Molecular Construction of Oriented Inorganic Materials: Controlled Nucleation of Calcite and Aragonite under Compressed Langmuir Monolayers

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The oriented nucleation of the calcium carbonate polymorphs calcite and aragonite under compressed langmuir monolayers of anionic surfactants was studied by optical and analytical electron microscopy. Whereas *n*-octadecanoic acid ($CH_3(CH_2)_{16}COOH$) monolayers induced the nucleation of the {1-1.0} face of calcite, *n*-eicosyl sulfate ($CH_3(CH_2)_{19}OSO_3H$), and *n*-eicosyl phosphonate ($CH_3(CH_2)_{19}PO_3H_2$) promoted nucleation of the calcite (00.1) face. The precipitation of the $CaCO_3$ polymorph araognite is favored by the presence of Mg^{2+} in the crystallization medium. Aragonite nucleation under compressed monolayers of these surfactants showed a similar dependence on headgroup stereochemistry. The (100) face was nucleated under eicosanoic acid monolayers, whereas the (001) face was observed in the presence of eicosyl sulfate or eicosyl phosphonate. The nucleation selectivity observed in these experiments can be explained by an interfacial mechanism that involves stereochemical complementarity between the oxygen atoms of the anionic headgroup and those of carbonate ions located in lattice positions in the crystal faces of nuclei forming at the monolayer/solution interface.

Introduction

The production of tailored inorganic materials to a specific design is desirable for many areas of materials processing since crystallographic selectivity frequently determines the exploitable properties of the inorganic phase. However, despite an extensive knowledge of the macroscopic and microstructural features of inorganic solids and the requirements for ceramic and composite production, the reproducible fabrication of crystalline materials from particles of modal size, defined habit, and uniformity of crystallographic orientation has yet to be achieved. One major limitation has been the difficulty of engineering the size and morphology of crystals, although this has been overcome to some extent with the advent of tailor-made habit modifiers.[1-4]

Another limitation in materials chemistry is the absence of readily available crystallization strategies that control nucleation such that uniformally oriented crystallites are produced. The construction of ordered arrays of crystallographically aligned particles is a much discussed goal since anisotropic materials frequently display physical properties which are orders of magnitude greater than their isotropic counterparts.[5,6] A certain degree of orientation can be introduced through the epitaxial overgrowth of the desired inorganic phase on a "sympathetic" inorganic surface.[7,8] In this case the host surface minimizes the activation energy for nucleation of a specific crystal face as a result of structural matching at the host-guest interface. Of the methods which exist for forming such oriented structures, however, few have sufficient generality to make them applicable to materials of differing chemical composition or physical properties.

An alternative strategy which has generated much interest is the use of supramolecular assemblies of organic molecules as templates to control the nucleation and growth of both organic[9,10] and inorganic crystals.[11-17] These studies indicate that controlled crystallization can be achieved as the result of molecular recognition events between a host organic surface and guest crystals, but the precise nature of the interfacial interactions remains difficult to define because of the complex structure of the

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macromolecular assemblies. To probe the organic–inorganic interface and resolve some of the molecular events mediating template-directed crystal nucleation and growth, a simple model surface was required. With this in mind, langmuir monolayers were adopted as a planar two-dimensional substrates on the assumption that the spreading of an insoluble amphiphile of the appropriate molecular design (headgroup identity, polarity, packing conformation) at the gas–liquid interface could potentially mimic the surface of three-dimensional crystals with the result that nucleation would be favoured at the monolayer–solution interface.[9,18] This premise has been shown to be correct in the oriented nucleation of inorganic[18–27] and organic crystals[28–33] under compressed langmuir monolayers. Calcite ($CaCO_3$) for example nucleates on a (1$\bar{1}$.0) face under compressed monolayers of long-chain alkyl carboxylates ($CH_3(CH_2)_{18-24}CO_2H$) because calcium ion binding to the pseudohexagonal motif of the close-packed surfactant molecules mimics the structure of this crystal face.[20] More recently, it has been shown that compressed monolayers can also influence both the nucleation and growth morphology of oriented barium sulfate crystals.[24,25]

The nucleation orientation of crystals relative to the monolayer appears to be determined by the translation of specific structural information at the organic–inorganic interface with charge accumulation, electrostatic interactions, lattice homology, and stereochemical complementarity being the key elements of this process.[20,23,33] While the importance of lattice matching and Coulombic interactions cannot be discounted, stereochemical complementarity appears to be a critical factor determining the alignment of inorganic crystal nuclei under the monolayer surface.[20,23] For example, stereochemical matching between the carboxylate oxygens of an octadecanoic acid monolayer headgroup and the bidentate orientation of carbonate anions in the calcite (1$\bar{1}$.0) face was responsible for oriented nucleation. On the basis of purely epitaxial considerations, the lattice coordinates of the hexagonally close-packed charged organic surface (a = 5.0A) would favor nucleation of either the {1$\bar{1}$.0} or (00.1) faces. If the preeminence of stereochemistry over other structural factors is accepted, then it follows that the tridentate surface arrangement of carbonates in the calcite (00.1) face (Figure 1a) should be stabilized under a similarly packed monolayer if the headgroups exhibit three oxygen atoms exposed at the air–water interface. This proposal is tested in this paper, in which we describe the influence of compressed monolayers comprising sulfate or phosphonate headgroups on the oriented nucleation of the calcite (00.1) face. Our results show that a dramatic change in the crystallographic alignment of calcite crystals occurs under these headgroups compared with analogous experiments under carboxylate monolayers,[20] indicating that a stereochemically induced mechanism of oriented nucleation is operative. Moreover, because the stereochemistry of the calcite (00.1) face is similar to that of the aragonite (001) face (Figure 1b), we predict and experimentally confirm that similar nucleation effects will be observed for this polymorph when crystallized under langmuir monolayers. In addition, our observations may be relevant to biomineralization studies of aragonite and calcite formation in mollusc shells because these crystals exhibit preferential alignment of their c axes perpendicular to highly organized organic surfaces.[34]

