JOURNAL OF MATERIALS SCIENCE 33 (1998) 4075–4077

The growth of self-aligned calcium carbonate precipitates on inorganic substrates

S. L. TRACY, H. M. JENNINGS*,[‡]
*Department of Materials Science and Engineering, and also *Department of Civil Engineering, Northwestern University, Evanston, IL 60208, USA*
E-mail: hjennings@nwu.edu

Calcium carbonate has been found to precipitate into tablets which were self-aligned with respect to each other on limestone aggregates in Portland cement-based materials. A surface layer of water and reaction in 100% relative humidity air environments were critical for alignment of precipitates. The organization of the calcium carbonate precipitates resembled the cross-section of nacre, but without an organic phase. Possible implications for organized material synthesis, as well as biomineralization, are discussed. © *1998 Kluwer Academic Publishers*

1. Introduction

The microstructure of seashell nacre is often described as having a brick-and-mortar configuration of aragonite tablets separated by thin layers of organic material [1, 2]. Essentially all published theories about the mechanisms of nacre formation emphasize the importance of organic phases in nucleating calcium carbonate crystals, orienting them, and controlling their growth into a highly organized composite biomaterial [1, 3–5]. No published study of the precipitation of $CaCO_3$ has demonstrated that a self-aligned microstructure can be formed synthetically. Furthermore, much research on biomineralization and biomimetics focuses on the importance of interactions between organic and inorganic components during the precipitation of organized material [6–11].

This paper reports the finding that calcium carbonate crystals can grow in a self-aligned configuration without an organic component, in this case on the surface of Portland cement-based materials. As shown in Fig. 1a and b, the precipitates were of plate or prismatic morphologies (although other morphologies such as needles have also been grown in different experiments), often appearing to be made of smaller lath-like components. In addition, the precipitates formed in a patchy nature on the substrates as shown in Fig. 2. The fine scale arrangement of these precipitates has similarities to the cross-section of nacre, however, notably without an organic phase, as seen in Fig. 1b.

2. Experimental procedure

The calcium carbonate precipitates were grown on the surfaces of cement-based materials under special conditions. The specimens, basically a Portland cement mortar that contained silica fume (water/binder ratio about 0.24) and limestone powder, were polished and then aged up to 24 h with a thin (about 30 μm, calculated from the weight of water removed from the surfaces) layer of water on their surfaces in closed chambers at 100% relative humidity and atmospheric CO_2(g) levels. The presence of excess water (i.e. submersion or a meniscus covering the sample) led to different morphologies, including large, isolated crystal growth or needle-shaped precipitates which sometimes coalesced into columnar shapes. Excess CO_2 (e.g. CO_2(g) flowing over the surfaces of the samples) led to rhombohedral precipitate growth over the entire surface. Moist samples (the thin layer of surface water had been towel-dried off) did not form precipitates. The cement-based substrates provided a source of free calcium ions for subsequent reactions. Additionally, the limestone powder aggregates in the cement-based material were found to be the phase underlying the precipitate growth, and therefore the reason for the patch-like tendency of precipitate growth. Further experiments were performed on limewater-soaked limestone, and organized precipitates also grew on those materials.

3. Results and discussion

A possible mechanism for inter-precipitate alignment could be a result of the combination of capillary action of a porous media and the thin layer of surface water, providing the means for calcium from the substrate and carbonate to meet and solidify, as shown in Fig. 3. This might be similar to a case which Buckley [12] has described of columnar ice crystals forming on a porous clay medium.

[‡] Author to whom all correspondence should be addressed.

