Perspective

Developing Chiral Surfaces for Enantioselective Chemical Processing

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DOI 10.1002/aic.12036
Published online August 13, 2009 in Wiley InterScience (www.interscience.wiley.com).

Keywords: chirality, surfaces, asymmetric synthesis, chromatography

Introduction

Any object that cannot be superimposed upon its mirror image is said to be chiral, and the two mirror image forms are called enantiomers. A person's left and right hands are one familiar macroscopic example of chiral objects. Chirality is of immense interest in chemistry, because many organic molecules are chiral. Any atom in a molecule that is tetrahedrally bonded to four different functional groups makes that molecule chiral. Alanine is a simple example of a chiral molecule, having a central C atom that is bonded to H, CH_3, NH_2, and COOH. More complex chiral molecules can have many chiral centers.

From a bulk physicochemical perspective, the chirality of organic molecules is rather uninteresting; the solubility, density, melting point, etc., of the two enantiomers of a chiral molecule are identical. This simple fact makes it impossible to separate enantiomers using the typical tools of chemical engineering. A related reality is that the typical methods of chemical synthesis do not distinguish between enantiomers of a chiral product, so a typical chemical synthesis generates a racemic mixture, that is, an equimolar mixture of the molecule's enantiomers.

The importance of molecular chirality lies in the biological effects of chiral chemicals. A fundamental property of all known living organisms is that they are homochiral. That is, life uses only a single enantiomer of each chiral molecule. As a result, the bioactivity of chiral chemicals is often highly dependent on which enantiomer of the chemical is ingested by the organism. A simple example is limonene, a chemical with two enantiomers which have quite different odors. A more striking example is the illicit drug cocaine. One enantiomer of cocaine has well documented biological effects, although the other enantiomer has no comparable effects.

The differing bioactivity of the enantiomers of chiral compounds is of great importance in the pharmaceutical industry. If the enantiomers of a pharmaceutical compound have different bioactivities, then a racemic mixture of the enantiomers will, at best, have lower efficacy than the enantiomerically pure form. In other cases, the undesirable enantiomer can cause unpleasant or dangerous side effects. To give just one example, levalbuterol, the enantiomerically pure form of an asthma medication, causes significantly fewer side effects than the racemic form, which is marketed in the U.S. as albuterol.

Creation and purification of enantiomerically pure[1] compounds has many ramifications in the pharmaceutical industry. Worldwide sales of enantiopure drugs exceeded $U.S.225 billion per year in 2006, with an annual growth rate of $\sim$10%.[2] If a compound is currently marketed in its racemic form, the corresponding enantiopure compound can be covered by a new patent, thus, extending its protected lifetime. Moreover, the U.S. FDA mandates that each enantiomer of a new compound be tested separately prior to FDA approval,[1] even if the compound that will be marketed will be a racemic mixture This situation means that all pharmaceuticals must be produced in enantiopure form in at least limited quantities.

Because of the importance of producing enantiopure chemicals, numerous methods exist for enantioselective chemical processing. A concise description of these methods has been given in this journal by Rekoske.[1] Broadly speaking, these methods can be divided into efforts to synthesize chemicals in an enantiopure form rather than a racemic mixture and methods for separating enantiomers from racemic (or other) mixtures. We will refer to both of these approaches as enantiospecific processing. The former approach is known as asymmetric synthesis, and it defines an important field within organic chemistry. Asymmetric synthesis is dominated by the use of homogeneous catalysts that are themselves chiral. Although asymmetric synthesis is practiced widely, the use of homogeneous catalysts can

