Kinetically the (Fe,Ni)S catalyst in our system promotes the productive reaction channel to peptides as compared to other nonproductive channels. It means that the reaction occurs in the ligand sphere of the sulfide mineral. Previously, copper ions have been used as catalyst for peptide formation in the presence of high salt concentrations (*9*). However, under anaerobic conditions with even a small sulfide activity, copper ions cannot exist.

Most prior attempts to produce peptides under primordial conditions have been beset by the formation of large amounts of unreactive diketopiperazines (*7, 12*). For example, in drying-wetting cycle experiments with glycine on montmorillonite, the molar ratio of diketopiperazine to diglycine was more than 4:1 (*13*). The formation of diketopiperazines was so far only suppressed, if the amino acid was activated in the form of a Leuchs anhydride, which required organic activation agents such as carbodiimides (*14*). In our system the diketopiperazines form minor byproducts. For example, in run 25, the amount of the diketopiperazine was 3.5 ± 0.5 μmol; while in run 13 the amount of the diketopiperazine of tyrosine is 5 μmol after 1 day and 8 μmol after 4 days (*15*). Both mechanisms shown in Fig. 2 would disfavor the formation of the diketopiperazine. They would also explain the racemization by resonance-stabilized enolization.

Our result supports the theory of a thermophilic origin of life with a primordial surface metabolism on transition metal sulfide minerals. It means that a continuously recycling library of peptides was generated on the surfaces of a library of (Fe,Ni)S structures. It raises the possibility that CO and Ni had a much greater role in the primordial metabolism than in any of the known extant metabolisms. All known extant organisms are found in habitats with low activities of CO and Ni. This could explain why they resorted to the formation of CO from CO_2 and to the elimination of nickel from many enzymes (*16*).

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Circular Polarization in Star-Formation Regions: Implications for Biomolecular Homochirality

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Strong infrared circular polarization resulting from dust scattering in reflection nebulae in the Orion OMC-1 star-formation region has been observed. Circular polarization at shorter wavelengths might have been important in inducing chiral asymmetry in interstellar organic molecules that could be subsequently delivered to the early Earth by comets, interplanetary dust particles, or meteors. This could account for the excess of L–amino acids found in the Murchison meteorite and could explain the origin of the homochirality of biological molecules.

The origin of the homochirality of biological molecules (living systems use almost exclusively L–amino acids and D-sugars) has been a puzzle since the effect was discovered in the 19th century. Homochirality may be a prerequisite for the origin of life (*1*). A number of processes have been proposed that might operate soon after the formation of Earth to produce an enantiomeric excess in prebiotic organic molecules (*2, 3*), including the action of circular polarization (CP) from the daylight sky and effects caused by the parity-violating aspect of the electroweak interaction. These are small effects and would require amplification by factors $\leq 10^{17}$ (*2, 4*) to account for homochirality. The difficulty with any proposed Earth-based mechanism led Bonner (*3*), in a detailed review of the origin of homochirality, to suggest an extraterrestrial origin. Support for this view comes from the discovery of an excess of L–amino acids in the Murchison meteorite (*5, 6*).

In the laboratory, high levels of enantiomeric excess in racemic substances can be produced by asymmetric photolysis by circularly polarized light (*3*). Twenty percent enantiomeric excess has been demonstrated in the laboratory (*7*) for 99% photolysis of camphor. The excess can be increased, by increasing the fraction of material photolyzed, but it will be reduced in proportion to the CP for CP of less than 100%. Astronomical sources of CP might

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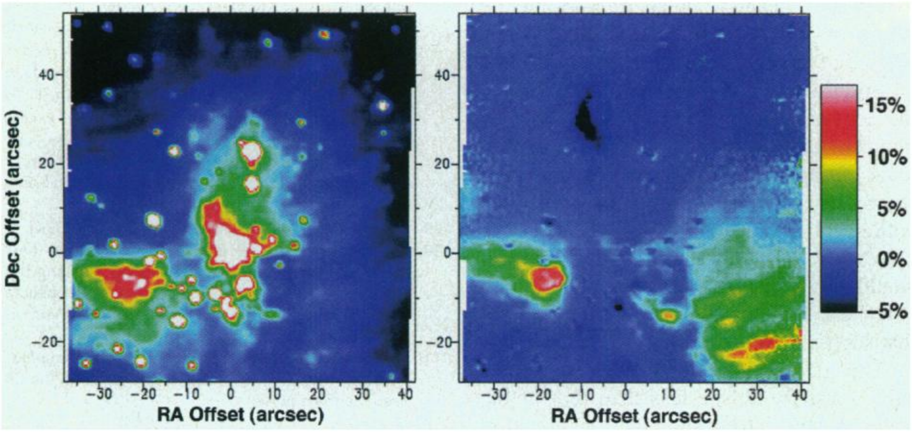

Fig. 1. Circular polarization image of the OMC-1 star-formation region in Orion at 2.2 μm (K_n band). (Right) Percentage circular polarization ranging from −5% (black) to +17% (white). Polarization accuracy ranges from about 0.1% in the brighter regions to 1% in the fainter regions. By convention, positive polarization means that the electric vector is seen to rotate counterclockwise in a fixed plane by an observer looking at the source. (Left) The total IR intensity. The bright source at coordinates (0, 0) is the Becklin-Neugebauer object. The size of a typical protostellar disk (~100 astronomical units) is less than 1 arc sec at the 450 pc distance of OMC-1 and therefore much smaller than the observed polarization structure.