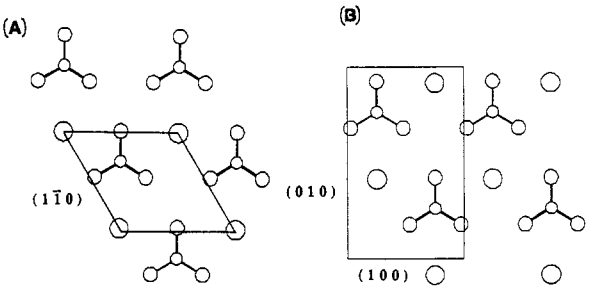

Figure 1. Schematic showing the carbonate layers in the structure of (A) calcite (1/6 [001]) and (B) aragonite (1/4 [001]) viewed down the [00.1] axis.

Materials and Methods

The experimental approach has been described in detail elsewhere.[19,24,25] Supersaturated solutions of calcium bicarbonate ($[Ca^{2+}]$ = 9 mol dm^{-3}; pH 5.8 – 6.0; temperature 293 K) were used as subphases. For experiments involving aragonite, magnesium ions were added ($MgCl_2$; Ca:Mg > 1:6) to these solutions prior to the formation of a compressed monolayer. Under these conditions the induction time (determined by light-scattering techniques) exceeds 3 h at room temperature. Within these time limits the surfactant can be applied and compressed to the desired limit before crystallization in bulk solution is initiated. Langmuir monolayers of eicosanoic acid ($C_{20}H_{41}CO_2H$, limiting area per molecule 22 Å^2), n-eicosyl sulfate ($C_{20}H_{41}OSO_3H$, limiting area per molecule 26 Å^2), or n-eicosyl phosphonate ($C_{20}H_{41}PO_3H_2$, limiting area per molecule 23 Å^2) were formed at the air–solution interface of freshly prepared solutions. Monolayers were prepared in a Nima Technology circular trough by first spreading the surfactant/solvent mixture over the solution surface and then reducing the surface area to the required limit by slow compression. The monolayer phase, surface pressure, and limiting area per molecule were determined from π–A isotherms recorded during compression.

The crystals were removed by collection on glass coverslips for XRD measurements and the nucleation density determinations and particle size distributions determined by optical microscopy.[19] Crystals grown in the absence of a monolayer were collected on glass coverslips placed at the bottom of the reaction vessel. Crystals grown on the monolayer were collected for morphological analyses by slowly dipping aluminum SEM stubs, glass slides,

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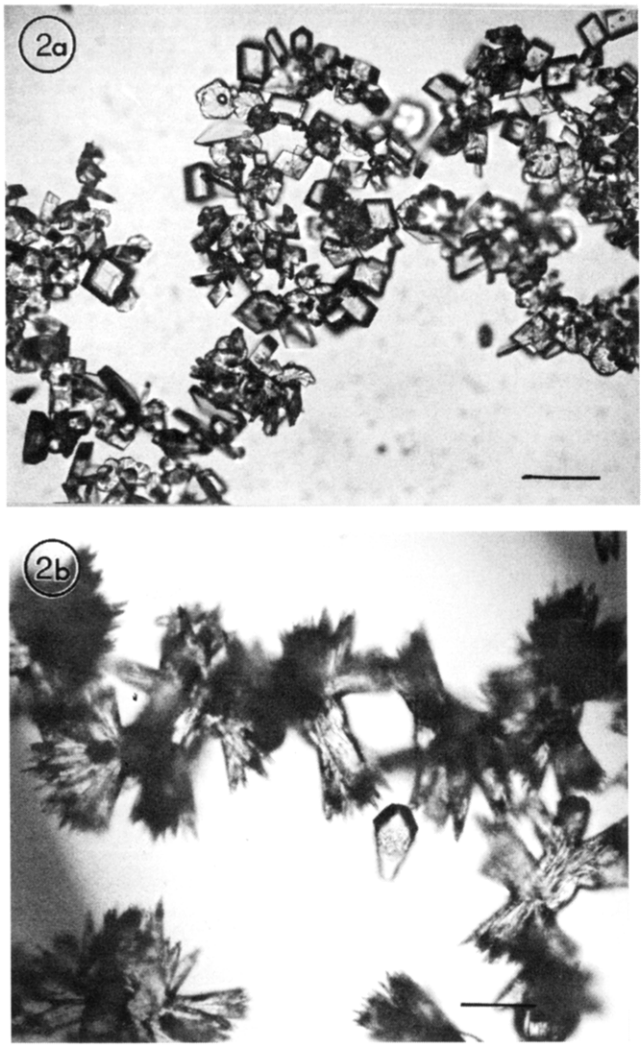

Figure 2. (a) Optical micrographs of rhombohedral {10.4} calcite crystals formed at the gas–liquid interface in the absence of a compressed monolayer. Bar = 50 μm. (b) OM of aragonite crystals formed in the absence of a monolayer. Bar = 25 μm.

