Chiral selection on inorganic crystalline surfaces

From synthetic drugs to biodegradable plastics to the origin of life, the chiral selection of molecules presents both daunting challenges and significant opportunities in materials science. Among the most promising, yet little explored, avenues for chiral molecular discrimination is adsorption on chiral crystalline surfaces periodic environments that can select, concentrate and possibly even organize molecules into polymers and other macromolecular structures. Here we review experimental and theoretical approaches to chiral selection on inorganic crystalline surfaces — research that is poised to open this new frontier in understanding and exploiting surface-molecule interactions.

ROBERT M. HAZEN*1 AND DAVID S. SHOLL²

¹Carnegie Institution of Washington and NASA Astrobiology Institute, 5251 Broad Branch Road NW, Washington DC 20015, USA ²Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA *e-mail: r.hazen@gl.ciw.edu

Chemical interactions that occur at the interface between crystalline surfaces and aqueous solutions are of central importance to a broad range of scientific and technological investigations, including the mechanisms of corrosion, the control of heterogeneous catalysts, the design of chemical sensors, and the development of a host of products from paints and glues to solvents and cleaners. Geochemists and environmental chemists have paid special attention to reactions that occur between crystalline mineral surfaces and aqueous species — interactions that play a central role in numerous natural processes, including weathering and soil formation, pH buffering, hydrothermal ore deposition, biofilm formation, catalytic organic synthesis, and the uptake and release of organic and inorganic species that affect water quality¹.

In this regard, chiral crystalline surfaces that selectively absorb chiral molecules — so-called lefthanded and right-handed molecules that are not superimposable on their mirror image — are of special interest. A strong chiral preference for amino acids, sugars and other essential biomolecules is a defining characteristic of biological systems. Abiotic processes that select left-handed versus right-handed molecules are thus central to geochemical models of life's origin and evolution^{2,3}. Chiral recognition and separation of molecules, furthermore, is vital to the pharmacological activity of many drugs, the biodegradation of packaging materials, the development of stronger polymers, and many other applications in science and industry⁴.



Nevertheless, interactions between chiral molecules and crystalline surfaces have received relatively little attention until recently. In a brief review of these interactions, Jacoby claims that "chiral surface chemistry has hardly been defined, let alone explored"⁵. The technical challenges of this pursuit are compounded by the inherent multidisciplinary nature of the field. Indeed, the interface between inorganic crystalline surfaces and organic molecules provides an appropriate metaphor for the subject.

Here we review the rapidly growing experimental and theoretical literature on selective adsorption of chiral molecules onto chiral inorganic crystalline surfaces. We do not address the related, but distinct, topics of chiral molecular organization on achiral crystalline surfaces^{6,7}, or adsorption onto chiral organic surfaces⁸—both subjects deserving of review articles.

Current research on chiral inorganic crystalline surfaces progresses on two complementary fronts:

Figure 1 Quartz crystal (~1mm diameter) displaying selective deposition of iron oxide coatings on $\{10\overline{1}1\}$ rhombohedral faces, compared with adjacent {0111} rhombohedral faces. This behaviour points to the possibility of differential, selective adsorption of chiral organic species on different quartz growth surfaces a phenomenon not easily documented in powdered material. The specimen, which formed hydrothermally as a crystal-lined pocket in basalt, was collected in 1967 in Paterson, New Jersev, by Robert Hazen.

Figure 2 The mineral quartz, SiO₂, occurs in both left- and right-handed variants, depending on the orientation of structural helices. External morphology of natural quartz crystals often serves to distinguish a, leftversus b, right-handed crystals. However, even morphologically distinct natural crystals are usually strongly twinned internally (c). Powdering natural crystals, therefore, produces a mixture of left- and right-handed material (after Dana²⁸). Copyright © (1949, Wiley). This material is used by permission of John Wiley & Sons, Inc.



phenomenological investigations using natural minerals, and fundamental studies using single-crystal samples of manufactured materials. For almost 70 years, origin-of-life specialists have focused on demonstrating the phenomenon of chiral molecular adsorption on a mineral surface — a process that might have jumpstarted the homochirality characteristic of life. Within the past decade, other materials scientists have used metal surfaces to tackle this experimental problem. The principal challenge here lies in detecting a chiral excess that may be as small as 1% for adsorbed molecular species in concentrations no more than ~1 nanomole cm⁻².