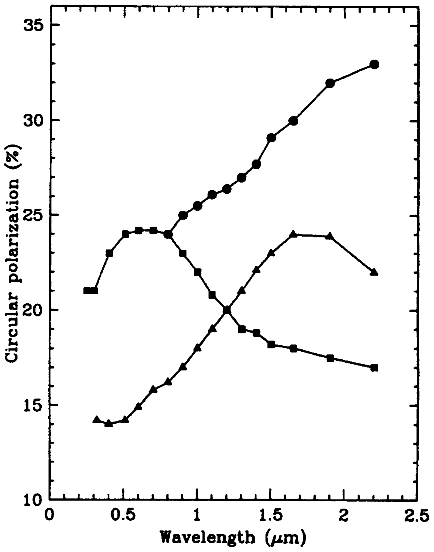

Fig. 2. Circular polarization caused by Mie scattering of unpolarized light from a size distribution of aligned spheroidal grains from 0.005 to 0.25 μm with a power law index of −3.5. The circular polarizations at a scattering angle of 90° are plotted for spheroidal grains of a dirty-ice type of material (refractive index 1.5 − 0.4*i*) with different axis ratios (*r* = *a*/*b*, where *r* < 1 for oblate spheroids, *r* > 1 for prolate spheroids). (■) *r* = 2.0, (▲) *r* = 0.5, (●) *r* = 0.33. The calculations were carried out with the use of code adapted from that of Barber and Hill (*28*). Owing to numerical difficulties with the code it was not possible to explore large axis ratios in the UV, although these are the instances that produce the largest polarizations. However, the models calculated at small axis ratios show that UV polarization is comparable to that in the IR, and IR polarizations are comparable to or greater than that seen in OMC-1.

therefore be capable of producing substantial levels of enantiomeric excess in interstellar chiral molecules (*8*).

It has been suggested that the required circularly polarized radiation could be due to synchrotron radiation from supernova remnants or pulsars (*3*, *9*). However, the best example of a young supernova remnant of a type that would be expected to be a source of ultraviolet (UV) light, the Crab Nebula and its pulsar, shows no CP either in the nebula (*10*) or in the pulsar (*11*), nor is any expected from synchrotron radiation under these conditions (*12*). Furthermore, the flat power law spectrum of such a source will irradiate circular dichroism bands of both signs, so that even if CP was present there would be little net enantioselective effect (*13*).

Here we report observations of the CP at infrared (IR) wavelengths in Orion OMC-1, a region of high-mass star formation. The observations were obtained on the 3.9-m Anglo-Australian Telescope with the use of the IRIS IR camera (*14*) and a polarimetry system (*15*). For CP observations, a half-wave plate is rotated continuously with a period equal to the detector integration time to remove any effects resulting from the incident linear polarization. A quarter-wave plate, stepped between two positions 90° apart, together with a Wollaston prism analyzer in the collimated beam of the camera is used to measure the CP. The detector is a 128 by 128 pixel HgCdTe array.

We measured levels of CP as high as 17% at IR wavelengths (Fig. 1). The highest CP is seen in regions that are reflection nebulae, scattering light from the highly obscured luminous source IRc2 (*16*). Previous observations of low-mass star-formation regions showed (*17*) CPs of only 1 to 2%. Because star-formation regions such as OMC-1 contain many organic molecules (*18*), these regions are a promising location for the origin of homochirality. Chiral organic molecules (including amino acids) are produced in experiments that simulate the action of UV light on interstellar grain surfaces (*9*).

Because of the high obscuration, these regions are directly observable only at IR and radio wavelengths, whereas the circular dichroism bands in amino acids and similar molecules are in the UV at wavelengths of about 200 to 250 nm. We therefore investigated whether the mechanism responsible for the CP at IR wavelengths will continue to operate at UV wavelengths. Scattering of unpolarized light from spherical grains can produce only linear polarization. However, CP is produced where spherical grains scatter light that is already linearly polarized, or where the grains are nonspherical and aligned by a magnetic field (*19*) as in OMC-1 (*20*). We have calculated the CP at UV and IR wavelengths for both these mechanisms (*21*) (Fig. 2) and find that in either case the levels of CP in the UV are comparable to those in the IR.

These results should not be taken as implying that the same regions will show similar amounts of CP in the IR and the UV. The greater optical depths in the UV may lead to a different pattern of polarization at these wavelengths. The UV polarization may be limited by the high extinctions to a local phenomenon, dominated by scattering from the nearest adjacent star, rather than from the bright sources such as IRc2 as in the IR. The important point is that a process does exist that might produce CP at UV wavelengths. Direct observation of this UV-polarized light may be difficult as little of it will escape from these dusty regions, but it might be detectable in some cases in regions with less obscuration than OMC-1.