or Formvar-coated, carbon-reinforced copper electron microscope grids (3 mm) through the monolayer. The crystals were generally collected after t = 20 h. In some cases, however, the crystals were harvested at earlier time points t = 1 min to 1 h. The structure and crystallographic orientation of the particles were analyzed by high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction using established procedures.[20]

Samples were examined using a JEOL T330 SEM (15 keV) or JEOL 2000FX high-resolution analytical transmission electron microscope operating at 200 kV. Selected area diffraction data were recorded from individual crystals. The electron diffraction patterns and lattice images were indexed by comparing their d spacings and interplanar angles with calculated values assuming, for calcite, a unit cell ($R\bar{3}c$, a = 4.96 Å, c = 17.002 Å) and for aragonite ($Pmcn$) with unit cell dimensions a = 4.959 Å, b = 7.698 Å, c = 5.741 Å.

Results

Control Experiments. In the absence of a monolayer, rhombohedral ({10.4}) crystals of calcite formed within 4–6 h. Some crystals were collected from the gas–liquid interface; they were extensively intergrown and of variable size (32 ± 11 μm). The majority of crystals were collected from the bottom and sides of the crystallization vessel (Figure 2a). In the presence of excess Mg^{2+}, calcite nuclei are destablilized and the formation of aragonite polymorph of calcium carbonate is favored.[36] Thus, when the crystallization media was doped with magnesium at Ca:Mg ratios greater than 1:6, only aragonite was precipitated. Bundles of long acicular crystals showing strong positive birefringence in polarized light formed at the gas–liquid interface (mean size 83 ± 28 μm, Figure 2b). These morphological observations were confirmed by XRD (data not shown).

Calcite Nucleation under Compressed Monolayers of *n*-Eicosyl Sulfate and *n*-Eicosyl Phosphonate. Compressed monolayers of *n*-eicosyl sulfate favored the rapid nucleation of calcite from the supersaturated subphase of calcium bicarbonate (induction time t = <45 min). The crystals formed exclusively at the monolayer/solution interface, and when viewed in situ by optical microscopy were seen to be uniformly oriented with respect to the monolayer. Each crystal was a distinct trigonal pyramidal unit (Figure 3a). Further analysis of the mature crystals (t = 16 h) by SEM showed that the surface in contact with the monolayer was triangular and roughened, rather than smooth (Figure 3b). The unique pyramidal structure was generated by the growth downward from the monolayer of three symmetry-related rhombohedral faces of {10.4} type which intersected to produce a clearly defined apex (Figure 3c). The symmetry properties of these crystals were consistent with nucleation on the calcite (00.1) face.

Immature crystals viewed by TEM were initially pseudohexagonal in profile (t = 2 min, Figure 4a) but rapidly developed a smooth triangular outline (t = 30 min, Figure 4b). Electron diffraction analyses of these particles (t = 2 min) indicated that the particles were single crystals of calcite oriented with their [00.1] crystallographic axes perpendicular to the monolayer–solution interface (Figure 4c). Nucleation therefore occurred on the (00.1) face, and the unique pyramidal morphology was determined by rapid growth along the [00.1] and ⟨11.0⟩ directions (Figure 4d).

Experiments undertaken with eicosyl phosphonate monolayers gave similar results except that the calcite nucleation density was significantly reduced (Table 1). Triangular-based pyramidal crystals, oriented with their [00.1] axis perpendicular to the monolayer surface were observed (Figure 5a). A significant number of discrete nonoriented rhombohedral calcite crystals was also observed (some 10% of total nucleation density). These results, and those for the eicosyl sulphate monolayers, were very different from analogous experiments involving octadecanoic acid[20] in which the calcite ($1\bar{1}.0$) face was preferentially nucleated.

Aragonite Nucleation under Compressed Monolayers of *n*-Eicosanoic Acid, *n*-Eicosyl Sulfate, and *n*-Eicosyl Phosphonate. The incorporation of magnesium ions into the subphase had no effect on the compression isotherm and limiting area per molecule of monolayers formed from *n*-eicosanoic acid, *n*-eicosyl sulfate, or *n*-eicosyl phosphonate. However, the addition of Mg^{2+} resulted in the formation of oriented aragonite crystals under these monolayers, although the nucleation densities were reduced compared with experiments involving calcite (Table 1). Under eicosanoic acid monolayers, each crystal comprised an intergrown bundle of acicular crystallites (Figure 6a). Individual crystallites were bounded by four symmetry-related {110} faces. At the point of contact with the monolayer there was a single