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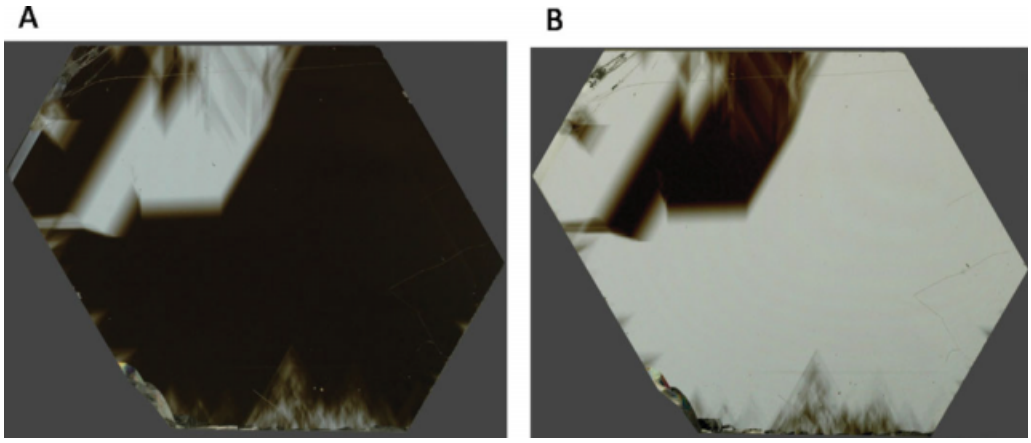

Figure 1. Two photos of a thin slice of a natural quartz crystal illuminated by polarized light.

The crystal is approximately 5 mm across. The plane of polarization was rotated 90° between images A and B. The change in transmitted light as a function of the plane of polarization demonstrates the chirality of the crystal. The appearance of twinned domains of opposite chirality within the crystal can be seen. Images provided courtesy of Prof. G. Rohrer, Carnegie Mellon University.

create challenging purification problems arising from the need to remove the catalyst from the product.

The two main techniques used in enantiospecific separations are chiral crystallization and chiral chromatography. Chiral crystallization can be successfully applied for some compounds by seeding a supersaturated solution of a racemic mixture with crystals of the preferred enantiomer. This approach cannot be used, however, for the initial separation of a new compound. The other common separation technique is chiral chromatography, in which a chiral stationary phase (CSP) is used to separate enantiomers during high-pressure liquid chromatography. Simulated moving-bed techniques play an important role in making chiral chromatography industrially practical. A large number of CSPs are available, and some general rules of thumb have been developed to guide the selection of CSPs for separation of new compounds.[3] Other separation methods such as using reactions to form diastereomers that can subsequently be purified using standard separation techniques are also available.[1] Rekoske emphasized that the effective application of chiral separation methods can have importance in both time-to-market and in process economics.[1]

The broad scope of chemicals that can be considered as potential pharmaceuticals or intermediates, and the enormous challenges posed by the need to develop processes for their enantiopurification create interest in any new class of chiral materials that can potentially open new avenues for enantiospecific processing. In this Perspective article, we describe efforts that have been made over the past decade to create solid surfaces that are chiral. These materials offer the possibility of creating fundamentally new approaches to enantiospecific processing that we hope will add to the list of methods already used to great effect industrially.

Creating Chirality on Solid Surfaces

Our focus in this Perspective article is to consider how solid surfaces can be made in a chiral form. The most obvious method is to irreversibly attach the single enantiomer form of some chiral organic molecule to an otherwise achiral surface. This is the principle underlying the limited number of known chiral heterogeneous catalysts.[4] These materials are described in the next section. This same principle describes many chiral stationary phases used in commercial chiral chromatography in which an achiral stationary phase is functionalized with chiral organic groups.

It is not surprising that the molecular crystals of enantiopure chiral species such as amino acids are chiral objects and that the surfaces of these crystals are chiral. It is slightly more surprising that the crystals of many inorganic materials are also chiral. An excellent example is the common mineral quartz (SiO_2). The tetrahedra that define the local environment of each Si atom in quartz are aligned in a helical structure along one crystallographic axis, endowing the entire crystal with chirality. This bulk chirality can be directly observed under polarized light, as shown in Figure 1. The two enantiomers of crystalline quartz can be identified from the shape of well developed crystals.[5] Many other common minerals are also chiral.[6] A review of metal oxide crystal structures by Halasyamani et al. lists 210 oxides whose structure is chiral.[7] When a crystal has a chiral crystal structure, all of its surfaces are also chiral. Working with materials of this kind, therefore, creates naturally chiral solid surfaces without using any organic functionalization.

