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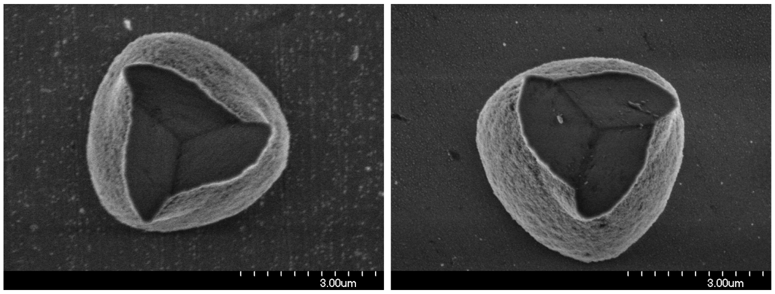

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Electrochemical Biomineralization: The Deposition of Calcite with Chiral Morphologies

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Biomaterials such as foraminifers, coccoliths, and shells exist predominately as one of two nonsuperimposable mirror images of each other known as enantiomers.[1] Calcite can form these chiral microstructures even though the material crystallizes in an achiral space group.[2] Researchers have shown that enantiomorphs of calcite can be produced either by treating calcite with chiral etchants or by crystallizing calcite in the presence of amino acids such as aspartic acid and proteins.[3] Electrodeposition, like biomineralization, is a near-equilibrium solution processing method in which solid inorganic materials are produced from solution precursors. The resulting morphologies depend strongly on the presence of solution precursors and additives. We have previously shown that chiral films of CuO can be electrodeposited in the presence of tartaric and amino acids.[4] Here, we show that chiral morphologies of calcite can be electrodeposited in the presence of tartaric, malic, and aspartic acid.

Studies in biomineralization have explored the influence of additives on the morphology of calcite crystals.[3,5] Magnesium additives are found to inhibit calcite growth by limiting the step growth and substituting for calcium in the calcite structure, consequently increasing the solubility of the deposit and often producing a different polymorph such as aragonite.[3e,5a] The addition of carboxylic acids to calcite deposition solutions produces elongated calcite crystals, terminated with $\{10\bar{1}4\}$ facets.[3d,5d] Similar structures have occurred in magnesium inhibition studies on calcite growth on carboxylate-terminated self-assembled monolayers.[5f] Chiral organic acids with carboxylate groups have produced chiral etch-pit morphologies[3a−d] and chiral growth hillocks on calcite.[3d,e]

Chiral morphologies of calcite exist in nature even though the material crystallizes in the achiral space group $R\bar{3}c$.[2] In fact, enantioselective adsorption of molecules on the chiral surface of minerals such as calcite has been invoked to explain the genesis of biogenic homochirality.[2c] The chirality of certain faces of calcite can be understood from symmetry considerations. A chiral plane lacks mirror or glide plane symmetry.[2a,b] In order to determine which planes of calcite are chiral, one needs to determine from the space group the locations of mirror or glide planes in the structure. Achiral planes are those which are parallel with directions normal to these planes and therefore satisfy the zonal equation ($hu + kv + lw = 0$). This process can be simplified by considering the point group of the material, $\bar{3}m$, in which the c-glides are replaced by mirrors. Table 1 shows selection rules for chirality for the point group $\bar{3}m$. The plane groups for the planes $\{11\bar{2}0\}$, $\{hki0\}$, $\{hh\bar{2}\bar{h}l\}$, and $\{hkil\}$ are chiral because they lack mirror symmetry.[6] Hence, the common $\{10\bar{1}4\}$ cleavage planes of calcite are achiral, whereas the $\{21\bar{3}1\}$ scalenohedral faces on dog-tooth calcite are chiral. For a chiral plane such as $(hkil)$, its enantiomer is $(\bar{h}\bar{k}\bar{i}\bar{l})$.