0022–2461 © *1998 Kluwer Academic Publishers*

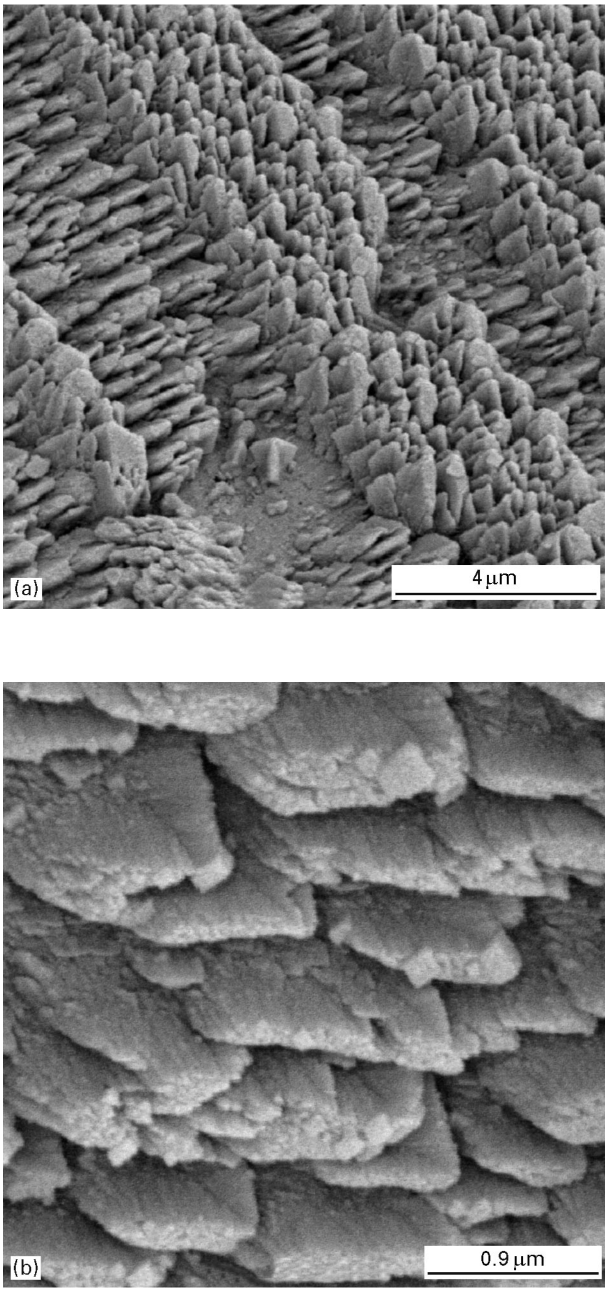

Figure 1 Scanning electron micrographs of calcium carbonate precipitates (a) showing tile and lamellar morphologies, specimen tilted at 30°; (b) higher magnification.

These observations have possible significance in several areas. The first area is in biomineralization and nacre growth mechanisms. Research by Digby [13] suggests the possibility of nacre growing in a sideways fashion from the mantle edge, although this theory seems not to be discussed today. To materials scientists, the idea sounds interesting based on the observations of this work and the fact that a bivalve shell grows more over its lifetime in a circumferential direction rather than in thickness.

Furthermore, fractured nacre from a bivalve shell has been aged in the conditions described above, and tiny crystals have grown on the surfaces of the fractured tablet planes (Fig. 4). This method may be useful to biomineralogists for studying nacre growth *in vitro.*

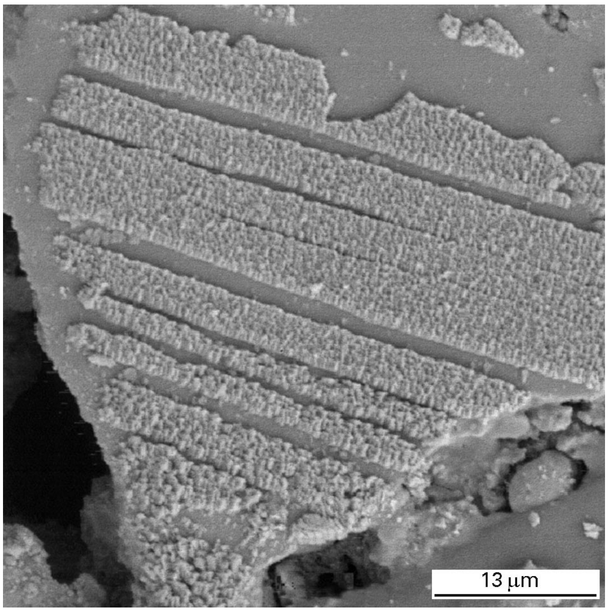

Figure 2 Example of patch growth of calcium carbonate precipitates on Portland cement-based material.

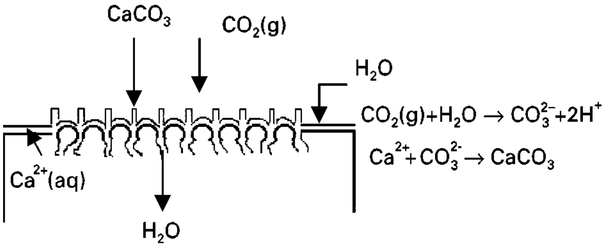

Figure 3 Schematic representation of mechanism for aligned precipitate growth due to capillary action over a porous medium, in the presence of a thin layer of surface water and calcium and carbonate ions.

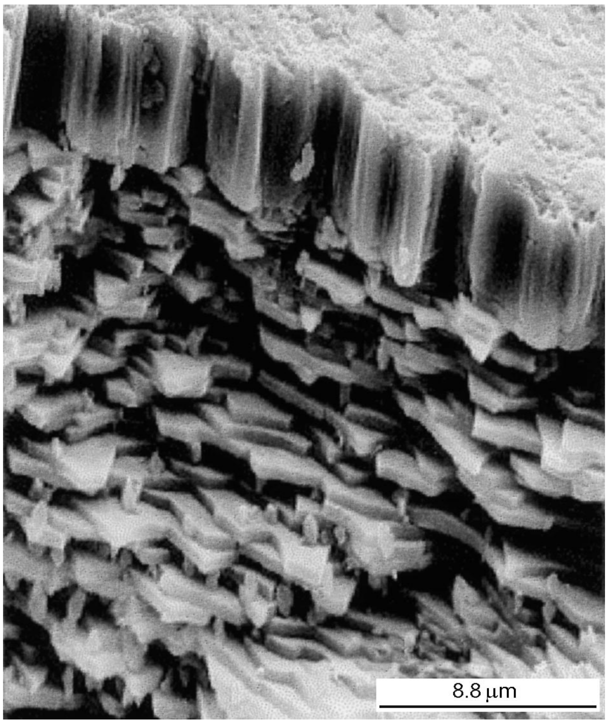

Figure 4 Bivalve seashell fracture surface aged in limewater in 100% relative humidity and air with small precipitates on the aragonite tablet surfaces.

