Biomineralization of Calcium and Iron

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The subtle interaction of biological organization and mineral growth results in the formation of amorphous and crystalline material of different form, symmetry and structure. These bioinorganic solids are replicated throughout the evolution. As they belong both to the living and inanimate world, their genesis is one of the most intriguing and fundamental topics in science. It is therefore a true interdisciplinary area of research that overlaps with such diverse fields as inorganic, physical, organic, geological and biological branches of chemistry, material science, orthopaedics, dentistry, paleontology, mineralogy, archaeology, crystallography, molecular and cell biology and evolution etc. There are approximately 60 different biogenic minerals known to date, occurring in about 55 different phyla [1]. Of these, calcium carbonate is the most utilized bioinorganic constituent [2]. Phosphates, and iron oxides are also widely distributed and formed in huge amounts in the biosphere. Most of the important studies in this field have been done in the last 10-15 years, upon the advent of modern characterization techniques.

Two fundamentally different processes of mineral formation can be distinguished. "Biologically induced mineralization" [3] is the process in which the mineralization occurs in the environment which is not specifically designed for it. The process in which a specific machinery is set up for the purpose is called "Biologically controlled mineralization" [4]. Most of the research in the field aims for a better understanding of the control processes. In this talk, the central focus will be calcium and iron biomineralization.

The important techniques used in the studies of biominerals are electron microscopy, advanced X-ray techniques and Mössbauer spectroscopy (for iron biominerals).

Calcium biominerals are deposited in the wide variety of bacteria, protozoa, algae, higher plants , invertebrates and vertebrates [5,6]. The major structural polymorphs identified in the biological systems are calcite, aragonite and valerite ($CaCO_3$ phases), hydroxyapatite [$Ca_{10}(PO_4)_{10}(OH)_2$]. There are evidences of amorphous and a range of Ca/Mg carbonate phases also.

The calcium carbonate/sulfate mineralization in the unicellular organisms is controlled by factors like ionic concentration (supersaturation), nucleation, and crystal growth. A model study involving the use of stearic acid and octadecylamine monolayers in the controlled crystallization of $CaCO_3$ from supersaturated solutions suggests an important role of the organic surfaces [7,8].

The mineral phase of the sea-urchin-skeleton is composed of Mg-bearing calcites (composite materials), which diffract the X-rays as single crystals. It has unique fracture properties, different from its inorganic counterpart. Internal texture of biogenic and synthetic calcite crystals have been studied to gain an insight into the unique protein- crystal composites [9,10]. X-ray absorption spectroscopy has been applied to study the perturbation due to a foreign cation on the biologically formed minerals [11].

Iron biominerals are known to occur in many organisms. This is due, perhaps, to the importance of iron in many metabolic processes [12]. The discovery of a very simple magnetotactic response in a certain species of bacteria is very interesting and important [13]. Electron diffraction techniques have been used to determine the structure of the magnetic particles extracted from different bacteria [14,15]. As the sample required for the Mössbauer is much larger than that available, very few bacterial magnetite studies using Mössbauer spectroscopy have been reported to date [16,17]. Crystals from *A. magnetotacticum* at early stages of growth have been studied in situ by HRTEM (High Resolution Transmission Electron Microscopy) [18].

The occurrence of several forms of iron sulfide in sulfur bacteria [19-21] has led to speculation as to whether sulfur bacteria have a homeostasis device based upon Fe/S rather than on Fe/O solids, and whether this was an earlier form (in anaerobic life) of iron storage [22-26]. The answer to this question will help in understanding the evolution of life on earth.

Application of the concepts of biomineralization to synthetic systems is an important goal [27,28]. Supramolecular protein cages have been used as constrained reaction environments in the synthesis of inorganic materials of nanometer dimensions [29]. The synthesis of a composite material in which cadmium sulfide crystals are embedded in the polymer matrix, thus mimicking certain biological materials, has been reported [30]. There is growing awareness in materials science that the adaptation of biological processes may lead to a significant advances in the controlled fabrication of superior composites, ceramics, and polymers.

References

1. Lowenstam, H. A.; Weiner, S. *On Biomineralization*; Oxford University Press: New York, 1989, p 324.

2. Ochiai, El-ichiro, "Biomineralization: Principles and Applications in Bioinorganic Chemistry - V," *J. Chem. Educ.* **1991**, *68*, 627-30.

3. Lowenstam, H. A., "Minerals Formed by Organisms," *Science* **1981**, *211*, 1126-31.

4. Mann, S., "Mineralization in Biological Systems," *Struct. Bonding* **1983**, *54*, 125-174.

5. Mann, S; Perry, C. C., "Solid-State Bioinorganic Chemistry: Mechanisms and Models of Biomineralization," *Adv. Inorg. Chem.* **1991**, *36*, 127-200.

6. *Biomineralization: Chemical and Biochemical Perspectives*, Mann, S; Webb, J; Williams, R. J. P., Eds.; VCH: Weinheim, 1989, p 541.