Electrodeposition has been used by other groups to deposit biominerals.[7] Although electrodeposition is usually a redox method in which metals are produced from metal ions by a cathodic process, it is also possible to deposit materials on an electrode surface by the electrochemical generation of acid or base.[8] The electrodeposition of biomaterials occurs by electrochemically generating hydroxide ions from water reduction, increasing the local pH at the electrode surface (eq 1). Base can also be electrochemically generated by reducing molecular oxygen, nitrate, or organic molecules such as quinones. The biominerals calcite and aragonite can then be electrodeposited by using the electrochemically generated base to react with HCO_3^- in solutions containing Ca^{2+} according to eq 2.

Table 1. Selection Rules for Chirality of the Calcite Crystal System (Planes Which Lack Mirror Symmetry are Chiral)[6]

system	point group	$\{0001\}$	$\{10\bar{1}0\}$	$\{11\bar{2}0\}$	$\{hki0\}$	$\{h0\bar{h}l\}$	$\{hh\bar{2}\bar{h}l\}$	$\{hkil\}$
trigonal (hexagonal axes)	$\bar{3}m$	$6mm$	$2mm$	2	2	$2mm$	2	2

$$2H_2O + 2e^- \leftrightarrows H_2 + 2OH^- \qquad (1)$$

$$OH^- + Ca^{2+} + HCO_3^- \leftrightarrows CaCO_3 + H_2O \qquad (2)$$

Scanning electron micrographs of electrodeposited calcite and aragonite are shown in Figure 1a and b. We observe that rhombohedral-shaped crystals of trigonal calcite are electrodeposited from a pure calcium bicarbonate solution (Figure 1a). The lattice parameters determined by Rietveld analysis are $a = 0.4980$ nm and $c = 1.7033$ nm for the electrodeposited calcite, compared with the literature values of $a = 0.4991$ nm and $c = 1.7062$ nm for trigonal calcite (JCPDS no. 81-2027). The addition of magnesium to the deposition bath inhibits the growth of the trigonal calcite and produces rosette formations of orthorhombic aragonite (Figure 1b). The lattice parameters are $a = 0.4950$ nm, $b = 0.7957$ nm, and $c = 0.5738$ nm for the orthorhombic aragonite, compared with the literature values of $a = 0.49598$ nm, $b = 0.79641$ nm, and $c = 0.57379$ nm (JCPDS no. 76-0606). When the deposition bath contains both dicarboxylic acids and magnesium ions, the structure reverts back to trigonal calcite with lattice parameters of $a = 0.4964$ nm and $c = 1.6930$ nm. The electrodeposited calcite contains 0.6−0.8 atom % Mg. The morphology also changes when carboxylic acids are added to the bath. Instead of rhombohedral-shaped morphologies, the electrodeposited calcite from solutions with achiral succinic acid (Figure 1c) or DL-malic acid (Figure 1d) are barrel-like structures with symmetrical facets. It is interesting to note that the racemic mixture of D- and L-malic acid does not produce a racemic mixture of chiral morphologies, but instead forms an achiral microstructure.

Calcite that is deposited in the presence of chiral molecules grows with a chiral morphology. Scanning electron micrographs of calcite

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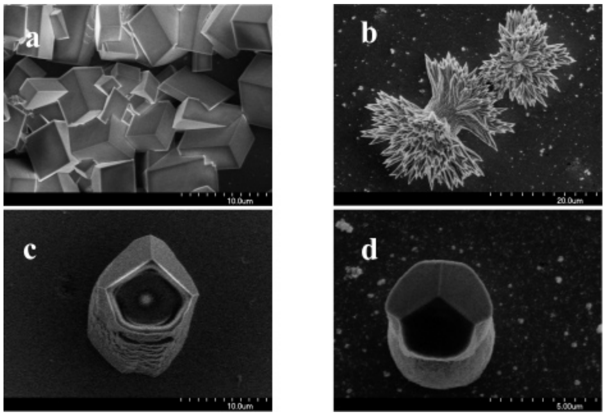

Figure 1. Deposition of calcite and aragonite by the electrochemical generation of base. Scanning electron micrographs of (a) trigonal calcite grown from a calcium bicarbonate solution, (b) rosettes of orthorhombic aragonite grown from the same solution with magnesium present, (c) calcite grown with added succinic acid, and (d) calcite grown with added DL-malic acid.