Researchers have also attempted to understand the theoretical basis of chiral interactions between molecules and surfaces. This task, which merges experimental studies with computational techniques, requires an exact knowledge of crystalline surface structures that are typically deformed in the vicinity of an aqueous medium^{9,10}, as well as molecular and crystal surface charge distributions that are strongly dependent on pH, aqueous ions and other chemical factors^{11,12}.

Ultimately, when the phenomenon of chiral discrimination has been established and some principles of the structural interactions clarified, we look to the computer-aided design of highly efficient crystalline surfaces to promote specific chiral separations and synthesis reactions. If successful, this approach could lead to valuable new laboratory and industrial processes for analysis and manufacturing.

ON THE NATURE OF CHIRAL CRYSTALLINE SURFACES

Selective adsorption of a chiral molecule on a crystalline surface is analogous to a ten-pin bowler's selection of a left- versus right-handed ball. Ten-pin bowling balls feature three non-colinear holes for the thumb and first two fingers. A left-handed bowler cannot use a righthanded ball and vice versa. Similarly, preferential selection of chiral molecules on a crystal surface implies at least three non-colinear points of interaction between the molecule and an acentric solid surface¹³ (that is, a surface without a centre of symmetry).

Chiral adsorption clearly requires both a chiral molecule and a chiral crystalline surface, although under special circumstances, adsorption of prochiral species on achiral surfaces can result in locally chiral adsorbate–surface complexes¹⁴. The properties of chiral molecules have been studied for more than a century and a half^{15,16}, and chiral chemistry is a thriving branch of organic chemistry^{17,18}. The subject of chiral crystalline surfaces, however, has received relatively little attention, and most previous studies of chiral adsorption have failed to exploit these surfaces effectively. It is worthwhile, therefore, to review the most important types of chiral crystalline surfaces available for adsorption studies.

Crystals that lack a centre of symmetry provide the most obvious chiral surfaces for experimental study. Quartz (SiO₂; trigonal space group $P3_221$ or $P3_121$), which is by far the most common acentric mineral in nature, has a structure that features a helical arrangement of corner-linked SiO4 tetrahedra; left- and right-handed quartz structures are defined by the sense of that helix. Many other acentric materials are known, including over 210 metal oxides¹⁹. Because of its abundance, almost all experimental studies of chiral adsorption have thus focused on the symmetrybreaking effects of right-versus left-handed quartz²⁰⁻²⁴. However, all of these studies used quartz crystals that were powdered — a procedure that for two reasons severely limits the possibility of determining the magnitude, or identifying structural mechanisms of adsorption on specific surfaces.

First, as with any crystalline substance, different crystallographic planes of quartz are known to possess dramatically different adsorption characteristics, even in the absence of chiral effects. For example, some specimens of quartz display differential formation of iron oxide coatings on the two symmetrically distinct rhombohedral faces (Fig. 1), designated r and z for $(10\overline{1}1)$ and $(01\overline{1}1)$, respectively (Fig. 2). This behaviour is duplicated by other surface properties in other phases; for example, it has been demonstrated that there are significant differences in the sensitivity of pyrite (FeS₂; cubic space group Pa3) to oxidation for the (100) and (111) planes²⁵. When studying chiral adsorption, powdering the quartz sample exposes the chiral adsorbate to all possible crystallographic faces simultaneously. It is quite possible, however, that one crystallographic plane of pure left-handed quartz selectively adsorbs one molecular enantiomer, whereas another plane on the same crystal adsorbs the other enantiomer. Powdered quartz averages potentially strong adsorption effects on different faces, while destroying all structural information that might reveal adsorption mechanisms.

A second argument against powdering quartz (an argument specific to natural specimens of that mineral) is that virtually every natural quartz crystal — even those with distinctive left- versus right-handed external morphology — are internally twinned (Fig. 2). Individual external quartz crystal faces may possess a uniform left- or right-handed surface structure suitable

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REVIEW ARTICLE

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for experimental study, but powdering a natural crystal inevitably blends left- and right-handed domains. Studies of chiral selection using such mixed samples are meaningless. We conclude that the only effective way to study chiral adsorption on quartz or any other acentric crystal is to examine well-developed chiral growth faces on well-faceted left- and right-handed crystals.

