 5.1.

Salam's approach (1990-1995) also invoked the electroweak interaction, but was original in appealing to further physical concepts that may apply during chemical evolution. He pointed out a particular cooperative phenomenon that may have taken place, namely, a phase transition beneath a certain critical temperature T_c . Amino acids

that had been synthesized earlier from various precursors entered into a new phase assumed to be a Bose condensed mode.

These concepts: cooperative phenomena and condensation led to the suggestion that the electromagnetic force is not the only force producing chemical effects. The Z^0 component of the electroweak force, in spite of the fact that its effects appear to be negligible at low energies, may play an active role in biochemistry. The reasons for the proposed chemical role of the parity-violating weak interactions may be found in quantum chemistry calculations (QCCs) of, amongst others, Mason, MacDermott and Tranter (MacDermott, 1993) and, independently, by Bakasov, Ha and Quack (Bakasov *et al*, 1996). We refer the reader to the reviews of Bonner (1991), Cline (1996), Keszthelyi (1995) and our own recent review (Chela-Flores, 1995b) where a comprehensive list of earlier references are available.

These calculations indicate that four amino acids, for which results have been obtained, are L-stabilized relative to their D-partners for configurations in aqueous media. (The above-mentioned amino acids are alanine, valine, serine, and aspartic acid.) Although the result of the calculations gives only a small energy shift in the ground state energies of the L- and D-amino acids, nevertheless, in the conjectured phase transition, sufficiently large effects may still have to be taken into account, such as the inclusion of the top quark (t) and its antiparticle, in an enlarged version of the standard model (Chela-Flores, 1991).

2.4. PHYSICAL CRITERIA FOR THE GENESIS OF HOMOCHEIRALITY

If homochirality originated on Earth, its geological record unknown, as metamorphism has destroyed all possible evidence. The corresponding period in Moon stratigraphy is well documented for instance in the Nectarian, 4.2-3.8 Gyr bp; even samples from the pre-Nectarian period are known from the Apollo 17 mission to the Taurus-Littrow region of the highlands bordering south-eastern Mare Serenitatis; this mission succeeded in retrieving a dunite-an intrusive igneous rock of ultramafic chemistry-some 4.4 Gyr bp.)

On the other hand, if T_c is much smaller than the ambient temperature of the Earth's surface during the period corresponding to chemical evolution, Salam's theory has some options:

An important aspect of the origin of homochirality concerns the thermal conditions that may have existed at a time when chemical evolution took place. Although the geological record is unknown on Earth, as metamorphism has destroyed all evidence, the corresponding period in Moon stratigraphy is well documented (the Nectarian, 4.2-3.8 Gyr bp), when presumably the presently observed homochirality of amino acids originated on the Earth-bound biomolecules. Solid evidence of the heavy bombardment period is known from the rocks retrieved by the Apollo missions. (Even samples from the pre-Nectarian period are known, as the Apollo 17 mission to the Taurus-Littrow region of the highlands bordering south-eastern Mare Serenitatis succeeded in retrieving a dunite-an intrusive igneous rock of ultramafic chemistry-some 4.4 Gyr bp.)

Since the ambient temperature of the Earth's surface is approximately 300K, if T_c is much smaller than this temperature, Salam's theory may not apply to the Earth, in which case some options are still open:

2.4.1. Pre-solar contributions may be necessary to get low enough temperatures. We may assume that such contributions may have arisen from a molecular cloud of dust and gas (predominantly in molecular form) out of which the Solar System originated. Since over seventy organic molecules have been detected in the last 25 years (cf., Sec. 1.1), it is possible that the effects that we are discussing in this review may have taken place in amino acids at a time prior to the formation of the Solar System. In those early

stages the temperatures may indeed have been low enough (possibly in the range 10-20K, as in current small molecular clouds).

2.4.2. Major contributions may come from the outer Solar System with ambient temperatures less than T_c . (For instance, the surface temperature of Uranus, which is

some three billion km from the Sun, is well below $-200\text{ }^\circ\text{C}$, a temperature in which both methane and nitrogen condense.) In the heavy-bombardment period (i.e., prior to about 3.8 Gyr bp) the Earth and Mars, for instance, may have exchanged matter and if life originated in Mars first, it is conceivable that it may have been transferred to the early Earth. So the assumption that chemical evolution of the Earth biomolecules may have been influenced by interplanetary exchange of chemicals cannot be ruled out.