It is even more surprising to learn that even materials whose bulk crystals are highly symmetric can have surfaces that are chiral. The bulk structure of the metals copper and platinum, for example, is the face centered cubic structure, which contains many planes of mirror symmetry, and, thus, is achiral. Most studies of the surfaces of these metals examine the small number of atomically-flat, low-Miller index surfaces defined by these crystals, which also possess mirror symmetry and, are, therefore, not chiral. If a metal surface is created, however, along a plane that is not coincident with the crystal's symmetry directions then the resulting surface is chiral.[8,9] This concept defines a fascinating set of intrinsically chiral surfaces from materials whose bulk structure is

achiral. Examples of intrinsically chiral surfaces that have been described in the literature include metals, metal oxides such as $SrTiO_3$,[10] and semiconductors such as Si.[11]

Throughout this article we focus on chiral surfaces that are the external surfaces of solid objects. We note, however, that there has been a surge of activity in recent years in making highly porous materials whose internal surfaces are chiral. A number of chiral metal-organic framework (MOF) materials have been synthesized by using chiral organic species as linkers between metal centers.[12] The nanoporosity created by these crystalline MOFs is chiral. Recently, zeolites with homochiral pores and enantioselective adsorption properties have been reported.[13] Further developments of chiral porous materials of this kind may open a variety of interesting opportunities in enantioselective processing.

Chirally Modified Heterogeneous Catalysts

Unlike the very large number of homogeneous catalysts that are known for asymmetric synthesis,[14] only a small number of effective chiral heterogeneous catalysts have been developed. In the best known example, supported Pt catalysts are modified by the irreversible adsorption of cinchonidine or one of the many derivatives of this multifunctional chiral molecule. These catalysts have been developed to perform highly enantioselective hydrogenation of α-ketoesters (e.g., methyl pyruvate), and this reaction has been demonstrated on the kilogram scale.[4] An interesting feature of this process is that the chirally modified metal catalyst not only imparts chirality to the reaction products, but the rate of the overall hydrogenation reaction is accelerated substantially. The other well studied chiral heterogeneous catalytic reaction is the hydrogenation of β-ketoesters using supported Ni catalysts modified with tartaric acid.[15]

Although high-levels of enantioselectivity can be achieved with the heterogeneous catalysts mentioned previously, the complexity of these materials has made it extremely difficult to generalize their properties to other classes of reactions or chirally modified heterogeneous catalysts. Extensive experimental studies have shown that the enantioselectivity of these reactions is dependent in a complex way on the precise structure of the chiral modifier, the solvent used in the reaction, as well as H_2 pressure and reaction temperature. The use of surface science and spectroscopic methods to probe the mechanisms that determine the enantioselectivity of these catalysts continues to be an active area in which multiple competing hypotheses for the origin of the catalyst's enantioselectivity are being tested.[16,17]

Chiral Minerals

Experiments attempting to use chiral minerals such as quartz in enantioselective chemical reactions date back to at least the 1930s.[18] More recently, Soai and coworkers have reported chemical syntheses with very high-levels of enantioselectivity in which powdered quartz is added as a "chiral promoter".[19] Although the mechanism of these syntheses is not understood, the interaction of reacting molecules with the chiral environment defined by surfaces of the powdered quartz presumably plays a decisive role in determining the chirality of the reaction products.

One aspect of using quartz surfaces in the way just outlined that greatly complicates any attempt to examine their role mechanistically is that natural mineral samples of quartz are commonly twinned. That is, natural quartz crystals often include separate domains of the two crystalline enantiomers of quartz, as shown in Figure 1. This situation implies that powdered samples of natural quartz include a mixture of the mineral's two enantiomers.[5] It is interesting to note, however, that the quartz grown synthetically for applications such as quartz crystal microbalances are typically high-quality single crystals without twinning.

