

Homochirality and Chiral Induced Spin Selectivity;
A New Spin on the Origin of Life

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The fundamental questions of “Where do we come from?” and “How did life begin?” date back millennia. Even today the scientific community seeks to understand abiogenesis, the origin of life. It is now generally agreed that any answer to this question must involve an explanation for the emergence of biological homochirality, that naturally appearing biomolecules from organisms occur with a particular handedness (enantiomeric form); e.g., L-amino acids and D-sugars. A unifying concept among deterministic theories for homochirality is the presence of a chiral bias, which breaks the symmetry for driving the formation of molecules with a given handedness over that of the other. The bias has previously been attributed to circularly polarized light, fluid dynamics, and magnetic fields, among many others (1). In **PNAS**, Ozturk and Sassellov (O&S) approach this age old question by proposing that the symmetry breaking involves a phenomenon known as chiral induced spin selectivity (2).

A central feature of the chiral induced spin selectivity (CISS) effect is the coupling between the intrinsic angular momentum of an electron, or its spin, and the molecular frame of a chiral molecule. Electrons exist in one of two possible angular momentum states and are commonly referred to as either spin-up or spin-down. Multiple studies have shown that electrons of one spin-type favorably transmit through an assembly composed of left-handed molecules, however the other spin-type does not (3). Conversely, the opposite preference for spin transmission becomes true when the assembly is composed of right-handed molecules. A chiral molecule’s spin-preference manifests for electrons transmitted through the molecules, for charge exchange between two chiral molecules, or for a chiral molecule and a magnetized surface (3, 4).

The latter example forms the basis of O&S’s conjecture that the spin of electrons can impart enantioselectivity for the production of chiral molecules from achiral precursors under conditions that are believed to be consistent with that of prebiotic Earth (2). Precedent exists for their hypothesis that magnetized surfaces can lead to enantioselective reactions and the formation of chiral molecules from achiral precursors (5, 6) and others have considered the implications of CISS for the origin of life (7). Experimental studies have shown that CISS operates on chemical processes of multiple length scales and of varying complexity; see the summary in Figure 1. Experiments involving more complex multi-step reactions have shown that a preferred molecular handedness can emerge for systems that do not initially possess any chirality (8). Features of CISS have also proven to be influential in biological processes, such as electron transport in proteins and across cell surfaces, as well in allosteric regulation (9, 10, 11).

In previous work, Sassellov and colleagues proposed chemical pathways for the origin of biomolecular building blocks that are consistent with prebiotic Earth conditions. This picture involves the accumulation of reactants (precursor chemicals) in shallow subaqueous basins that undergo photochemical reactions through UV radiation, believed to be extant at that time (12). That picture

did not account for molecular chirality however; and in **PNAS**, O&S extend that model to account for chirality by invoking the CISS effect and magnetite as the origin of a chiral bias. Magnetite, a ferrimagnetic material, is an abundant constituent of subaqueous sedimentary mineral deposits on the anoxic Earth, circa 1.8 to 3.7 billion years ago. (13). O&S propose that UV irradiation generates spin-polarized photoelectrons from uniformly magnetized magnetite, which then initiate enantioselective chemical reactions near the magnetite surface because of the CISS effect. Studies have shown that a spin selectivity dependence exists between the molecular frame of a molecule relative to that of the incoming electron (14), so that freely diffusing molecules would likely display less CISS-based enantiospecificity than do those that might be oriented, e.g., surface adsorbed. This constraint likely limits any CISS-based chiral bias mechanism to an interfacial regime with the magnetite, as pointed out by O&S. It is known however that spin-polarized photoelectrons from magnetite surfaces are produced in a face selective manner - negative spin polarization from the (111) face and positive from the (001) face (15) – so that a chemistry involving surface adsorbed species and/or face-specific catalysis may also prove to be a viable hypothesis.

The cyanosulfidic chemistry (16) that O&S propose is an attractive candidate to explore, and provides a way to produce chiral molecules which are known to propagate into some of life's most fundamental building blocks (17). It is important to appreciate that the enantioselectivity arising from the spin-polarized electrons need not be 100%, as experiments have shown that nonlinear amplification schemes can lead to homochirality from a relatively small chiral bias, or enantiomeric excess. The time evolution of a small initial excess of one molecular handedness towards a much larger excess is thought to be possible through autocatalytic processes (18, 19), as well as other nonlinear processes (1,20). Along similar lines, CISS-based processes could reinforce and propagate the benefit of homochirality in biology; CISS has been shown to manifest in biomolecules and biochemical mechanisms, see Figure 1 (7, 9).

The next step for developing a CISS-based origin of life theory necessitates experiments which show that a defined electron spin can control the handedness of the resulting molecules in chemical reactions under prebiotic conditions. The proposed experiment by O&S (2) is one such example that should be pursued and if validated would cement CISS as a potential mechanism for an initial chiral bias in prebiotic chemistry. In tandem, studies of CISS-based mechanisms that lead to, or reinforce, homochirality should be pursued. More broadly, studies of this sort will further demonstrate the importance of considering the electron spin's role in regulating and directing chemical reactions, as well as guiding life's processes.

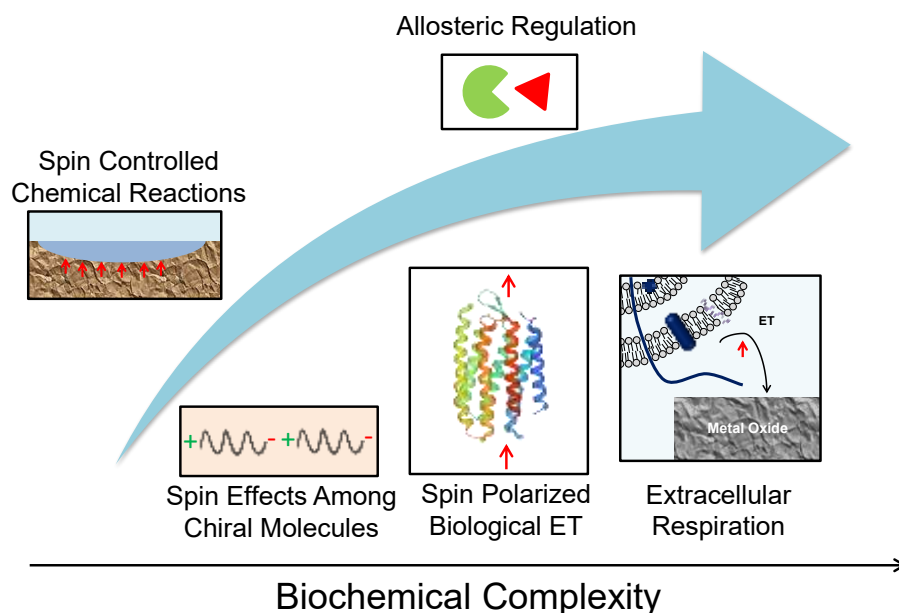


Figure 1. Examples of CISS-related processes in chemical and biological systems which may have contributed to the evolutionary progression responsible for the origin of life. Spin effects for facilitating chemical reactions are discussed in references (5, 6, 8), spin interactions among chiral molecules is reviewed in reference (9), the spin-filtering capabilities of proteins are reviewed in references (7, 9), CISS-based allostery is described in reference (11), and the effect of CISS on extracellular respiration is discussed in reference (10).

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