2.4.3. If T_c is found to be considerably less than $300\text{ }^\circ\text{K}$, one would be led to accept that the Earth only acted as a junction place, where L-amino acids came together with D-sugars, so as to give rise to early replication. It may be reasonable to assume that the Earth did accrete prebiotic organic molecules important for the origin of life from impacts from carbonaceous asteroids and comets during the period of heavy bombardment in the Hadean Earth (Chyba *et al.*, 1990). Remarkably, we may also assume that the alanine molecules, for instance, could withstand temperatures as high as about $700\text{ }^\circ\text{K}$ for one second, whereas the other amino acids could withstand temperatures in the range 600 to $800\text{ }^\circ\text{K}$ for a similar period of time, and remain stable and intact upon impact with the Earth. Another physical question is whether phase transitions of the type of Bose condensation may occur in the living cell. We may recall that in the case of certain specific macromolecules relevant to living processes, this subject has been studied in both biochemistry, as well as in genetics, during the last thirty years.

In biochemistry, the ability of lipids to adopt a variety of phases is well documented (Luzzati, 1968; Eze, 1995). This has been called lipid polymorphism; an important aspect of this topic is that the macroscopic structure adopted by lipids depends on the experimental conditions; for instance, temperature is an important parameter which determines the macroscopic structure of hydrated membrane lipids (De Kruiff *et al.*, 1985). At present a conservative position is still that the possible biological significance of some of the polymorphic membrane transitions is striking, but we have not yet bridged the gap with physiological phenomena.

On the other hand, evidence for phase transitions in the life sciences is not limited to biochemistry, but a separate line of research in genetics also suggests the occurrence of phase transitions in the living state: A factor that may influence the onset of DNA replication is intracellular *ion concentration* (Maino *et al.*, 1974; Dulbecco and Elkington, 1975). In fact, experiments with rat liver-cell nuclei may indicate that chromatin structure and nuclear volume display abrupt transitions as function of ion concentration in the nuclear environment (Nicolini *et al.*, 1984): this experiment has suggested to its authors that the chromatin structural changes may be discussed in terms of phase transitions. The phenomenon being proposed may be thought of as a quantum mechanical enhancing factor in molecular evolution from the initial racemic mixture to the present day chiral amino acids. The concept of condensation is not new in biology; indeed, it goes back some 30 years (Delbruck, 1963). In the context of the origin of life condensation in the nucleic acids had already been suggested to have played a role in the origin of Darwinian evolution (Chela-Flores, 1985).

3. Experimental tests of phase transitions in amino acids.

3.1. IS THERE A PHASE TRANSITION UNDERLYING HOMOCHEIRALITY?

These results from the biochemistry of the cell membrane and from the genetics of chromatin structure lead us naturally to raise the question: What direct evidence is

there for a clear hallmark of the phase transition underlying the origin of chirality? There are some alternatives:

3.1.1. Melanin - a dark brown pigment of many animals- is the product of tyrosine metabolism, which causes pigmentation of eyes, skin and hair in vertebrates. It is often located in melanophores (cells with permanent radiating processes lying superficially in vertebrates). Data taken from natural melanins, as well as from melanosomes isolated from human melanoma, may indicate that it undergoes a phase transition. In fact, its heat capacity shows a discontinuity near 1.9 °K. This anomaly, though relatively small, is significant beyond the scatter of the data points. It is probably associated with a magnetic transition, possibly from paramagnetism to antiferromagnetism (Mizutani *et al.*, 1976). In an analogous manner, a means of detecting the putative phase transition may be by measuring differences of specific heats and looking for anomalies in the curve for specific heat (a cubic polynomial) as has already been done for the above-mentioned non-amino acids.

3.1.2. One direct means of testing the new theory for the origin of chirality in amino acids is by taking a 50-50 racemic mixture of crystalline L- and D-amino acids and lowering the temperature. Salam has discussed extensively an experiment involving a 50-50 racemic mixture subjected to a temperature gradient ranging from the melting temperature for the amino acids to the absolute zero temperature.

3.1.3. In view of the discovery of organic superconductors with critical temperatures similar to metals and alloys, an alternative experimental procedure may be to test directly for conductivity and magnetic (Meissner effect) properties of amino acid crystals.