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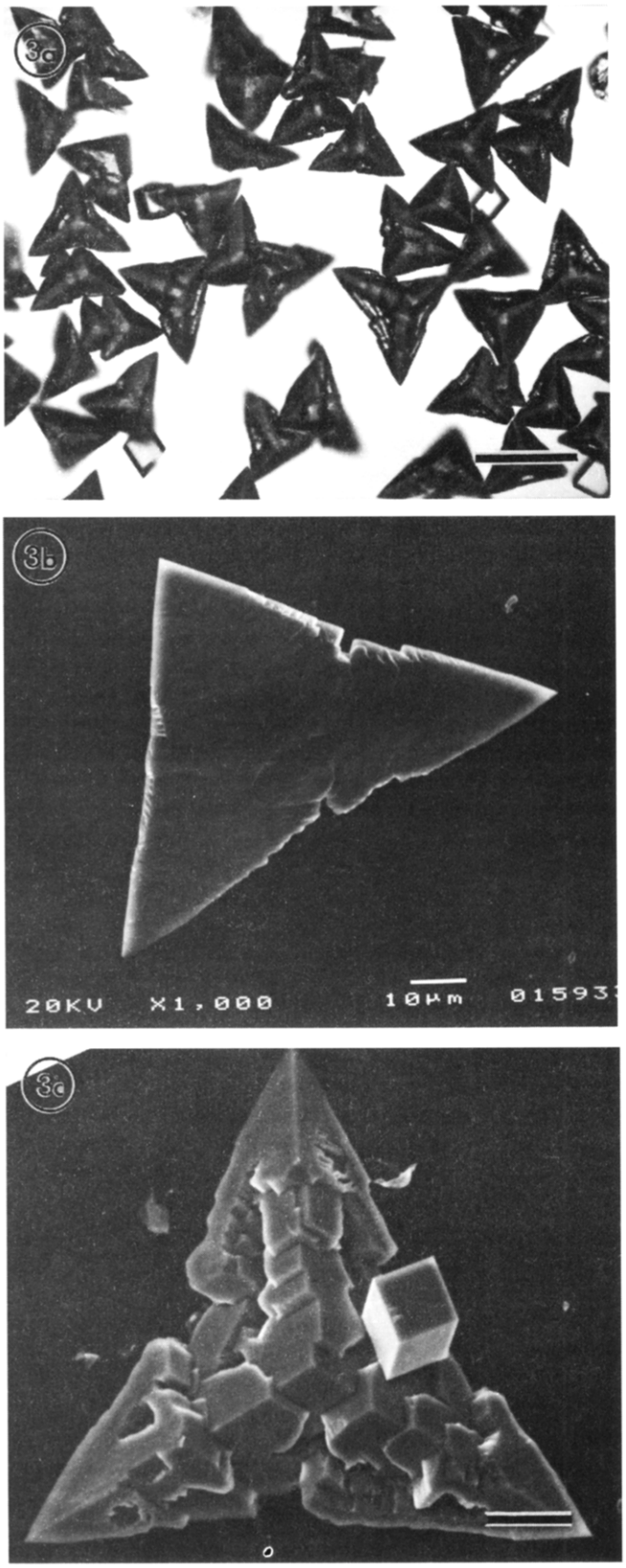

Figure 3. (a) In situ optical micrographs of calcite crystals formed under a compressed monolayer of *n*-eicosyl sulfate. Bar = 50 μm. (b) Scanning electron micrograph (SEM) of a mature crystal viewed from above a monolayer. Bar = 10 μm. (c) SEM of a single mature crystal viewed from below a compressed monolayer. Bar = 10 μm.

ridge formed by the intersection of two symmetry-related {110} faces and interupted by a single elevated feature. These data suggested that the majority of crystals were oriented with the [100] axis perpendicular to the monolayer and that growth continues preferentially along the [001] direction (Figure 6b).

Significant changes in aragonite nucleation were observed under eicosyl sulfate and eicosyl phosphonate monolayers. Under eicosyl sulfate monolayers, discrete oriented crystals were localized at the monolayer/solution interface. Viewed in situ, the mature crystals appeared to have a distinct central feature from which emanated numerous crystalline extensions (Figure 7a). The crystals were no longer positively birefringent when viewed in polarized light. SEM analysis confirmed the existence of a discrete central feature and the presence of crystalline outgrowths (Figure 7b). At the center of each unit was an hexagonal disk which was roughened on the surface apposed to the monolayer by a series of raised striations and grooves radiating from the center to the exposed edges. These textural features divided the crystal into six equal quadrants. Outgrowths of numerous acicular crystallites in random orientation were observed on the surface facing the supersaturated solution. SEM micrographs of immature crystals (t = 45 min, Figure 7c) revealed small, elongated crystals which were clearly hexagonal in cross section. These developed from the roughened hexagonal tablets which formed initially (t = 5 min, Figure 8a). Electron diffraction of these tablets showed them to be aragonite crystals oriented with the [001] axis perpendicular to the substrate (Figure 8b). These results are consistent with oriented nucleation of the aragonite (001) face under the sulfate monolayer (Figure 8c).

Nucleation of aragonite under eicosyl phosphonate monolayers mirrored that observed under eicosyl sulfate monolayers, with [001] oriented crystals being preferentially formed. The aragonite crystals showed an oriented central pseudohexagonal unit with a series of acicular outgrowths on the ventral side (Figure 5b). The presence of vaterite was noted in some experiments (approximately 5% of crystals) and confirmed by XRD (data not shown).

Discussion

As with previous studies of monolayer-directed crystallization of inorganic solids, the work reported here indicates that organized anionic langmuir monolayers can induce the oriented nucleation of crystalline materials. This template effect is dependent upon specific molecular motifs that can promote the construction of oriented nuclei at the inorganic–organic interface. For example, calcite crystals oriented along axes lying orthogonal to each other can be produced simply by changing the surfactant headgroup from carboxylate to sulfate.