Somewhat counter intuitively, centric crystals can also provide a rich variety of chiral solid surfaces for study^{3,26,27}, because any crystal plane with a surface structure lacking mirror symmetry is intrinsically chiral. Most common rock-forming minerals display crystal growth faces that meet these conditions^{28,29}. Chiral surfaces of centric calcite (CaCO₃; rhombohedral space group $R\overline{3}c$) have been studied by Hazen et al.27. The existence of chiral surface faces of centric materials is of course not limited to natural minerals; crystal surfaces of simple metals that have atomic steps that are not straight lines were found to be chiral²⁶. Chiral adsorption has since been demonstrated both experimentally and theoretically on a number of chiral metal surfaces^{30–39}. As in the case of acentric crystals, chiral adsorption experiments must be performed on crystallographically uniform surfaces.

In addition to the intrinsically chiral surfaces discussed above, there is a considerable amount of literature related to achiral surfaces that have been templated by irreversible adsorption of chiral organic species. The most developed examples of heterogenous enantioselective catalysis fall in this class^{40–45}. Considerable activity has also been focused on the chiral properties of amino acids adsorbed on achiral metal surfaces^{46–50}. Although these composite materials may provide valuable avenues for exploring enantioselective chemistry, they fall outside the scope of this review.

THE PHENOMENOLOGY OF CHIRAL ADSORPTION ON NATURAL MINERALS

Research efforts spanning more than 65 years have focused on documenting chiral selectivity on crystalline surfaces. These studies provide convincing proof of the phenomenon and point to tantalizing directions for further study.

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As noted above, the first efforts concentrated on polycrystalline quartz. Although several of these early studies reported success, the experiments were not repeatable, and it was concluded that all previous reports were erroneous⁵¹. One of the previous problems was alleviated by using untwinned commercial crystals of left- and right-handed quartz, although the samples were powdered^{22,23}. A 1.4±0.4% asymmetric preferential adsorption of D- and L-alanine on rightand left-handed quartz, respectively, was found. It has also been demonstrated that left- and right-handed powdered quartz (again using chirally pure synthetic material) promote the chiral synthesis of pyrimidyl alkanol with a chiral excess of $95 \pm 2\%^{24}$. These experiments establish the phenomenon of chiral interactions between molecules and crystal surfaces, though the extent and mechanisms of the effect are obscured by the use of polycrystalline quartz.

Perhaps the most dramatic, albeit indirect, demonstrations of strong interactions between chiral molecules and growth surfaces of a centric mineral involve crystal growth morphology. Strongly asymmetric crystal growth morphology of gypsum (CaSO₄·2H₂O; monoclinic space group A2/a) was found when grown in the presence of 28 different chiral organic molecules, including amino acids⁵²; such asymmetric growth morphologies were also found in natural gypsum from evaporite deposits in Poland⁵³. Gypsum's common {110} and {111} crystal faces, which are chiral growth surfaces, thus represent likely candidates for chiral selective adsorption.

A similar asymmetric growth phenomenon has been described for calcite⁵⁴. In this work, atomic force microscopy was used to image the asymmetric patterns



Figure 3 Calcite, CaCO₃, displays stepped-growth features on (1014) cleavage surfaces when placed in a supersaturated aqueous calcium carbonate solution. The image is courtesy of H. Teng (adapted from Orme et al.⁵⁴). Liquid-immersion atomic force microscopy was used by Teng and co-workers to study these calcite growth features in the presence and absence of chiral solutes. a, In pure water, growth steps possess the mirror symmetry of the cleavage face. b, In solutions of L-aspartic acid (left image) and D-aspartic acid (right image), however, steps display asymmetric crystal growth. This phenomenon reveals chiral interactions between the calcite surface and chiral molecules. which selectively block growth sites (after Orme et al.54).