3.2. PHASE TRANSITIONS IN ORGANIC MATERIALS

The suggestion has been made that a superconducting-like phase transition may actually occur in amino acids. Physics has been rather slow in studying alternative candidates for superconductors. The first class of (low-temperature) superconductors was discovered in 1911; these early superconductors were unlike any form of matter that occurs in living systems. In fact, they were metals and alloys. The discovery of a radically new class of superconductors had to wait some time. In 1986 a more interesting superconductor from the point of view of chemistry was identified in certain ceramics

The simple potassium-doped fullerene (Hebard *et al.*, 1991) has been shown to be superconducting with a reasonably high critical temperature i.e., the onset of the critical temperature is 18 °K. However, we should recall that organic superconductors have been known for some time, such as graphitic compounds with typical formulae C_8A ($A = K, Rb, Cs$) with values of T_c smaller than 1K (Hannay *et al.*, 1965).

Another example is that of the organic superconducting metal bis(ethylene dithiolo) tetrathiofulvalene triiodide with formula $(C_{10}H_8S_8)_2I_3$ (Yagubskii *et al.*, 1984) with a value of $T_c = 1.5$ °K at normal pressure. Hence, the most we can say at present is that superconductivity-, or superfluidity-like effects may not be excluded from organic materials. This suggests to extend the search for quantum liquid behaviour observed in the organic materials to a particular form of organic materials, namely, amino acid crystals. This point will be discussed further in Sec. 5.5.

3.3. BIOMOLECULAR RELICS OF EVOLUTION

The search for physical mechanisms underlying the causal origin of homochirality are mainly motivated by the fact that the most characteristic of all relics of evolution is provided by the chiral nature of the biomolecules.

Other relics, however, are known. This may be illustrated with the widespread use of the standard genetic code by a very large number of organisms. (Exceptionally some protozoans and *Mycoplasma* use a modified code.)

The general question of whether it is possible for further relics of the earliest stages of evolution to have survived till the present has been raised in the past by various authors. Some well known examples are certain nucleotide sequences (introns) in genes of mainly eukaryotic organisms; they do not code for the gene product (neither proteins nor nucleic acids).

The presumed antiquity of these sequences is based on the finding that some introns are ancient (Saldanha *et al.*, 1993). More recently, the question of further molecular relics from one of the earliest stages of the evolution of life on Earth (the RNA world) has been raised in the context of the origin of RNA plant pathogens, such as the viroids (Diener, 1993). The relevance of this putative relic has been discussed recently (Chela-Flores, 1994b; 1995a; 1996).

Inserted in this broad range of problems regarding biomolecular relics, the all-important question of homochirality of amino acids as an evolutionary relic has been recently reviewed, particularly from the point of view of experiments (Bonner, 1994, Keszthelyi, 1995, Cline, 1995), while the relevance of chirality in biology has also been discussed extensively in an excellent review (Crossly, 1992).

The continued efforts to come to terms with the experimental question of Salam's two conjectures (cf., Sec. 5.3 below), have not been completed so far, but these set of experiments (Figureau *et al.*, 1993, 1995; Navarro-Gonzalez *et al.*, 1993; Wang *et al.*, 1995) are, nevertheless, illuminating an area of condensed matter physics which has so far not been extensively studied, and which potentially may be of wider interest than strictly within the domain of chemical evolution and the origin of life.

Preliminary experiments (Wang *et al.*, 1995) have attempted the first part of the task (the specific heat curves); the complementary magnetic properties should also be considered. The intrinsic importance of testing new materials for the key technologies of the future should be emphasized, as technological innovation should not stop at ceramics, which already produced the revolution of the high T_c superconductors in 1986 (Chela-Flores *et al.*, 1988), but biological materials should be thoroughly discussed and tested, as we already emphasized in our earlier paper (Chela-Flores, 1991).

4. Asymmetric adsorption of amino acids at crystal surfaces

4.1. L-AMINO ACIDS MAY BE ADSORBED ON L-QUARTZ CRYSTALS

There is a long history of experimental efforts with inorganic substances which have the ability to rotate the plane of polarization of light passing through a crystal (cf., Sec. 2.1). This ability is due to their chiral crystal structure. In this respect quartz, the most common of the six polymorphs of crystalline silica (SiO_2) is found in nature in the form of well defined enantiomorphic crystals, in which chirality is caused by the spiral structure of linked silicon-oxygen tetrahedra.

Quartz, therefore, is an obvious candidate for the stereoselective adsorption of a given enantiomer from a racemic mixture. A long series of experiments has led to the conclusion that asymmetric adsorption on quartz is a well authenticated phenomenon, but it is also equally clear that in this process, quartz acts merely as a passive 'filter' of homochiral domains, passive in the sense that quartz itself does not induce any catalytic process that may convert racemic or achiral reactants into optically active products (Bonner, 1991).