Earlier studies with calcium carbonate crystallization established that monolayers of long-chain alkyl carboxylates will nucleate calcite on the $(1\bar{1}.0)$ face.[19,20] In this face, the oxyanions lie with their C_{2v} axis perpendicular to the plane of the face, an orientation which mimics the alignment of carboxylates in the compressed monolayer. Cation binding to the hexagonal close packed anionic monolayer (a = 5.0 Å) generates a structural motif which is similar to the crystal lattice planes of the $(1\bar{1}.0)$ face; further addition of carbonates from solution would perpetuate this motif and thereby promote oriented nucleation. Similar molecular recognition events have been invoked to explain the oriented nucleation of barium sulphate on a (100) face under sulfate or phosphonate monolayers,[23,24] suggested that stereochemical comple-

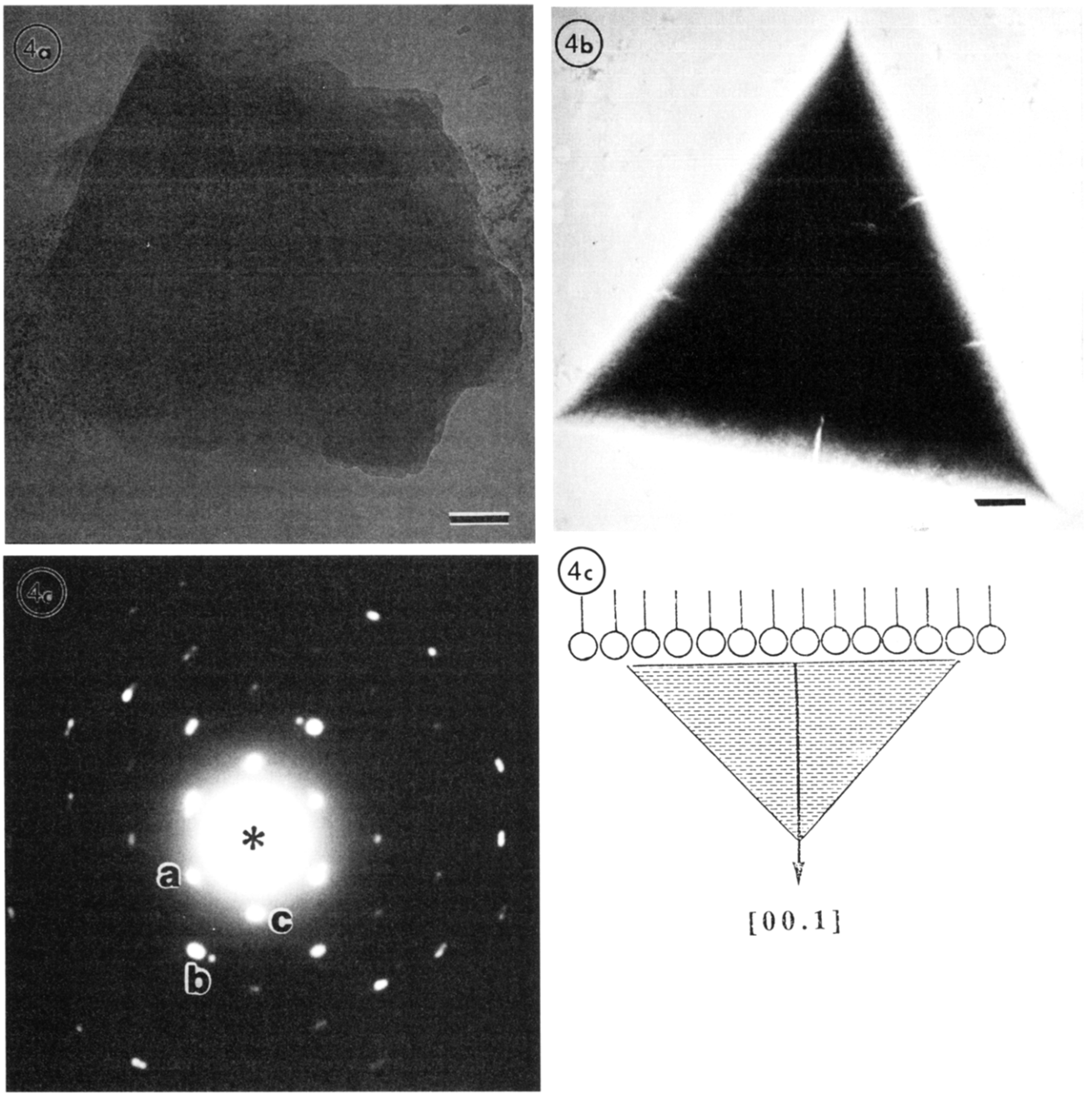

Figure 4. Transmission electron micrographs (TEM) of immature calcite crystals nucleated under *n*-eicosyl sulfate monolayers. (a) t = 2 min; bar = 50 nm. (b) t = 30 min; bar = 200 nm. (c) Electron diffraction pattern obtained from particle imaged in Figure 4a. The pattern corresponds to the [00.1] zone of calcite. Reflections: A = 11.0 (2.49 Å); B = 10.0 (4.99 Å); C = 1–1.0 (4.99 Å). Angles: (11.0) Λ (100) = 30°, (10.0) Λ (1$\bar{1}$.0) 60°. The broadening of the spots results from radiolytic damage during exposure to the electron beam. (d) Schematic showing the relationship between the morphology and crystallographic ultrastructure of the calcite crystals and their orientation relative to the *n*-eicosyl sulfate monolayer.

