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Comments on "Mirror Symmetry Breaking" of the Centrosymmetric CaCO₃ Crystals with Amino Acids

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*I*n a recent Communication "*Phase selection of Calcium Carbonate Through the Chirality of Adsorbed Amino Acids*" published in this Journal, Tremel and co-workers reported crystallization of calcium carbonate in the presence of chiral-resolved and racemic α-amino acids.[1] As an illustration of their results, shown in Figure 1, they found that L-alanine induced precipitation of vaterite, the least stable of the three CaCO₃ polymorphs, whereas the presence of D-alanine yielded, predominantly, the stable polymorph calcite. Racemic alanine induced crystallization of calcite only. The L- and D-forms of proline led to the crystallization of aragonite, the third CaCO₃ polymorph, and calcite (with minor aragonite contamination) respectively. The corresponding forms of α-amino butyric acid, which behaved similarly, yielded aragonite and calcite respectively.

These results appear to provide a deterministic route to "mirror-symmetry breaking", which may have far-reaching ramifications, in particular for the emergence of homochirality on Earth. In our view, however, they violate basic principles of symmetry.

The three CaCO₃ polymorphs are centrosymmetric in structure. Crystals with this symmetry are delineated by pairs of opposite faces (h,k,l) and $(-h,-k,-l)$. If these faces are chiral, they are enantiotopic to each other, but if achiral, they are congruent. The interaction between the face (h,k,l) with a chiral additive of L configuration, will be equienergetic to the interaction of the $(-h,-k,-l)$ face with the additive of D configuration.

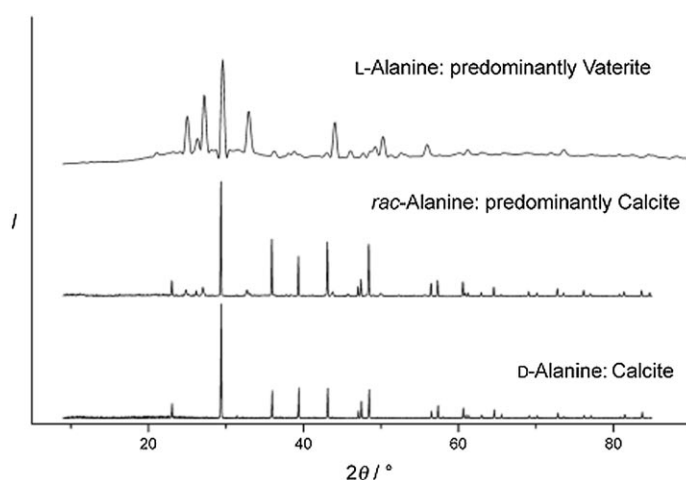These symmetry relationships are depicted in Figure 2 by a representative

Figure 1. X-ray diffraction patterns[1] of CaCO₃ samples obtained with the addition of 1 mg mL⁻¹ L-, D-, or racemic alanine.
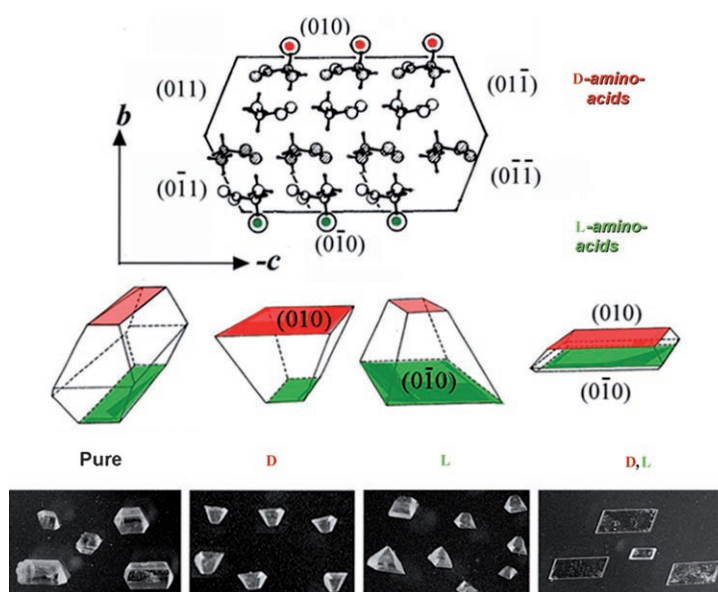

Figure 2. Morphology and photographs of centrosymmetric crystals of α-glycine as well as those grown in the presence of D-, L-, and D,L α-amino acids as additives.