Figure 4 The common {2131} trigonal scalenohedral ('dogtooth') form of calcite features adjacent crystal faces with enantiomorphic surface structures (after Dana²⁸). The markedly acentric surface structures of both the $(3\overline{1}\,\overline{2}1)$ face (left) and the $(21\overline{3}1)$ face (right) consist of corner-linked chains of CaO₆ octahedra (yellow), crosslinked by planar CO₃ groups, which here are seen almost on edge. L-aspartic acid is observed to adsorb preferentially on the $(3\overline{1}\,\overline{2}1)$ face, whereas p-aspartic acid adsorbs preferentially on the $(21\overline{3}1)$ face.



f.c.c (643)

Figure 5. A top view of an ideal face-centred-cubic (f.c.c.) (643) surface, with step-edges highlighted with solid lines (after Sholl *et al.*³²). The terraces separating the single-atom high steps have a local (111) orientation, and the step edges are comprised of two distinct local orientations, periodically replicated along the step edge.

that form when calcite is grown in the presence of Dversus L-amino acids (Fig. 3). Calcite was subsequently chosen for chiral adsorption experiments because of its geochemical relevance to origin-of-life studies²⁷. Calcite was one of the most abundant marine minerals in the Archaean Era^{55,56}, and calcite crystal surfaces would thus have been widely present in prebiotic environments. Calcite is also biochemically relevant because it adsorbs amino acids57,58; biomineralized calcite is strongly bonded to proteins in the shells of many invertebrates^{57,59,60}. An additional pragmatic reason for using calcite is that it is readily available in large (>10 cm long) crystals with prominent $\{21\overline{3}1\}$ trigonal crystal forms known as scalenohedra (Fig. 4)²⁸. Pairs of adjacent scalenohedral faces, for example $(21\overline{3}1)$ and $(3\overline{1}\overline{2}1)$, possess surface structures that are related by mirror symmetry (Fig. 4) and thus have the potential for chiral selectivity.

As a test of chiral selective adsorption, four calcite crystals were immersed for 24 hours in a 0.05 M solution of racemic aspartic acid²⁷. Enantiomeric faces equivalent to $(21\overline{3}1)$ and $(3\overline{1}\overline{2}1)$ displayed up to 10% preferential adsorption of D- and L-aspartic acid, respectively. By contrast, no selective adsorption was observed on rhombohedral (10 $\overline{1}4$) cleavage faces, which have centric surface structures and thus serve as an experimental control. This study of the calcite–aspartic acid system is the first experimental demonstration of significant chiral selectivity by a centric natural crystal.

CHIRAL ADSORPTION ON CHIRAL METAL SURFACES

The study of chiral adsorption on chiral metal surfaces began with the observation that many crystal surfaces of simple metals are chiral²⁶. The ideal structure of the (643) face of a face-centred-cubic (f.c.c.) metal is shown in Fig. 5. The chirality of this surface and those like it stems from the repeated intersections of unlike step edges on the surface^{26,32,37}. In fact, the (*hkl*) Miller index surface of any f.c.c. metal is chiral, provided that³² $h \neq k \neq l$ and $h \times k \times l \neq 0$. The net chirality of singlecrystal samples can in many cases be demonstrated directly by the existence of an asymmetric low-energy electron diffraction pattern^{26,37,39}.

One theme in research on chiral metal surfaces has been to characterize the enantiospecific adsorption of small chiral molecules on clean surfaces in ultra-high vacuum (UHV). Experimentally, temperature programmed desorption (TPD) can be used to measure the difference in desorption energies for R- and Senantiomers of the species of interest desorbing as pure species from a chiral surface $^{26,33-35,61}$, $|\Delta\Delta E_{des}|$. The first experiments²⁶ of this type examined 2-butanol, the smallest chiral alcohol, desorbing from Ag(643). In this case, $\Delta\Delta E_{des}$ was zero within the limits of experimental resolution. An advantage of examining adsorption in UHV is that this situation is amenable to atomically detailed modelling provided an adequate description of adsorbate-surface interactions is known. The first indication that chiral metals could have enantiospecific adsorption properties came from atomistic simulations of small chiral hydrocarbons adsorbed on chiral Pt surfaces³⁰. These simulations relied on interatomic potentials for hydrocarbon-Pt interactions parameterized to fit a variety of molecular beam scattering experiments on flat and stepped Pt surfaces62,63. After performing initial studies to examine the influence of adsorbate flexibility³¹ and substrate relaxation⁶⁴, a series of calculations was used to assess the enantiospecific adsorption of a homologous series of four chiral cycloalkanes on four chiral Pt surfaces³². Adsorption enantiospecificity in these calculations can be characterized by the energy difference between the global minimum energy states of the adsorbed R- and s- enantiomers, $|\Delta\Delta E_0|$, and the observed values for $|\Delta\Delta E_0|$ range from ~0.0 to 0.6 kcal mol⁻¹. Roughly a quarter of the examples examined had $|\Delta\Delta E_0| < 0.1$ kcal mol⁻¹, which was the approximate experimental sensitivity in the original experiments of McFadden et al.²⁶ Subsequent experiments have demonstrated measurable enantiospecific desorption effects for propylene oxide on Cu(643) $(|\Delta\Delta E_{des}| \approx 0.06 \text{ kcal mol}^{-1})^{34,35} \text{ and } 3\text{-methyl}^{-1}$ cyclohexanone (3MCHO) on Cu(643)