Asymmetric adsorption of amino acids at the surface of chiral crystals is a possible physical mechanism that may have led to the onset of homochirality in one

class of biomolecules. It is well documented that about one per cent more L-amino acids than D-amino acids are adsorbed on L-quartz crystals (Bonner, 1979).

This experimental fact may be taken together with the theoretical work that has shown that due to the effect of the weak interactions, L-amino acids (and similarly, D-sugars) have smaller ground-state energy than their corresponding enantiomers, a property that has been shown by independent QCCs (cf., Sec. 2.3).

The experiments on the stereoselective adsorption of amino acid enantiomers on the surface of either D-quartz or L-quartz suggest (together with the QCCs) that L-amino acids (which may be adsorbed in the surface of L-quartz) may serve as a reservoir of chirally-pure samples. Some amplification mechanism may have acted on, so as to enhance the small chiral bias that the QCCs suggest in favour of L-amino acids.

The analogous D-amino acids (that may be similarly adsorbed by the surface of D-quartz), presumably may not have benefited from the small advantage due to the weak interactions in favour of the L-amino acids. Hence, it is forced upon us to discuss possible physical mechanisms that while acting on both L- and D-amino acid crystals may, nevertheless, act as amplification mechanisms on chirally-pure samples.

4.2. THE POSSIBLE RELEVANCE OF QUARTZ IN CHEMICAL EVOLUTION

The abundance of quartz and its presence in a variety of conditions typical of the Archean era, militate in favour of the possibility that quartz may have provided early chirally-pure environments for amino acids.

We shall consider a few arguments that favour a physical mechanism in which L-quartz is the first step in the pathway that leads to the observed homochirality of protein amino acids: the environment in which quartz is found is ubiquitous. Although quartz is one of the thousand silicate minerals that make up the bulk of the Earth's outer crust, it is however one of its commonest minerals (12 % by volume). Furthermore, all terrestrial planets have a crust similar to the silicate crust of the Earth. In the case of Mars, for example, samples ('fines') have been analyzed by the Viking missions.

It was demonstrated that quartz is a prominent mineral in the fines that were retrieved from both the Chryse and the Utopia Planitiae, which are located on opposite sides of the planet: the Chryse Plains being at 20° N, 40-50° W, whereas the Utopia Plains are 47.89° N, 225.86° W (cf., Soffen, 1976, and the articles that follow his summary). Quartz is known to crystallize directly from igneous magma (i.e., from molten rock material that may have poured out from volcanos or hardened before reaching the surface). It occurs in deep-seated coarse-grained ('plutonic') rocks such as granites, as well as in volcanic rocks such as rhyolites, which are igneous rocks containing megascopic crystals of quartz.

In the following tables we illustrate the ubiquity of quartz in an extraterrestrial environment, but first we consider the elemental composition which demonstrates that in spite of both landing sites being separated by thousands of kilometers, the abundances are similar to those found in several common terrestrial soils and rocks.

TABLE 2: Elemental composition of Mars soil (Adapted from De Vincenzi, 1983)

| <i>Element</i> | <i>% of total composition (average over the sites at the Chryse & Utopia planitiae)</i> |
|--|---|
| Silicon | 21 |
| Iron | 13 |
| Magnesium | 5 |
| Calcium | 4 |
| Sulfur | 3 |
| Aluminium | 3 |
| Chlorine | 0.5 |
| Titanium | 0.5 |
| All others (probably mostly oxygen) | 50 |

TABLE 3: Minerals of martian samples

| <i>Mineral</i> | <i>% of total composition of a sample (Chryse planitia)</i> |
|--|---|
| Quartz (SiO ₂) | 27 |
| Feldspar (KAlSi ₃ O ₈ / CaAl ₂ SiO ₃) | 19 |
| Pyroxene (MgSiO ₃ CaSiO ₃) | 30 |
| Hematite (Fe ₂ O ₂) | 22 |

An additional reason to focus our attention on quartz is that it is stable in sedimentary conditions: it may occur in marine and desert sands, but also as cement in compacted rocks such as sandstone, in which quartz appears as rounded grains between the diameters of 0.06 and 2 mm, with a variable content of other mineral grains. What seems even more pertinent is that quartz is also stable under low- and high-grade metamorphic conditions. In fact, a high-pressure, high-temperature form (coesite) is found in meteorite impact rocks. Another form (stishovite) is found to occur naturally in meteorite craters, such as Meteor Crater, Arizona.