Table 1

monolayer	subphase ([Ca^{2+}] 9 mol dm^{-3})	polymorph[a]/orientation[b]	mean size[d]	nucleation density[e]
none	Ca:Mg = 1:0	calcite {10.4}[c]	32.07 (±11)	nd
	Ca:Mg = 1:6	aragonite {110}[c]	83.62 (±28)	nd
eicosanoic acid	Ca:Mg = 1:0	calcite (1$\bar{1}$.0)	106.19 (±22)	67
	Ca:Mg = 1:6	aragonite (110)	168.00 (±37)	31
n-eicosyl sulfate	Ca:Mg = 1:0	calcite (001)	60.09 (±25)	73
	Ca:Mg = 1:6	aragonite (001)	37.80 (±15)	68
n-eicosyl phosphonate	Ca:Mg = 1:0	calcite (001)	53.04 (±13)	32
	Ca:Mg = 1:6	aragonite (001)	32.98 (±17)	23

[a] $CaCO_3$ polymorph identified by morphological and structural analyses. [b] Face preferentially nucleated under named monolayer. [c] Predominant morphological form in the absence of a monolayer. [d] Longest physical dimension (μm ● σ). [e] Nucleation density; the number of crystals mm^{-2}.

mentarity and geometric matching are generic requirements of oriented nucleation.

The results of the present work indicate that a sulfate monolayer with its tridentate motif of oxygen atoms

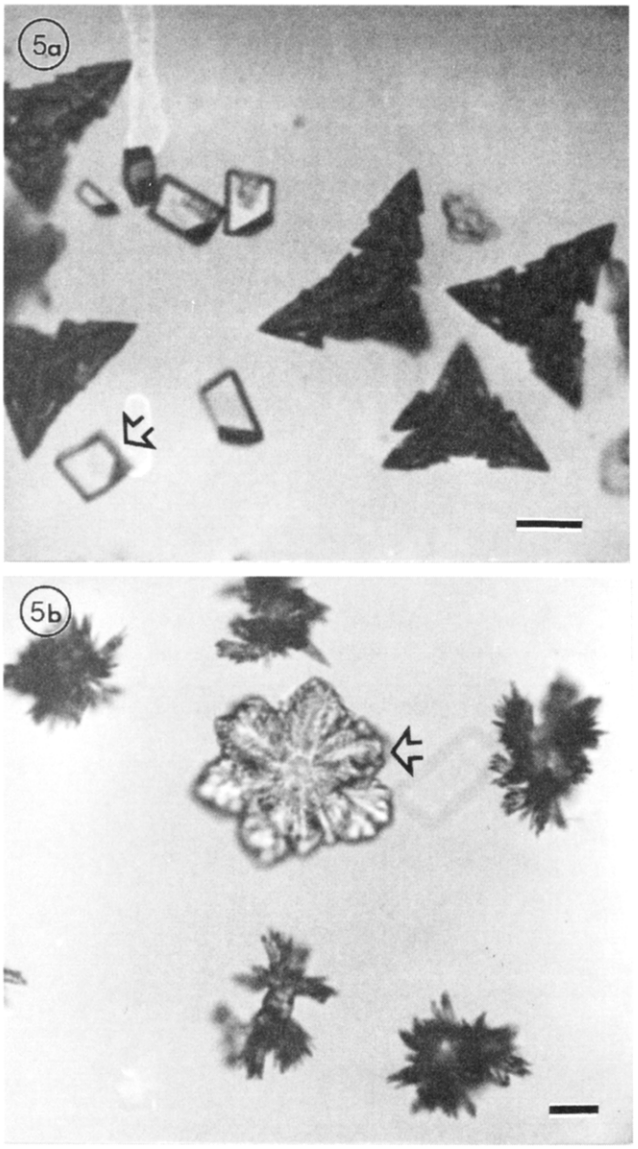

Figure 5. (a) In situ optical micrographs of calcite crystals formed under compressed monolayers of eicosyl phosphonate. Bar = 50 μm. (b) In situ optical micrograph of aragonite crystals formed under a compressed monolayer *n*-eicosyl phosphonate. Bar = 50 μm.

induces the nucleation of the calcite (00.1) surface since the carbonates in this face are oriented with their C_3 symmetry axis perpendicular to the plane of this face (Figure 1a). The pseudohexagonal close packing of both sulfate (a = 5.5 Å) and phosphonate (a = 5.2 Å) monolayers is similar in symmetry to the hexagonal array of calcium ions in the (00.1) face (a = 4.96 Å) such that calcium binding to the charged monolayer will create a geometric pattern which mimics to the calcite (00.1) lattice plane. It is noteworthy that the nucleated (00.1) face is not smooth, probably because this face is intrinsically unstable,[37] and steps are generated as the crystal grows laterally. Indeed, a (00.1) face is not observed at the subphase side of the crystal because the stable rhombohedral {10.4} faces become dominant as the influence of the monolayer diminishes.

As the interion distances and angles within the basal faces of calcite and aragonite are very similar, it is perhaps

