Edited by
Peter Behrens and Edmund Baeuerlein

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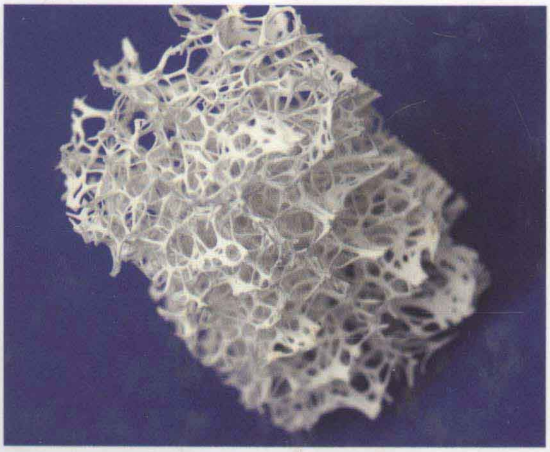
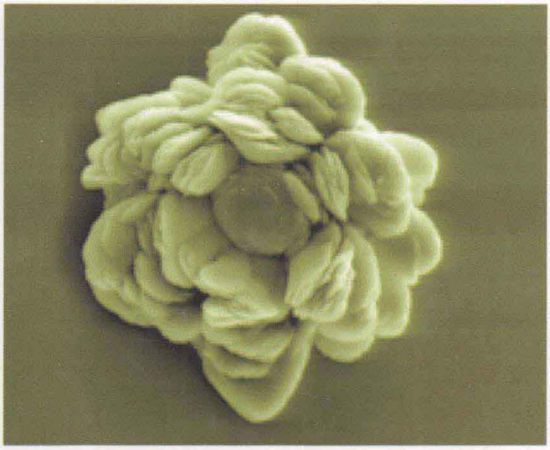
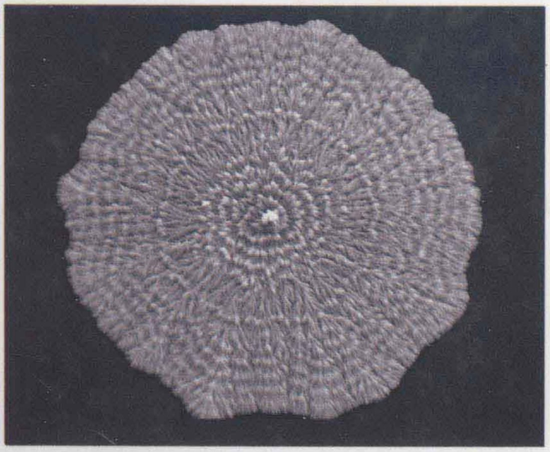
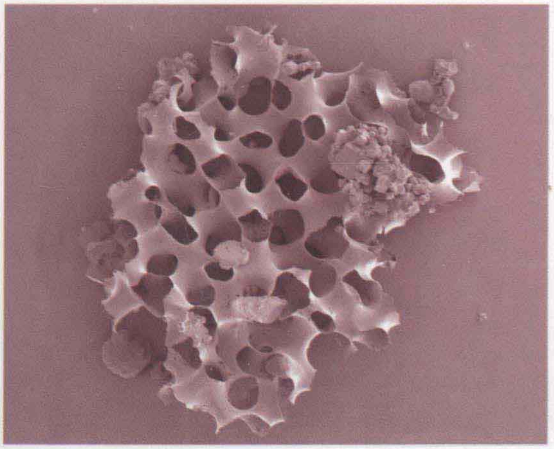
Handbook of Biomineralization

Biomimetic and Bioinspired Chemistry

Foreword by Stephen Mann

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Cover Illustration (designed by Felix Bäuerlein)
Top left: A Silicat-1 *Luffa* monolith, created in shape-preserving, *in situ* thermal reactions after complete coverage of the sponge *Luffa* as biotemplate with Silicalite-1.
(A. Zampieri et al., Chap. 14, Fig. 14.8 b)
Top right: This vaterite structure resulted from a rapid, kinetically controlled formation in presence of a macrocyclic polyacid with the highest charge density used.
(D. Volkmer, Chap. 4, Fig. 4.10, bottom right)
Bottom left: Formation of planar aragonite-type crystals of barium carbonate with silicate anions on a chitosan substrate
(H. Imai, Y. Oaki, Chap. 5, Fig. 5.9 b)
Bottom right: Calcium carbonate particle formed as a thin film over the membrane surface of polymer replicas of sea urchin skeletal plates
(F. Meldrum, Chap. 15, Fig. 15.4 c)

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Preface

On passing back through history and prehistory, one finds the Stone Age, the Bronze Age, and the Iron Age. Clearly, Man has in the past related the achievements of former generations to things solid and material – most likely because these materials have been rediscovered as artifacts, long after their day-to-day use. But today, we live in an era dominated by vast progress in the possibilities of information exchange, to a point where this period indeed may be referred to as the "Silicon Age". So, what might be the materials of the future?