Hence the probable presence of quartz in favourable environments during the heavy-meteorite impact-period (the Hadean) may have been a factor influencing the origin of life in the selection homochirality, which has persevered as a distinctive feature of the earth's biota.

5. On the breaking of chiral symmetry

5.1. AMPLIFICATION MECHANISMS

One of the principal difficulties in understanding the asymmetry of biomolecules is the question of the amplification mechanism that would boost a primordial small physical effect (Keszthelyi, 1995). New suggestions of amplification mechanisms should be considered in addition to the earlier possibilities such as those considered in the past:

5.1.1. Amplification of the Vester-Ulbricht processes, namely amplification mechanisms that may apply to the interaction of polarized particles with biomolecules.

5.1.2. Amplification of the Yamagata processes, namely those processes (such as those discussed in this work) in which the breakdown of the discrete P symmetry is considered as a possible source of biochirality.

5.1.3. Amplification known as the Kondepoudi-Nelson catastrophic mechanism (Kondepoudi and Nelson, 1985). According to this proposal the small electroweak energy difference between the enantiomers is sufficient to determine which of the two single-enantiomer reaction sequences was adopted at the metastable stage in a flow reactor that is off thermodynamic equilibrium.

The suggestion of Salam that Bose-Einstein condensation may act as a novel amplification mechanism still suffers from a difficulty: the underlying theory requires that large activation energy barriers be overcome in the process of turning a racemic mixture into optically pure amino acids. This requires that the phase transition may induce molecular changes that lead to the breaking of chemical bonds. Amongst various options that the phase transition hypothesis may be faced with is that the origin of life may be extraterrestrial, provided that the critical temperature is too small for the phase transition to have been supported by the environment of the early Earth.

5.2. MECHANISMS FOR IMPLEMENTING PARITY VIOLATION

The possibility of an alternative model incorporating P violation of a 'third kind' has been suggested in the past (Chela-Flores, 1994a), in which the phase transition acts on a racemic mixture of amino acids inducing spontaneous separation of the chiral phases due to their environment. The ground states of the two optical pure phases are taken to differ in energy (the L-amino acid having the lower ground-state energy), as discussed in Sec. 2.3.

This mode of symmetry breaking should be distinguished from either Quack's *de facto* symmetry breaking (the ground state does not show the same symmetry as the hamiltonian), or from *de lege* symmetry breaking (parity violation occurs in the hamiltonian, as in the case Salam discussed in his 1991 paper). For more details of the

first two types of parity violation we refer the reader to the original paper (Quack, 1993).

In fact, it has been found that a small electroweak energy increment adds to the binding energy of a given state in one enantiomer and subtracts from that of the corresponding state of the other, giving an electroweak binding energy difference between the two optical isomers.

This rationalizes the observed bias of protein amino acids for the left-handed chirality, a phenomenon that has been preserved by biological (i.e., neodarwinian) evolution. The interpretation of the postulated phase transition provided in this note does not suffer from the difficulty of implying large activation energy barriers for the production of optically pure amino acid concentrations from an initial primordial racemic mixture.

The BCS-like phase transition in the amino acids may occur at a certain critical temperature T_c . Preliminary experiments reporting negative results (cf., Sec.3.3) have attempted to find the value of T_c for the original theory. This situation motivates the search of further insights into the sources of homochirality. We suggested that one possible insight may be found in the connection between chiral symmetry breaking and pattern formation.

It has been observed that two-dimensional liquids composed of achiral units can spontaneously separate into right- and left-handed regions. This induces a breakdown of natural mirror symmetry, an effect which is related to ferroelectricity at the interfaces (Schwartz, 1993).

However, one of the important aspects of these experiments is that a new example has been provided, in which structure and symmetry at the molecular level have implications at the macroscopic level. This phenomenon has been observed at molecular length scales in some experiments (Eckhardt *et al*, 1993). The molecular lattice of a racemic organic monolayer has been imaged and was observed to spontaneously undertake separate chiral regions.

5.3. SALAM MADE TWO DIFFERENT PROPOSALS

This point that has not been widely appreciated (Chela-Flores, 1994a):

5.3.1. He proposed the existence of a phase transition in a *racemic mixture* of amino acids in which large activation energies need to be overcome. This proposal does not refer to the environment in which the racemic mixture was inserted. This is the aspect of Salam's conjecture that was tested in two experiments (cf., Sec 4.1).