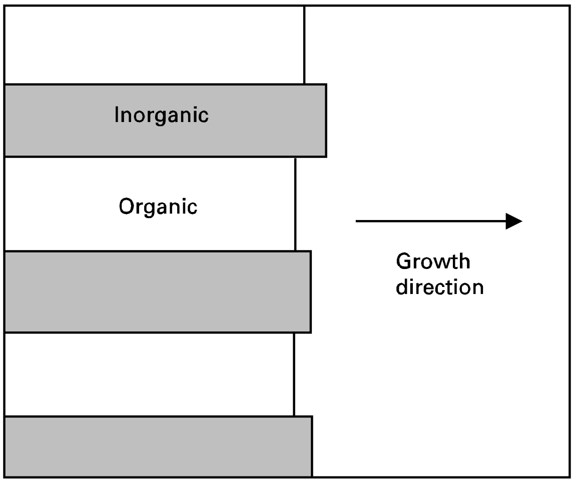

Figure 5 Schematic representation of potential eutectic growth of inorganic–organic hybrid material.

In addition, the use of inorganic substrates is a new approach to organized material synthesis and biomimetics, to the authors' knowledge. This and other work [14] have shown the importance of the role of variables other than organic phases in influencing precipitate deposition behaviour.

Lastly, in terms of synthetic material synthesis, this work points to possibilities of new routes for tough hybrid inorganic/organic material creation. The growth direction of these crystals is akin to lamellar eutectic growth directions. It may be possible to find a polymer or protein phase that could co-precipitate with the calcium carbonate tablets such that a lamellar composite is formed, as shown schematically in Fig. 5. In addition, perhaps a polymer could be infiltrated into the interstitial spaces after the organized structure forms.

4. Conclusion

The growth of aligned calcium carbonate precipitates has been observed on inorganic substrates including Portland cement-based materials and limestone. Requirements for alignment include the presence of a thin layer of surface water, a source of calcium and carbonate ions, and possibly a porous substrate. Implications in the areas of biomineralization, biomimetics, and materials science have been discussed.

Acknowledgements

S. L. T. thanks the Department of Defence for awarding her a Graduate Fellowship and the USG Corporation for donating funds for this research. J. Hsieh and C. M. Neubauer are also acknowledged for helping with experimental procedures.

References

1. K. M. WILBUR and A. S. M. SALEUDDIN, in "The Mollusca", edited by A. S. M. Saleuddin and K. M. Wilbur, Vol. 4 (Academic Press, New York, 1983) pp. 235–87.
2. C. GRÉGOIRE, in "Mollusca", "Chemical Zoology", Vol. 7, edited by M. Florkin and B. T. Scheer (Academic Press, New York, 1972) pp. 45–102.
3. S. WEINER and W. TRAUB, *Phil. Trans. R. Soc. Lond. B* **304** (1984) 425.
4. S. MANN, *Nature* **332** (1988) 119–124.
5. S. MANN, D. D. ARCHIBALD, J. M. DIDYMUS, T. DOUGLAS, B. R. HEYWOOD, F. C. MELDRUM and N. J. REEVES, *Science* **261** (1993) 1286.
6. S. MANN, D. D. ARCHIBALD, J. M. DIDYMUS, B. R. HEYWOOD, F. C. MELDRUM and V. J. WADE, *MRS Bull.* **17** (1992) 32.
7. B. R. HEYWOOD and S. MANN, *Chem. Mater.* **6** (1994) 311.
8. A. BERMAN, D. J. AHN, A. LIO, M. SALMERON, A. REICHERT and C. CHARYCH, *Science* **269** (1995) 515.
9. J. S. BECK, J. C. VARTULI, W. J. ROTH, M. E. LEONOWICZ, C. T. KRESGE, K. D. SCHMITT, C. T.-W. CHU, D. H. OLSON, E. W. SHEPPARD, S. B. McCULLEN, J. B. HIGGINS and J. L. SCHLENKER, *J. Am. Chem. Soc.* **114** (1992) 10 834.
10. D. WALSH and S. MANN, *Nature* **377** (1995) 320.
11. S. OLIVER, A. KUPERMAN, N. COOMBS, A. LOUGH and G. A. OZIN, *ibid.* **378** (1995) 47.
12. H. E. BUCKLEY, "Crystal Growth" (Wiley, New York, 1951).
13. P. S. B. DIGBY, *Symp. Zool. Soc. Lond.* **22** (1968) 93.
14. S. L. TRACY, PhD dissertation, Northwestern University (1997).

Received 8 December 1997
and accepted 15 May 1998