7. Mann, S; Heywood, B. R.; Rajam, S.; Birchall, J. D., "Controlled Crystallization of $CaCO_3$ under stearic acid monolayers," *Nature* **1988**, *334*, 692-695.

8. Mann, S.; Heywood, B. R.; Rajam, S.; Walker, J. B. A., "Crystal Engineering of Inorganic Materials at Organized Organic Surfaces," in *Surface Reactive Peptides and Polymers*, Sikes, C. S.; Wheeler, A. P., Eds., ACS Symposium Series 444, American Chemical Society: Washington, D. C., 1991, pp 28-41.

9. Berman, A.; Addadi, L.; Weiner, S., "Interaction of sea-urchin skeleton macromolecules with growing calcite crystals--a study of intracrystalline proteins," *Nature* **1988**, *331*, 546-48.

10. Berman, A.; Addadi, L.; Kvick, A.; Leiserowitz, L.; Nelson, M.; Weiner, S., "Intercalation of Sea-Urchin Proteins in Calcite: Study of a Crystalline Composite Material," *Science* **1990**, *250*, 664-67.

11. Taylor, M. G..; Greaves, G. N.; Simkiss, K., "Intercalation of Sea-Urchin Proteins in Calcite: Study of a Crystalline Composite Materials," *Eur. J. Biochem.* **1990**, *192*, 783-89.

12. *Iron Biominerals* , Frankel , R. B.; Blakemore, R. P., Eds; Plenum: New York, 1991, pp 435.

13. Blakemore, R. P., "Magnetotactic bacteria," *Science* **1975**, *190*, 377-79.

14. Mann, S.; Moench, T. T.; William, R. J. P., "A high resolution electron microscopic investigation of bacterial magnetite. Implication for crystal growth," *Proc. R. Soc. London, Ser. B* **1984**, *221*, 385-93.

15. Mann, S.; Frankel, R. B.; Blakemore, R. P., "Structure, morphology and crystal growth of bacterial magnetite," *Nature* **1984**, *310*, 405-7.

16. Bazylinski, D. A.; Frankel, R. B.; Jannasch, H. W., "Anaerobic magnetite production of a marine, magnetotactic bacterium," *Nature* **1988**, *334*, 518-9.

17. Pierre, T. G. St.; Bell, S. H.; Dickson, D. P. E.; Mann, S.; Webb, J.; Moore, G.R.; Williams, R. J. P., "Mössbauer spectroscopic studies of the cores of human, limpet and bacterial ferritin," *Biochim. Biophys. Acta* **1986**, *870*, 127-134.

18. Mann, S.; Sparks, N. H. C.; Blakemore, R. P., "Structure, morphology and crystal growth of anisotropic magnetite crystals in magnetotactic bacteria," *Proc. R. Soc. London* **1987**, *B 231*, 477-87.

19. Fassbinder, J. W. E.; Stanjek, H.; Vali Hojatollah., "Occurrence of magnetic bacteria in soil," *Nature* **1990**, *343*, 161-3.

20. Farina, M.; Esquivel, D. M. S.; Lins de. Barros, H. G. P., "Magnetic iron sulfur crystals from a magnetotactic microorganism," *Nature* **1990**, *343*, 256-58.

21. Mann, S.; Sparks, N. H. C.; Frankel, R, B.; Bazylinski, D. A.; Jannasch, H. W., "Biomineralization of ferrimagnetic greigite (Fe_3S_4) and iron pyrite (FeS_2) in a magnetotactic bacterium," *Nature* **1990**, *343*, 258-61.

22. Williams, R. J. P., "Iron and the origin of life," *Nature* **1990**, *343*, 213-4.

23. Wächtershauser, G., "Evolution of the first metabolic cycles," *Proc. Natl. Acad. Sci. USA* **1990**, *87*, 200-4.

24. Drobner, E.; Huber, H.; Wächtershauser, G.; Rose, D; Sletter, K. O., "Pyrite formation linked with hydrogen evolution under anaerobic conditions," *Nature* **1990**, *346*, 742-44.

25. Russell, M. J.; Hall, A. J.; Gize, A. P., "Pyrite and the origin of life," *Nature* **1990**, *344*, 387.

26. Popper, K. R., "Pyrite and the origin of life," *Nature* **1990**, *344*, 387.

27. *Surface Reactive Peptides and Polymers,* Sykes, C. S.; Wheeler, A. P., Eds.; ACS Symposium Series 444, American Chemical Society: Washington, D.C. 1991.

28. *Material Synthesis Utilizing Biological Processes*, Rieke, P. C.; Calvert, P. D.; Alper, Mark., Eds.; MRS Symposium Proc. Vol. 174; Material Research Society: Pittsburgh, 1990, pp. 3-92.

29. Meldrum, F. C.; Wade, V. J.; Nimmo, D. L.; Heywood, B. R.; Mann, S., "Synthesis of inorganic nanophase materials in supramolecular protein cages," *Nature* **1991**, *349*, 684-7.

30. Bianconi, P. A.; Lin, Jun.; Strzelecki, A. R., "Crystallization of an inorganic phase controlled by a polymer matrix," *Nature* **1991**, *349*, 315-17.