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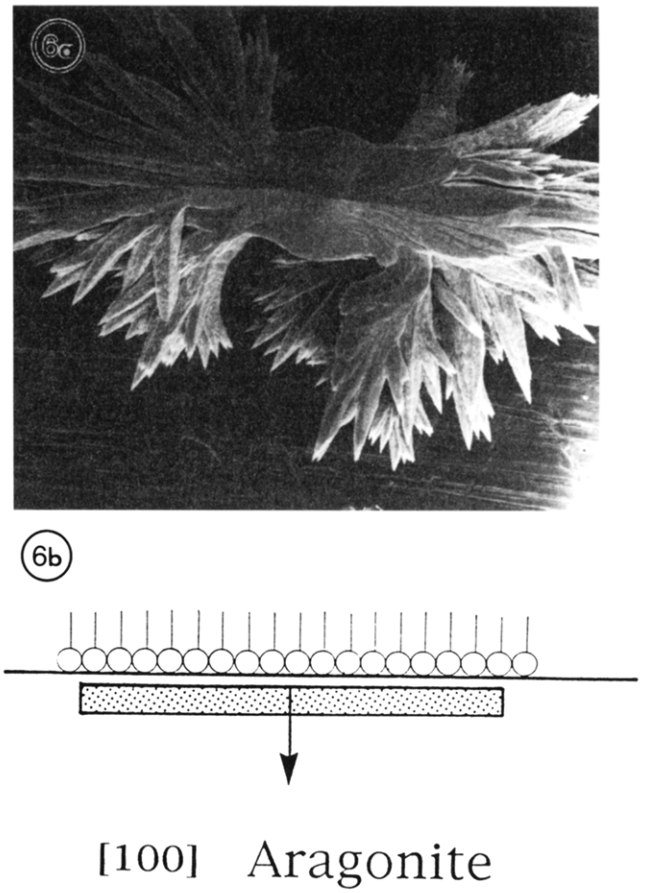

Figure 6. (a) SEM of an aragonite crystal aggregate formed under a compressed monolayer of eicosanoic acid. Bar = 5 μm. (b) Schematic showing the relationship between the morphology and crystallographic ultrastructure of aragonite crystals and their orientation relative to the eicosanoic monolayer.

not surprising that the influence of compressed monolayers on calcite nucleation can be extended to aragonite crystallization. The carbonate anions in calcite lie parallel to the (00.1) plane and midway between each pair of planes of Ca atoms, while in aragonite, the oxyanions lie parallel to the (001) plane but are staggered in two layers between each Ca layer with alternate CO_3^{2-} groups rotated by ±30°. This geometric and stereochemical arrangement can be mimicked by Ca^{2+} binding under sulfate or phosphonate headgroups, in a manner analogous to calcite crystallization, such that the aragonite (001) face is nucleated parallel to the monolayer surface.

The nucleation of the (100) face of aragonite under carboxylate monolayers can be accounted for on the basis of potential geometric and stereochemical relationships at the monolayer–crystal interface. This face contains a subset of carbonate anions, spaced at 5.72 Å, that are aligned perpendicular to the crystal plane in a bidentate arrangement (Figure 1b). The displacement of calcium by magnesium at the monolayer surface may account for the reduced nucleation efficiency of this system compared with carboxylate-mediated calcite nucleation in the absence of Mg^{2+} (ref 19, Table 1), although we observed no qualitative differences in the compression isotherms to indicate competitive binding. Alternatively, the decrease may reflect the reduction in the potential number of stereochemically equivalent carbonates per unit area, since whereas all the carbonates are equivalent on the calcite ($1\bar{1}.0$) face, there are two distinct orientations in the aragonite (100) surface. The adoption of the acicular

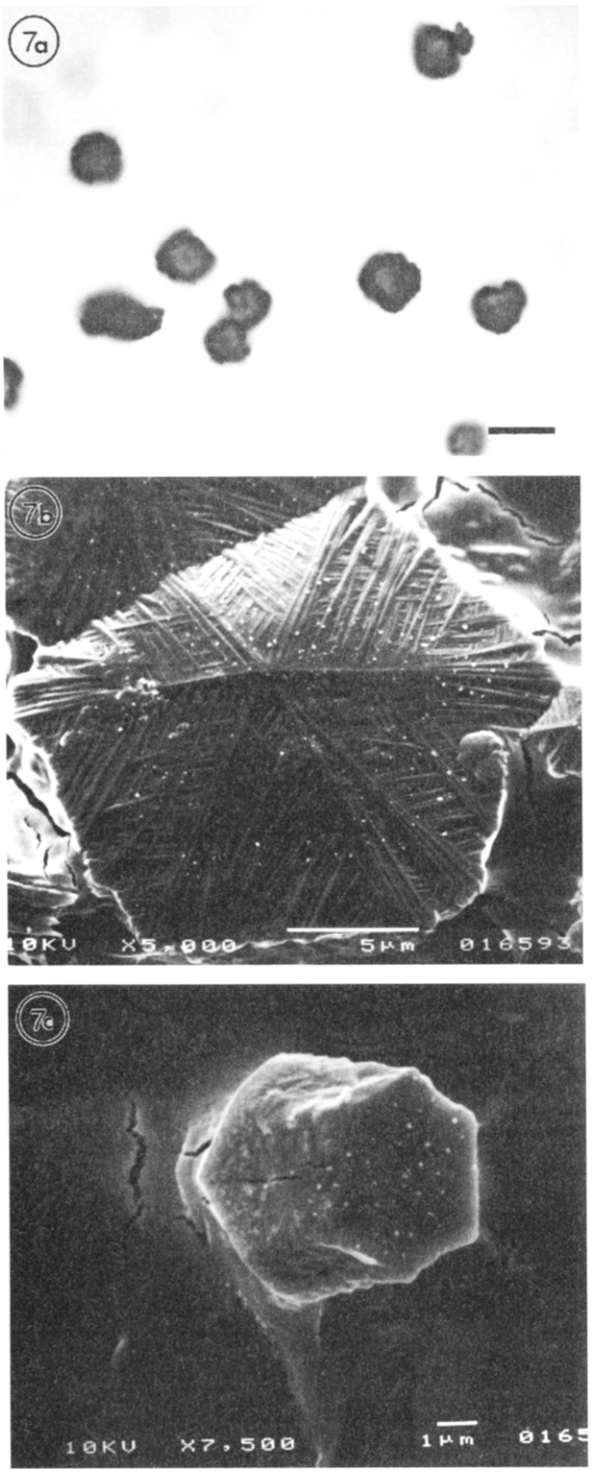

Figure 7. (a) In situ optical micrograph of aragonite crystals formed under compressed monolayer of *n*-eicosyl sulfate. (b) SEM of a mature aragonite crystals viewed from above a compressed monolayer of *n*-eicosyl sulfate. (c) SEM of immature aragonite crystal (t = 45 min) viewed from above the *n*-eicosyl sulfate monolayer.