 $(|\Delta\Delta E_{\rm des}| \approx 0.22 \pm 0.05 \,\rm kcal \, mol^{-1})^{35,61}.$

Several points need to be made when considering the values of $|\Delta\Delta E_{des}|$ and $|\Delta\Delta E_0|$ listed above. First, these quantities do not measure precisely the same property. Simulations of TPD experiments based on detailed atomic models of molecular adsorption on chiral Pt surfaces have been performed65. The main observation from this work is that the energy differences measured by TPD, $|\Delta\Delta E_{des}|$, tend to be in the same range of energies observed using $|\Delta\Delta E_0|$, even though the latter is defined using only the global minimum energy states, and the former involves a thermal average over multiple local energy minima. Second, although the absolute energy differences seem quite small, they are enough to induce physically significant effects. For example, the observed $|\Delta\Delta E_{des}|$ for 3MCHO on Cu(643) corresponds to a 30% difference in the desorption rates of the two enantiomers at room temperature. Recent experiments⁶¹ have shown that this difference in rates can lead to substantial enrichment of

an initially racemic mixture of 3MCHO by establishing an adsorption/desorption equilibrium with the gas mixture at temperatures associated with enantiospecific peaks in TPD. Furthermore, energy differences of considerably less than 1 kcal mol⁻¹ have been shown to be sufficient to allow effective chiral separations using gas chromatography with permethyl- β -cyclodextrin as a chiral stationary phase⁶⁶.

A complementary means for examining chiral adsorption on chiral metal surfaces that potentially has more relevance to the mineral studies described above, is to use these surfaces as electrodes for probing the electrochemistry of chiral molecules in aqueous solution. Cyclic voltammetry (CV) has been used to examine glucose and a range of other sugars interacting with chiral Pt electrodes^{36–39}. Strong chiral discrimination between L- and D-glucose was observed on Pt surfaces with various types of chiral kink sites. This work was in fact the first to demonstrate experimentally that intrinsically chiral metal surfaces can discriminate between molecular enantiomers. Experiments³⁷ over a range of temperatures indicate that the energy difference between barriers to electrooxidation of L- and D-glucose on Pt(643) is ~0.33 kcal mol⁻¹. One strength of these experiments is that the observed CV peaks can be related directly to individual terrace and step sites on the electrode surface - a procedure that yields microscopic insight into the surface locations leading to chiral discrimination. As with the UHV experiments discussed above, not all chiral molecules exhibit chiral discrimination during CV on chiral Pt electrodes. For example, dihydrocinchonidine, a species closely related to the chiral templates used in widely studied heterogeneous enantioselective catalysts, showed38 no chiral discrimination on Pt(643) or Pt(321). A recent observation that has important implications for understanding chiral adsorption on minerals is that the identity of anions present in solution can dramatically affect the ability of chiral Pt electrodes to discriminate between chiral species. Specifically, CV of glucose in a 0.1 MH₂SO₄ solution shows strong discrimination between L- and D- forms on several chiral Pt surfaces, but this discrimination is negligible if the solution is changed to 0.1 M perchloric acid³⁹. The origin of this behaviour remains an open problem. These experiments suggest that understanding the role of aqueous species may be vital in extending observations of chiral adsorption to realistic geochemical scenarios.