Hazen and coworkers have performed experiments to examine the enantiospecific adsorption of amino acids on specific crystal faces of calcite, another chiral mineral, using large untwinned natural crystals.[20] These experiments showed that the adsorption properties of some, although not all, amino acids on these mineral surfaces are enantiospecific. Han and Sholl have used quantum chemistry calculations to analyze the adsorption of several amino acids on a specific chiral quartz surface,[21] and theoretical descriptions at this level may ultimately make it possible to predict which chiral species would show strong enantiospecific interactions with crystalline surfaces of quartz and other chiral minerals.

Chiral Metal Surfaces

As we have already mentioned, it is possible to make chiral surfaces from achiral single crystal metals. It is useful to examine how this is possible by considering the set of all surfaces that can be created by truncating a bulk metal with a simple structure such as the face-centered cubic crystal. Each possible surface can be defined by a vector normal to the surface; this vector is referred to as the surface's Miller index, denoted by the components of the normal vector (*hkl*). Viewing a projection of a sphere is a compact way to visualize the complete set of Miller indices, and this projection is shown in Figure 2. This so-called stereographic projection or stereographic triangle can be used to classify all possible ideal surfaces that can be exposed by a single crystal of a face-centered-cubic lattice. Each point in the triangle represents a unique surface. Similar diagrams can be constructed for other achiral crystal structures.[22] The points at the vertices of the triangle, the (100), (110) or (111) surfaces, are atomically flat and highly symmetric. These achiral surfaces are known as the low-Miller index planes. The points along the edges of the triangle have Miller indices given by (*hkk*), (*hhl*) and (*hk0*). These surfaces have regions of the low-Miller index planes separated by surface steps that are a single atom high running along a high-symmetry direction on the surface. Because of the symmetry of these surface steps, these surfaces are also achiral.

By far the largest set of possible surfaces in the stereographic triangle is the surfaces not associated with the edges or vertices of the triangle. These surfaces have Miller indices that satisfy $h \neq k \neq l \neq h$ and $h \bullet k \bullet l \neq 0$. These surfaces have regions of the low-Miller index planes separated by steps that are a single atom high that do not point along a high-symmetry direction on the surface. Figure 2 shows the