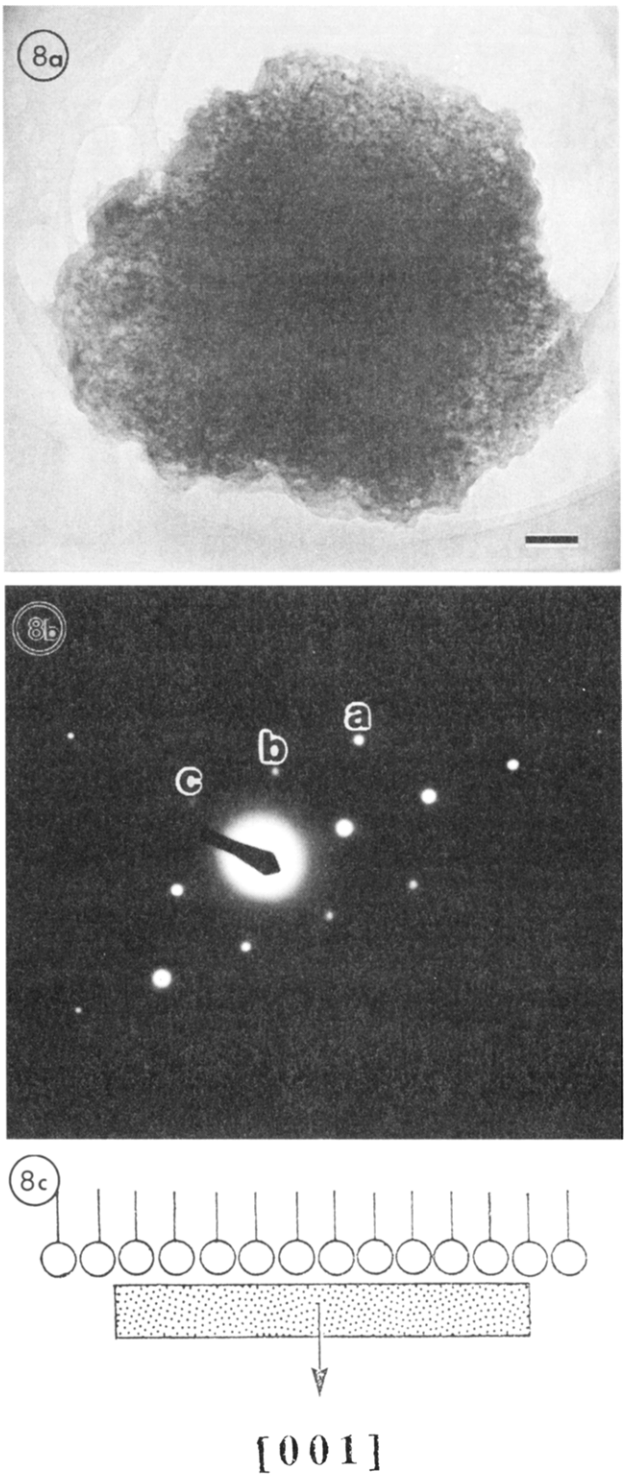

Figure 8. (a) TEM of immature aragonite crystals nucleated under compressed *n*-eicosyl sulfate (t = 2 min). Bar = 50 nm. (b) Single-crystal electron diffraction pattern of crystal imaged in (a). The pattern corresponds to the [001] zone of aragonite. Reflections: A = 200 (2.5 Å); B = 110 (4.2 Å); C = 020 (3.9 Å). Angles: (100) Λ (010) = 90°; (100) Λ (110) = 32°. (c) Schematic showing the relationship between the morphology and crystallographic ultrastructure of aragonite crystals and their orientation relative to the *n*-eicosyl sulfate monolayer.

morphology of the outgrowths from the mature aragonite crystals suggests that the rate of growth into solution exceeds growth under the influence of the monolayer and that the crystal–monolayer interactions are essentially redundant in the later stages of crystallization.

Finally, it is interesting to consider our results in light of studies of calcium carbonate biomineralization. There are numerous biological examples of uniformly oriented calcite and aragonite crystals[38] in which the crystals are preferentially aligned with their crystallographic c axes ([00.1] and [001], respectively) perpendicular to an underlying organized biopolymeric substrate. It is a commonly held view that the growth of the mineral phase

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is directed by the organic phase through a series of molecular recognition events[39,40] although the supporting evidence is largely circumstantial. The results of the present study, coupled with data concerning the primary structure of the matrix constituents (including post translational modifications),[41] offer some new insights into the possible mechanism by which oriented $CaCO_3$ crystals might be formed in vivo. In particular, we note that a high percentage of the functional residues in the biological matrices are sulfated or phosphorylated by post translational processing[42] and that the putative nucleation potential of these moieties in aligning the *c* axes of calcite and aragonite has now been confirmed by our studies of monolayer-directed nucleation.

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