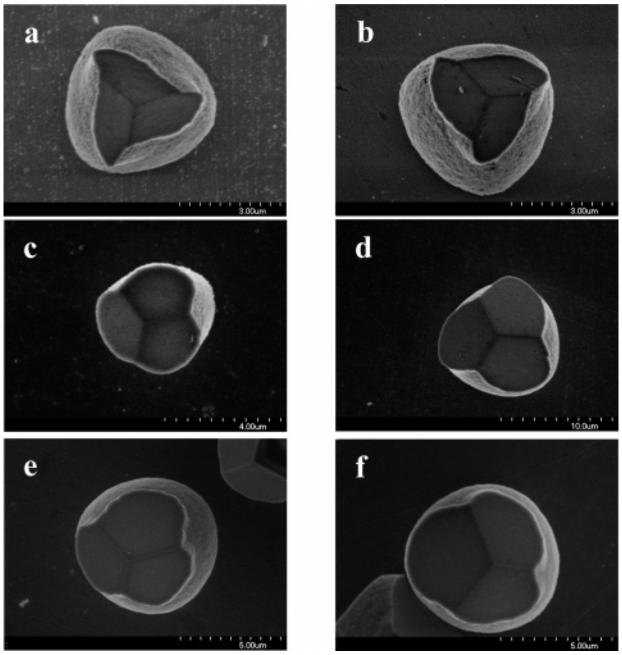

Figure 2. Electrodeposition of calcite with chiral facets. Scanning electron micrographs of calcite grown on polycrystalline stainless steel from calcium bicarbonate in the presence of magnesium and (a) L-tartaric acid, (b) D-tartaric acid, (c) L-malic acid, (d) D-malic acid, (e) L-aspartic acid, and (f) D-aspartic acid. Each chiral agent produces a chiral morphology with either a right- or left-handed spiral.

deposited with tartaric, malic, and aspartic acid additives are shown in Figure 2. For each of the acids, a seashell-like spiral morphology is produced, with the two enantiomers of the molecule producing chiral morphologies. Notice that L-tartaric acid produces calcite with a spiral that rotates to the left when viewed from above, while L-malic acid and L-aspartic acid produce calcite with spirals which rotate to the right. Hence, there is not a direct correlation between the L/D designation for the chiral molecule and the chiral orientation of the resulting calcite. We note that the L/D designation is an arbitrary label based on the glyceraldehyde molecule. Our results correlate better with the Cahn−Ingold−Prelog priority rules for assigning absolute configurations to chiral molecules. L-Tartaric acid has two chiral sites and is labeled *R*,*R*, whereas L-malic acid and L-aspartic acid are both designated as *S*.

The electrodeposited calcite morphologies seen in Figures 1c,d and 2a−f are similar to the columnar calcite with three rhombohedral-like facets chemically deposited from supersaturated calcium bicarbonate solutions with organic additives such as malonic acid[5d] and aspartic acid.[3d] The overall chiral shape evolution of right- and left-handed morphologies is reported to be related to the reduction of symmetry of the $\{10\bar{1}4\}$ plane and the step edge selectivity of the enantiomer.[3d] Orme et al. have shown by molecular modeling that D-aspartic acid will preferentially bind to a $(01\bar{1}\bar{4})$ riser over a $(1\bar{1}0\bar{4})$ riser.[3d] Our results suggest that D-tartaric acid may, in contrast, preferentially bind to $(1\bar{1}0\bar{4})$, producing calcite with the opposite handed morphology.

Chiral electrodeposition should also be applicable to other biominerals such as hydroxyapatite. Because other workers have shown that epithelial cells will preferentially adhere to specific chiral faces of solids such as calcium tartrate,[9] it is interesting to speculate whether the surfaces of electrodeposited biominerals such as hydroxyapatite on metal bone implants can be made more biocompatible if they are deposited in the presence of the correct hand of a chiral imprinting agent.