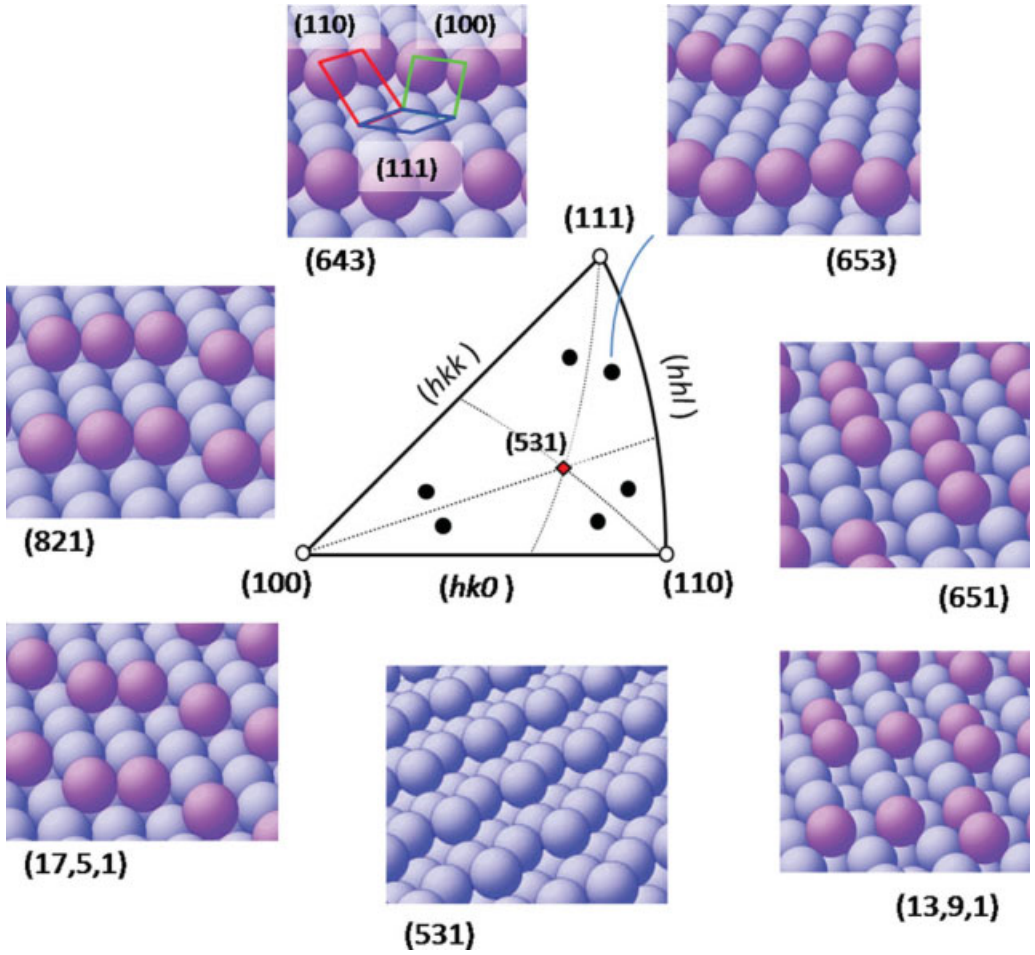

Figure 2. An illustration of the stereographic triangle (center) that defines all possible ideal surfaces that can be obtained from a face-centered cubic (fcc) crystal.

Labels in parentheses indicate the Miller indices of individual surfaces. All surfaces inside the triangle are chiral, having structural motifs based on three crystallographically distinct, low-Miller index microfacets, as illustrated for the (643) surface (top). Six other chiral surfaces are shown, including the (531) surface, which lies at the center of the stereographic triangle and has the highest density of chiral kinks of any ideal fcc surface.

structure of seven surfaces of this kind. Most importantly for our purposes, all surfaces in this large group are chiral.[11] One can appreciate the origin of the chirality of such high-Miller index surfaces by examining the local structure of the surface around the kinks that exist on the steps of these surfaces. As shown on the illustration of the (643) surface in Figure 2, the terrace can be thought of as being a (111) microfacet, although the straight step edge and the kink are formed by (100) and (111) microfacets, respectively. The ideal structures of all chiral, high-Miller index surfaces have this structural motif, they differ only in the choice of low-Miller index microfacets forming the terrace, step and kink, and in the widths of the terrace and the lengths of the step edge; the ideal kinks are always one atomic spacing in width.

The real structures of the chiral metal surfaces differ from those of the ideal crystal cleavage plane. In general, all surfaces are subject to relaxation which does not change their symmetry or chirality, however, gross reconstructions or phenomena such as faceting or step bunching could eliminate local chirality. The magnitude of these effects will depend on the metal and the surface being exposed. Even in the absence of these energetically driven phenomena, surfaces are subject to entropically driven "thermal roughening" arising from diffusion of atoms. The diffusion of atoms along step edges causes coalescence of kinks, and the formation of nonideal kink structures at the intersections of long step edges. Thermal roughening has been studied for a number of chiral Cu and Pt surfaces, and it has been shown that although step edges do roughen at elevated temperatures they retain their net chirality because the kinks still occur at the intersections of three different low-Miller index microfacets with the same sense of rotational orientation.[23,24] These effects are shown in Figure 3.