One important challenge in quantitatively understanding chiral adsorption on chiral metal surfaces is to describe accurately the atomic-scale structure of these surfaces. Figure 5 is an idealized representation made simply by terminating a bulk f.c.c. crystal along the appropriate surface plane. In reality, step edges on metal surfaces held at moderate temperatures become disordered due to thermally activated diffusion of surface atoms67,68. This phenomena can be seen in the room-temperature scanning tunnelling microscope (STM) image of the Cu(5890) surface shown in Fig. 6. The ideal termination of this chiral surface has (100)-oriented terraces separated by periodic single-atom-high step edges, analogous to the surface shown in Fig. 5. In the STM image, the single-atom-high steps are clearly



visible, but their periodicity has been disrupted by thermal fluctuations.

Thermal disorder potentially poses a severe problem for efforts to observe chiral adsorption on metal surfaces, because the chirality of these surfaces is inherently due to the existence of specific step-kink structures. This issue has been tackled by developing a detailed model of the step roughening of Pt surfaces with well-separated steps^{32,65,69}. The model in this work uses first-principles density functional theory (DFT) calculations for Pt atom diffusion near Pt surface steps, but uses coarse-grained lattice methods that allow direct simulation of surfaces containing many thousands of atoms on the timescales of minutes and hours relevant to experiments. An example of a chiral Pt surface structure predicted by this model after annealing an initially ideal surface for 1 hour at 500 K is shown in Fig. 7. The central conclusion of this work is that although thermal diffusion can lead to significant local disorder, the resulting surfaces maintain their net chirality and thus still exhibit chiral adsorption. In some instances, numerical measures of adsorption enantiospecificity such as $|\Delta\Delta E_0|$ are actually enhanced by thermal disorder⁶⁵. A second observation from these simulations is that thermal disorder tends to diminish the differences in chiral adsorption between chiral surfaces that have different Miller indices but similar terrace-step-kink structures. This observation may significantly reduce the number of chiral metal surfaces that need to be examined to describe comprehensively chiral adsorption on the chiral faces of a particular metal.

Figure 6 Scanning tunnelling microscope (STM) image of a 24.3×24.3 nm region of a Cu(5,8,90) surface reproduced from Dieluweit *et al.*¹⁰¹. The ideal Cu(5,8,90) surface is chiral and has (100) oriented terraces. Roughly 30 individual singleatom-high steps are visible. Deviations from the surface's ideal structure due to thermal roughening of the step edges can clearly be seen in the STM image.



Figure 7 The structure of a chiral Pt surface after annealing an initially ideal surface at 500 K for 1 hour using the DFT/lattice model described in the text (after Sholl et al.32). Step edges are highlighted with solid lines. The initial structure used in this calculation had periodic step edges with a structure similar to that of the ideal f.c.c.(643) surface shown in Fig. 5. Thermal roughening of the step edges causes substantial deviations from the ideal surface structure. but the resulting surface is still globally chiral.

A second challenge for quantitatively predicting the effects of chiral adsorption on chiral metal surfaces is that some metal surfaces spontaneously reconstruct. The 'missing-row' reconstruction of $Pt(110)-(2\times 1)$ provides one well-known example of this phenomenon⁷⁰. Whether surface reconstructions occur for specific chiral metal surfaces, and the impact that such reconstructions would have on chiral adsorption, remain open questions. A related topic of interest is that of adsorbate-induced reconstruction. Some atomically flat metal surfaces can be induced to reconstruct by the adsorption of species as simple as atomic oxygen⁷¹. Two experiments have shown that the adsorption of enantiopure species on achiral metal surfaces can induce reconstruction of the metal surface into a chiral form^{72,73}. These experiments suggest an intriguing middle ground between chiral heterogeneous catalysts, where chirality is imparted on otherwise achiral surfaces by an enantiopure template species, and the chiral metal surfaces discussed above that are chiral due to their surface structure.