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Supporting Information Available: Experimental procedures and symmetry aspects of chirality. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Addadi, L.; Weiner, S. *Nature* **2001**, *411*, 753.
(2) (a) Hazen, R. M.; Sholl, D. S. *Nat. Mater*. **2003**, *2*, 367. (b) Downs, R. T.; Hazen, R. M. *J. Mol. Catal. A: Chem.* **2004**, *216*, 273. (c) Hazen, R. M.; Filley, T. R.; Goodfriend, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 5487.
(3) (a) Thomas, J. M.; Renshaw, G. D.; Roscoe, C. *Nature* **1964**, *203*, 72. (b) Honess, A. P.; Jones, J. R. *Bull. Geol. Soc. Am.* **1937**, *48*, 667. (c) Barwise, A. J.; Compton, R. G.; Unwin, P. R. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 137. (d) Orme, C. A.; Noy, A.; Wierzbicki, A.; McBride, M. T.; Grantham, M.; Teng, H. H.; Dove, P. M.; De Yoreo, J. J. *Nature* **2001**, *411*, 775. (e) De Yoreo, J. J.; Dove, P. M. *Science* **2004**, *306*, 1301.
(4) (a) Switzer, J. A.; Kothari, H. M.; Poizot, P.; Nakanishi, S.; Bohannan, E. W. *Nature* **2003**, *425*, 490. (b) Bohannan, E. W.; Kothari, H. M.; Nicic, I. M.; Switzer, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 488. (c) Kothari, H. M.; Kulp, E. A.; Boonsalee, S.; Nikiforov, M. P.; Bohannan, E. W.; Poizot, P.; Nakanishi, S.; Switzer, J. A. *Chem. Mater.* **2004**, *16*, 4232.
(5) (a) Davis, K. J.; Dove, P. M.; De Yoreo, J. J. *Science* **2000**, *290*, 1134. (b) Teng, H. H.; Dove, P. M.; Orme, C. A.; De Yoreo, J. J. *Science* **1998**, *282*, 724. (c) Teng, H. H.; Chen, Y.; Pauli, E. *J. Am. Chem. Soc.* **2006**, *128*, 14482. (d) Mann, S.; Didymus, J. M.; Sanderson, N. P.; Heywood, B. R.; Samper, E. J. A. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1873. (e) Mann, S.; Archibald, D. D.; Didymus, J. M.; Douglas, T.; Heywood, B. R.; Meldrum, F. C.; Reeves, N. J. *Science* **1993**, *261*, 1286. (f) Han, Y.-J.; Aizenberg, J. *J. Am. Chem. Soc.* **2003**, *125*, 4032.
(6) *International Tables for X-ray Crystallography*; Henry, N. F. M., Londsdale, K., Eds.; Kynoch: Birmingham, 1952; Vol. 1, pp 37−38.
(7) (a) Redepenning, J.; Schlessinger, T.; Burnham, S.; Lippiello, L.; Miyano, J. *J. Biomed. Mater. Res.* **1996**, *30*, 287. (b) Monma, H. *J. Ceram. Soc. Jpn*. **1993**, *101*, 737. (c) Xu, S.; Melendres, C. A.; Park, J. H.; Kamrath, M. A. *J. Electrochem. Soc.* **1999**, *146*, 3315. (d) Beaunier, L.; Gabrielli, C.; Poindessous, G.; Maurin, G.; Rosset, R. *J. Electroanal. Chem.* **2001**, *501*, 41. (e) Gabrielli, C.; Maurin, G.; Poindessous, G.; Rosset, R. *J. Cryst. Growth* **1999**, *200*, 236.
(8) (a) Switzer, J. A. *Am. Ceram. Soc. Bull.* **1987**, *66*, 1521. (b) Limmer, S. J.; Kulp, E. A.; Switzer, J. A. *Langmuir* **2006**, *22*, 10535. (c) Liu, R.; Vertegel, A. A.; Bohannan, E. W.; Sorenson, T. A.; Switzer, J. A. *Chem. Mater.* **2001**, *13*, 508.
(9) Hanein, D.; Geiger, B.; Addadi, L. *Science* **1994**, *263*, 1413.

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