5.3.2. Salam went further in a separate proposal of a new mechanism for the amplification of the small effect of the neutral electroweak interactions on the ground state energy of the amino acids. This possibility was suggested on the bases of the QCCs (cf., Sec. 2.3). The macroscopic quantum mechanical amplification mechanism is analogous to Bose-Einstein condensation, currently assumed to occur in other forms of condensed matter, such as in liquid helium II and superconductors. It is this aspect of Salam's conjectures that has been preliminarily tested in the most recent experiment, which clearly requires independent confirmation (Wang *et al.*, 1995).

The proposal (5.3.1) has the difficulty that large activation energies have to be overcome, so that chemical bonds are broken for a given right-handed amino acid to be converted to its left-handed form. The second proposal (5.3.2) will be discussed below.

5.4. EXPERIMENTS TESTING THE QUESTION OF HOMOCHIRALITY

Unlike Salam's first suggestion which referred to a racemic mixture, we advocate the second part of his proposal (5.3.2). The main reason is the evident considerable

difficulty in explaining the means of overcoming the large activation energies which would inhibit the phase transition in the racemic mixture of amino acids.

At present, in order to test the theory, one needs to address the question of the possible occurrence of a phase transition in a chirally-pure sample of L-amino acids. For instance, experiments could address the question of chirally-pure samples of amino acids that have been adsorbed preferentially on the surface of L-quartz crystals, as explained in the above illustration (cf., Sec. 4).

In spite of the difficulties in the original phase-transition theory of 1991, non-linear mechanisms of amplification of the small parity-violating energy-difference may still be relevant, but one should search those theories that are free from the considerable difficulty implied by the underlying large activation energies needed in the transition from the racemic mixture to the chirally-pure samples. One possibility of an acceptable phase transition theory, free from the above-mentioned difficulties, may be found in the generation of chirally-pure domains by the action of L-quartz surfaces, a process that was already discussed in Sec. 4.2.

5.5. CHIRAL AMINO-ACID CRYSTALS AND SUPERCONDUCTIVITY

Evidence for the phase transition in chirally-pure samples of L-amino acids should be searched for with similar experiments to those preliminary experiments which tested the possible existence of the phase transition, in which a range in temperature was scanned for the signature of the putative phase transition (cf., paragraph 5.3.1).

We were already aware that in the special case of melanin, a derivative of the amino acid tyrosine, a phase transition may already have been detected experimentally (cf., Sec. 3.1) (Salam, 1991, Appendix D; Chela-Flores, 1991). A similar experiment directly on a sample of the amino acid L-tyrosine would serve as a test of the conjectured unusual behaviour of amino acids.

Further, the importance of testing for high-temperature superconductivity, in the present case of biological relics of the earliest steps in chemical evolution (homochirality in protein amino acids), was pointed out in the same above-mentioned section of our 1991 paper. Having raised the question of spontaneous onset of homochirality, experimental attention finally seems justified at present to search for signs of a phase transition in single chirally-pure crystals of amino acids.

6. Discussion and conclusions

The postulated parity violation of a third kind (in which the homochiral domains may form spontaneously due to their environment) may be illustrated in the case of the chiral quartz crystals discussed in Sec. 4, or in the case of phenomena that is known to occur in the liquid crystal state (Schwartz, 1993; Selinger *et al.*, 1993; Eckart *et al.*, 1993).

An important further example that has been extensively studied is provided by clays, as illustrated in Table 4:

TABLE 4: Some adsorption experiments related to chemical evolution (Adapted from Negron-Mendoza, 1996).

| <i>Adsorbate</i> | <i>Adsorbent</i> | <i>Comments</i> |
|---|--------------------|--|
| Amino acids (Shimoyama, and Ponnamperuma, 1980.) | Na-montmorillonite | Adsorption increases with decreasing pH and increasing amino acid concentration |
| Racemic mixture of amino acids (Friebele, Shimoyama & Ponnamperuma, 1981)) | Na-montmorillonite | There is no large preferential adsorption of either enantiomer |
| Proteins (Albert & Harter, 1973)) | Na-montmorillonite | Highest adsorption at pH around the isoelectric point |

From what we have said above we feel that experiments testing parity violation of the third kind (such as the Wang *et al* experiments) are justified and should be repeated (i.e., tests of phase transitions in single amino acids).

In this manner we have been led naturally to suggest testing a form of condensed matter that has not, from the present point of view, been exhaustively tested (although considerable information already exists on the crystal structure of amino acids).

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