To provide an enantioselective effect on amino acids, the spectrum of UV-polarized radiation must be such that absorption will be confined to a single narrow band, because circular dichroism bands will alternate in sign and sum to zero over the whole spectrum (the Kuhn-Condon rule). Because the long-wavelength absorption limit in amino acids is at about 230 nm, a spectrum with a steep short-wavelength cut-off below 200 nm will provide absorption limited to the 200- to 230-nm band (*2*). Chiral selection of amino acids by means of circularly polarized light passed through a >200-nm cut-off filter has been experimentally demonstrated (*22*). The spectra of most normal stars have just such a short-wavelength cut-off with the flux density falling by typically a factor of ≥100 from 220 to 150 nm (Fig. 3). Pre–main sequence stars, which are likely to be common in a star-formation region, may show an additional UV excess, but at spectral types A and F the steep drop below 200 nm is still observed (*23*).

We therefore propose that an enantiomeric excess in organic molecules in the protosolar system was generated by CP as a result of scattering of UV light from a nearby star (not the central star of the protosolar nebula). To maximize the CP seen by the grains, the distribution of dust must have obscured the direct view of the nearby star (and any other bright nearby sources) while allowing the scattered light to be seen with little obscuration. In a clumpy, dusty environment such as a star-formation region, such a geometry is feasible. The sign of CP seen by the protostellar material will depend on the scattering geometry. For the solar system, it must have favored the L–amino acids, but other solar systems would be formed with an excess of D– or L–amino acids equally likely.

Experiments (*9*) produce substantial enantiomeric excess in amino acids with 1.8×10^{17} UV photons cm^{-2}. An A5 main sequence star at a distance of 0.02 pc (10 arc sec at OMC-1, comparable with the scale of observed reflection nebulae) provides 3×10^{9} photons cm^{-2} s^{-1} for a bandwidth of 30 nm at ~220 nm. (An A5 star at a pre–main sequence stage could be substantially brighter). Scattering of only 0.1% of this light as circularly polarized radiation will produce irradiation comparable to that in the experiments in about 2000 years.

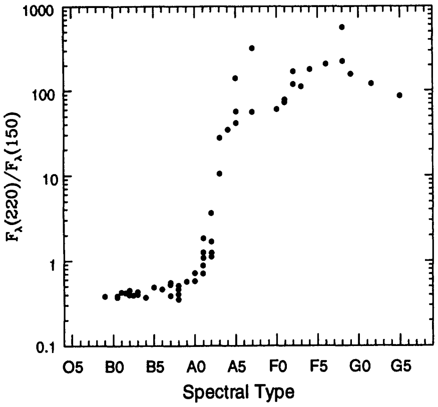

Fig. 3. The ratio of the observed flux density of main-sequence stars at wavelengths of 220 and 150 nm plotted against spectral type (which is determined mainly by the temperature of the stellar surface ranging from 28,000 K at B0 to 5000 K at G5). The data are from the International Ultraviolet Explorer (IUE) Low Dispersion Spectra Reference Atlas (*29*). Stars with spectral energy distributions distorted by interstellar extinction were omitted. Although the hottest stars have rising flux into the UV, there is a sharp transition at spectral type A3, and all stars cooler than A3 have a very steep fall in their spectrum below 200 nm, with the flux density at 150 nm being typically less than that at 220 nm by a factor of ≥100. Stars cooler than G5 were too faint to be observed with IUE but should continue to show the steep fall owing to their low temperatures.

For this material to be relevant to the origin of life it must be delivered to the surface of Earth without destruction or racemization of the chiral molecules. Studies of the delivery of organic material to Earth by interplanetary dust particles, comets, or meteors during the heavy-bombardment phase show that exogenous delivery is comparable with local production by Miller-Urey processes (*24*, *25*). How much of this material would survive delivery without racemization is unclear, but the Murchison results suggest that survival is possible.

The global enantiomeric excess on the early Earth would be less than that of the original material because the racemization time scale (*26*) (ranging from about 10^6 years at 0°C to 10^3 years at 50°C) will typically be less than the lifetime (~10^7 years) set by thermal degradation of the material in hydrothermal vents (*25*). Dilution by racemic material produced locally on Earth will also reduce the excess. On this basis we estimate that the global enantiomeric excess would be in the range 5×10^{-3} to 10^{-7} (*27*). This must be compared with ~10^{-17} resulting from the parity-violating energy difference (*3*), the only other global effect operating. Thus, even under very conservative assumptions, impact-delivered organic material can be the dominant global chiral influence on the early Earth by a large factor. Impacts of small comets could also provide high local concentrations of organic material with enantiomeric excess as high as that found in Murchison, which is again higher than can be produced by any plausible Earth-based process. Thus, whether a very high enantiomeric excess is a prerequisite for the origin of life, or a very small effect is amplified in the process, the ultimate source is likely to be of extraterrestrial origin.

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