IMPLICATIONS FOR ORIGINS OF BIOCHEMICAL HOMOCHIRALITY

The demonstrated ability of minerals to select and adsorb organic molecules has long been recognized as a possible mechanism for one of life's most distinctive biochemical signatures — its strong selectivity for Lamino acids and D-sugars. Almost all prebiotic synthesis reactions yield essentially equal amounts of L- and Denantiomers^{3,74}. Thus, to explain life's chiral excess, two broad categories of symmetry-breaking phenomena have been invoked^{4,75–77}. On the one hand, some researchers favour nebular-scale processes, such as chirally selective photolysis by circularly polarized synchrotron radiation from a rapidly rotating neutron star⁷⁸⁻⁸⁰, magnetochiral photochemistry⁸¹ or parityviolating weak interactions of nuclear particles⁸². These processes are consistent with the small but significant excess of L-amino acids reported from some carbonaceous chondrite meteorites^{83–85}.

On the other hand, many investigators^{2,86–88} have focused on more local 'asymmetric agents'. Some mechanisms rely on local amplification of slight chiral excesses, for example by Bose–Einstein condensation⁸⁹ or by chiral self-assembly of polymers^{90–92} or crystals^{7,93}. These and other chiral selection mechanisms⁷⁵ require further investigation, but the conceptually simpler and geochemically relevant chiral selection mechanism of adsorption on chiral crystal growth surfaces of minerals, described above, has been largely overlooked. According to Lahav³, "if a selective adsorption of chiral amino acids ... on certain crystal faces were observed, then the problem of biological homochirality would be possible to comprehend."

We should note that some authors argue that quartz and other minerals cannot contribute to the origins of biochemical homochirality⁷⁷ because left- and righthanded surfaces are present on Earth in equal abundance^{94,95}. This argument is based on the questionable assumption that multiple origin events occurred at different geographical locations on Earth; the preponderance of L-amino acids in biology is taken as evidence for a global prebiotic excess of L-amino acids rather than an excess of L-adsorbing environments.

We hold a different view: we assume that the nucleation of self-replicating molecular systems is infrequent, whereas the growth of such systems once nucleated is relatively rapid and efficient. In this scenario, a single successful self-replicating chiral synthesis (for example, on one chiral crystal face of one calcite crystal) purely by chance became the dominant biochemical overprint in spite of initially racemic mixtures both of molecules and surfaces.

THE FUTURE: DESIGNING SURFACES FOR CHIRAL SELECTION

The ultimate objective of research on chiral molecular discrimination by crystalline surfaces is to predict adsorption behaviour and design new, more efficient molecule-surface pairs. This challenging task requires knowledge of both the surface structure under practical conditions, and an accurate description of surface-adsorbate interactions. In addition to direct experimental measurements, computational techniques such as ab initio DFT are likely to play a key role in attempts to 'design' efficient chiral surface interactions. Hammer et al. have used DFT to examine the enantiospecific binding of R- and S-2-amino-3-(dimethylphosphino)-1-propanethiol on an ideal Au(17119) surface under vacuum conditions⁹⁶. Both enantiomers of this species form strong chemical bonds to the surface, but the s-enantiomer is predicted to bind to the surface 2 kcal mol⁻¹ more strongly than the R- enantiomer. By describing the total binding energy in terms of the binding of individual functional groups in the adsorbate, this study suggests a route to extending these methods to a broad range of adsorbates%. By extending DFT-based methods for predicting the structure of real chiral metal surfaces by including information about how thermal step fluctuations develop^{32,65,69}, it may be possible to extend calculations of the type performed by Hammer et al. to determine which metal surface would give the strongest enantiospecificity for a particular adsorbate.

The prediction of chiral adsorption properties under aqueous conditions on natural minerals will be even more challenging than the treatment of chiral metals. Perhaps the most pressing current need in this area is to determine accurately the relevant surface structures. High-resolution experimental methods⁹⁷ and DFT calculations^{98–100} have been applied to determine the surface structure of a number of hydrated mineral and oxide surfaces. To date, work of this type has only examined achiral low-index surfaces. It is our hope that similar efforts in the future will bear fruit when applied to chiral mineral surfaces and ultimately allow the predictive control of chiral adsorption on these fascinating materials.

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Correspondence and requests for materials should be addressed to R.M.H.

Competing financial interests

The authors declare that they have no competing financial interests.