Naturally chiral metal surfaces have enantiospecific interactions with chiral adsorbates. These interactions are the origin of enantioselectivity in surface chemistry. For example the orientations of chiral adsorbates depend on the handedness of the underlying substrate.[25] The adsorption energies of chiral molecules on naturally chiral metal surfaces are

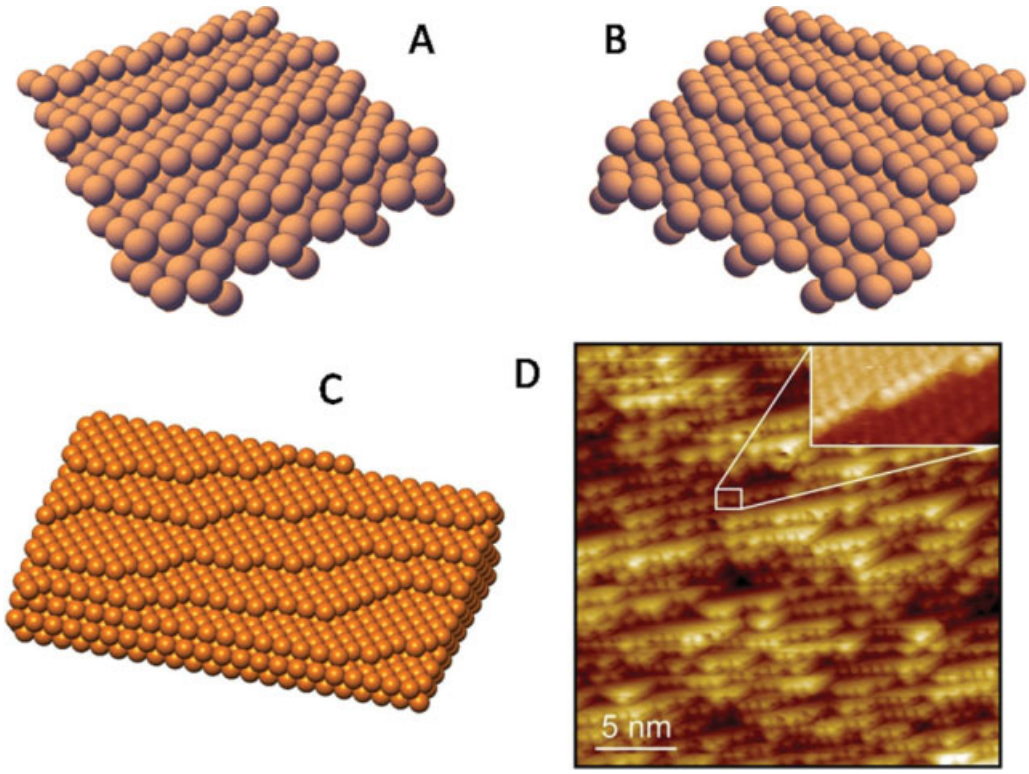

Figure 3. (A) and (B): The ideal structure of the two enantiomers of the ideal fcc(643) surface, respectively.

These two surfaces are mirror images of one another and cannot be superimposed, (C) a simulated structure of a chiral fcc(643) metal surface after thermal diffusion of surface atoms has caused restructuring of the surface steps,[23] (D) An atomically-resolved scanning tunneling microscopy image of a chiral Cu(643) surface.[24] The inset shows the atomic structure of a single step edge on the surface. (Images in (C) and (D) reproduced with permission from the American Chemical Society).

enantiospecific.[26] The largest measured enantiospecific differences in adsorption energies for molecules adsorbed on metal surfaces are of order $\Delta\Delta E_{des} = 1$ kJ/mole, although computational modeling studies have identified chemisorbed systems with larger differences in adsorption energy.[27]

Enantioselective reaction kinetics have been observed in the dehydrogenation of alkyl groups on Cu surfaces,[28] and in the electrooxidation of sugars on naturally chiral Pt electrodes.[29] The greatest enantioselectivities observed in those processes are rate differences of a factor of three. The conclusions of this body of work are that enantiospecificity can be observed in a number of interactions of chiral molecules with chiral surfaces. The naturally chiral metal surfaces form well-defined, model systems for study of chirality and enantioselectivity, and they deserve study as models that can lead to the level of understanding that is needed for development of new chiral materials for practical enantioselective chemical processes.