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example involving the changes induced by the presence of D- and L-α-amino acids in the growth and morphology of the centrosymmetric α-polymorph of glycine.[2] The relationships are also in agreement with dissolution experiments involving etch pit formation at dislocation sites. For example, the cleaved opposite (010) and (0$\bar{1}$0) enantiotopic faces of α-glycine, dissolved for several seconds in the presence of D- and L-

alanine respectively, exhibit mirror symmetry[2] (Figure 3). Similar principles were found to operate in the polymorphic behavior of glycine.[3,4]

Tremel and co-workers, in interpreting their results, discussed the interaction of a (104) face of calcite with the D- and L-α-amino acids, describing the symmetry of this face as chiral *P*1. In fact, the (104) surface is achiral, its symmetry being *pg*. The plane of glide

g is perpendicular to the face shown in Figure 4, which also depicts the CaCO$_3$ packing arrangement in the (104) layer. The symmetry of this layer, as opposed to its surface, is centrosymmetric *P*2*g*, where the twofold axis (2) passes through the C−O bond. All six symmetry-related (104) type-faces are crystallographically identical. Therefore, the energy of interaction between D- or L-chiral additives with calcite crystals will be the same. Furthermore, the above considerations are consistent with the enantioselective adsorption and etching behavior of α-amino acids on various faces of calcite, reported by Hazen et al.,[5] and De Yoreo et al.[6] For example, the shape of the etch pits on the (104) face of calcite induced by glycine, exhibit mirror symmetry, and the etch pits induced by D- and by L-aspartic acid appear related to each other by mirror symmetry,[5] in keeping with the enantiotopic relationship between chiral steps related by the glide plane.

The above-mentioned rules of symmetry must hold during formation of the centrosymmetric CaCO$_3$ crystals, including nucleation and the formation of reaction intermediates, irrespective of the presence or absence of defect sites, which, on average, obey the rules of symmetry. By comparison, an analogous set of symmetry rules holds for the asymmetric synthesis of prochiral molecules in solution.[7,8]

We do not dispute the possibility that different polymorphs of CaCO$_3$ may be obtained from the enantiomers of α-amino acid in (isolated) experiments, in which there are random variables. Moreover, kinetic considerations cannot be invoked to account for the results obtained since they would apply equally to both enantiomers in a set of repeated experiments.

In summary, we are of the opinion that the crystallization experiments reported by Tremel and co-workers violate basic rules of symmetry. We suspect the presence of chemical, biological, or other homochiral or achiral contaminants[9] present in the system.
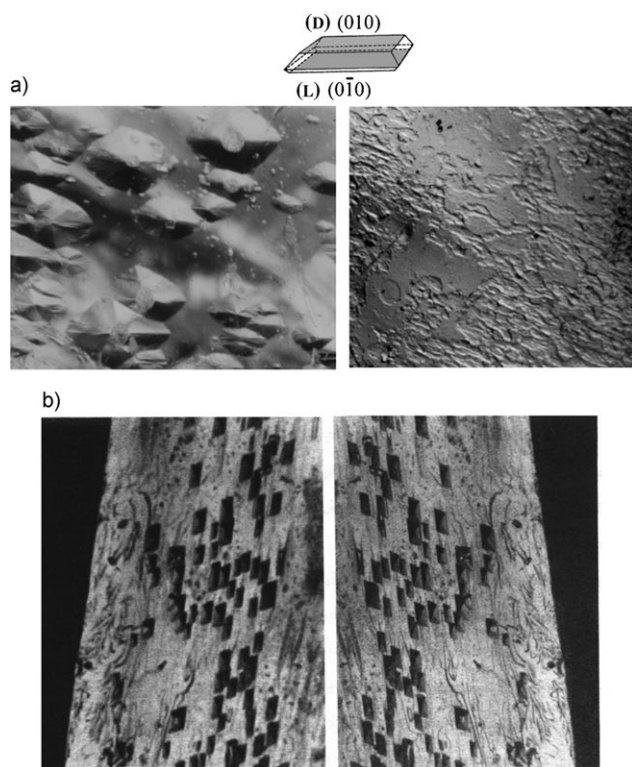
Figure 3. a) Photographs of the (010) and (0$\bar{1}$0) faces of platelike α-glycine after etching each in the presence of D-alanine. b) An α-glycine crystal cleaved to form (010) and (0$\bar{1}$0) faces, subsequently etched in the presence of D- and L-alanine respectively, to yield enantiomorphous etch pits.
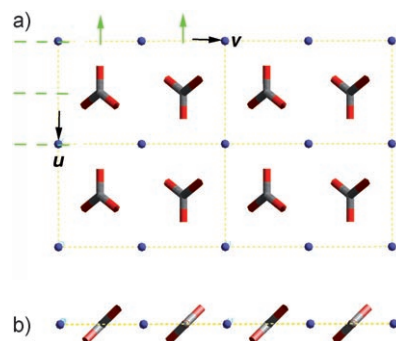

Figure 4. Packing arrangement of the (104) layer of calcite. a,b) Views perpendicular and parallel to the layer plane. The ***u*** and ***v*** axes are parallel to the crystal axes ***b*** and ***a*** + 0.5***b*** − 0.25***c***, respectively. The glide planes (dashed green line) and twofold axes (green arrows) are shown.

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