One of the critical challenges to the engineering application of chiral surfaces is that of preparing them in practically useful quantities. To date, much of the laboratory study of the naturally chiral surfaces has been performed using single crystalline samples with very low-surface area. For applications such as sensors, this might be sufficient. For applications such as catalytic conversion, however, it is not. For materials with naturally chiral bulk structures, one could imagine taking enantiomerically pure bulk samples and pulverizing them to obtain high-surface area powders. The potential complications of materials twinning associated with this approach have already been discussed previously in relation to experiments performed with powdered quartz. Several avenues exist that raise the possibility of preparing naturally chiral metal surfaces on a large scale. There is experimental evidence that the adsorption of L-lysine on achiral Cu(100) surfaces can result in reconstruction of the surface to yield homochiral, high-Miller index facets, thus, imprinting the chirality of the compounds onto the surface.[30] This suggests that use of chiral reagents to imprint the surfaces of metal powders might yield moderately high-surface area chiral metals. Another interesting and relevant technology is that of the RABiTS^{TM} process, in which metal foils are cold rolled from bulk metals in such a way that they crystallize during rolling to yield biaxially textured foils with the (100) axis normal to the foil surface.[31] It may be possible to modify foils of this kind through shearing along low symmetry directions such that the surface has a net orientation along a high Miller index direction. Finally, it has been demonstrated that chiral CuO films can be electrodeposited a from a solution of Cu tartrate.[32] This kind of film deposition may make it possible to conformally coat macroporous solid supports with chiral films.

Perhaps the two application areas in which naturally chiral surfaces might be best suited are as sensors or for crystal nucleation. Both of these applications require surfaces of limited area. Sensors based on the use of adsorption from a gas phase or from solution could be made enantioselective if

their surfaces were chiral. As nuclei for crystallization, naturally chiral surfaces might be useful because they could be designed such that one enantiomer of the crystallizing compound forms on one enantiomer of a chiral surface, although the other enantiomer is deposited on the other enantiomer of the surface. Naturally chiral surfaces may be advantageous over surfaces modified with organic ligands because of their inherent thermal stability; they will retain their desirable surface properties even after heating to temperatures at which organic ligands would decompose.

Chiral Surfaces and Biological Homochirality

We close by turning to a topic with limited engineering applications but profound scientific implications, namely the origin of biological homochirality. Various hypotheses have been advanced to account for the emergence of biological homochirality, but all hypotheses to date are highly speculative. Hazen has raised the possibility that chiral surfaces may play a role in this problem,[6] noting that chiral minerals such as quartz were extremely common on the prebiotic Earth.

Chiral surfaces on minerals could only be related to biological homochirality if this homochirality was initiated at an isolated location rather than in multiple independent locations, because a racemic mixture of chiral minerals must exist by symmetry on any global scale. An intriguing hint that local symmetry breaking is possible comes from studies of the organic species that were found on the Murchison meteorite.[33] These organic species are thought to have originated via chemistry occurring on surfaces of mineral grains of the meteorite in interstellar space, a conclusion supported by the presence of multiple non-natural amino acids that would not have appeared from terrestrial sources. Importantly, these non-natural amino acids existed in enantiomeric excess, not as racemic mixtures.[33] This observation is at least suggestive that chemistry occurring on a finite collection of chiral surfaces can lead to spontaneous symmetry breaking and net chirality.

Although a chemical process occurring on a chiral mineral surface could lead to a local enantiomeric excess, the persistence of this homochirality on large scales only seems plausible if the local chemical process suppresses formation of chemicals with the opposite chirality in some way. A phenomenon similar to this principle is realized in some implementations of chiral crystallization where nucleation of one enantiomer can reduce the supersaturation of the opposite enantiomer to levels where nucleation of the second enantiomer is negligible.[34] Closely related mechanisms are thought to control several well studied asymmetric synthesis reactions.[35] This discussion is of course very far from postulating a specific mechanism that led to the emergence of biological homochirality, but the possibility of making progress on this fascinating and unresolved scientific problem is likely to spur continued research activity.

Acknowledgments

Our joint work on chiral materials has been supported by the NSF, the DOE Catalysis Futures Program, and the Merck Foundation. We have greatly benefited from collaborations with F. Zaera, W. T. Tysoe, and E. C. H. Sykes.

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