Many well-established materials such as metals, ceramics, or plastics can no longer fulfill all of the needs of a technologically advanced society, and today a clear trend can be seen towards more complex functions that may be realized only with the use of materials of more complex composition and structure. At an early stage, engineers and scientists realized that, compared with their pure counterparts, mixtures of materials tend to show superior properties. Excellent examples of this are composite and hybrid structures, and especially those which contain an elastic, malleable organic component together with a hard, inorganic substance. For example, the addition of silica particles to the rubber used to make rubber tires enhances the tire's lifetime, while the properties of even a material as mundane as concrete can be "spiced up" with polymers,

Although, in terms of materials sciences, biominerals belong to this class of composites and hybrids, they also feature well-defined structures on several length scales, from the atomic scale to centimeter-sized functional arrangements of crystals in an organic matrix. In this way they demonstrate properties – or combinations of properties – which have not yet been achieved with synthetic hybrid materials. Thus, when using natural biominerals as a model, it is possible to prepare materials with both improved properties and applications.

Several different terms have been used to describe this approach, notably those appearing in the title of this Handbook, namely "biomimetic" and "bio-inspired". The process of mimicry involves constructing something that resembles the original as closely as possible, although this of course requires a detailed knowledge of the archetype. Inspiration, on the other hand, provides novel ideas which often appear as a "flash", even when observing the "original" only superficially. In fact, inspiration may even be hampered by too good a knowledge of the original, and by trying to follow it too closely. In this sense, we use the

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term "biomimetic" when the scientific approach follows biomineralization so closely that it also allows conclusions to be drawn about the natural process. Bio-inspired materials are, correspondingly, much more loosely attached to archetype biominerals.

Part I of this volume begins with two chapters, by Behrens, Jahns, and Menzel, and by Brunner and Lutz, which focus on the biomimetic chemistry of silica deposition. On moving away from this amorphous material to crystalline substances, Cölfen's chapter on mesocrystals provides information on a novel model for crystallization processes and their products. Calcium carbonate is not only the most prominent natural biomineral, but also is highly suited to laboratory investigations, and this point is highlighted in chapters on the crystallization of calcium carbonate under monolayers (Volkmer), in layered organic systems resembling mollusk nacre (Imai and Oaki), or in eggshells (Arias, Arias, and Fernandez). de Masi and her co-workers then report on the biomimetic mineralization of protein aggregates. The next chapters, by Orme and Giocondi and by Faivre, describe the calcium phosphate and iron oxide systems, respectively.

Part II of the volume presents bio-inspired approaches to model certain structural features of biominerals, based either on a three-dimensional approach using ice crystals as a template (Deville, Saiz, and Tomsia), or by applying two-dimensional analogues (Helmecke, Behrens, and Menzel; and Tremel and co-workers). In Part III, we have collected "bio-supported" approaches, which do not aim to follow the self-aggregation and self-ordering processes of natural biomineralization, but rather use natural materials in shape-preserving reactions to imprint certain structural features on the resulting product. "Bioclastic" approaches using inorganic preforms are described by Sandhage et al. The use of organic plant tissues to generate inorganic macrostructures is summarized by Schwieger and Greil and their co-workers. In "bio-casting", the pores of biomineral skeletons are used as templates for the generation of macroporous structures (Meldrum).

Moving to smaller biological entities such as templates, Part IV contains details of studies conducted on the mineralization of protein cages (by Douglas and co-workers) and viruses (by Bittner). In Part V, the chapter of Boissière, Allouche, and Coradin on the medical applications of silica capsules formed with biopolymers, builds the first stages of a bridge to Volume 3 of this Handbook. The imaging methods described in the final part of this volume by Zolotoyabko and Stock, respectively, are of course important not only to the study of products of biomimetic, bio-inspired, bioclastic, biocast and synthetic products, but also to the investigation of biominerals themselves.

As editors, we hope that our collection of articles timely reflects the current importance of the field, and also highlights future trends – perhaps at the advent of the "Age of Complex Materials"? We thank all of the contributing authors for their commitment to this book, and especially Dr. Gudrun Walter from Wiley-VCH, without whose enthusiasm this Handbook of Biomineralization may not

have materialized. We also thank Cornelia Meinertz-Bäuerlein and Birgit Förster for their ongoing secretarial support.

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Foreword

Where does scientific creativity come from? If we knew the answer to this question then the world would be a very different place. Civilisation depends at its core on the creative inspiration found at the bedrock of science and art, yet we have very little understanding or control over the conditions and circumstances that set off the sparks of invention or reveal the sudden clarity of insight. Understandably, transforming existing scientific paradigms is an event that we expect to be very rare indeed, not only because of the fundamentally progressive, step-wise nature of the scientific endeavour but because the system is exemplified by its intellectual and empirical robustness. But most scientists do encounter moments of "jaw-dropping" originality that arise from time to time in their research fields through newly unveiled experiments and methodologies. (This is often recognised by a bemused state of half-envy/half-awe as one contemplates why one hadn't thought of it first!). Often, we tend to look to young scientists for this type of local scale revelation, which suggests that at least some aspects of the creative process fade with age.

If the essence of scientific creativity cannot be captured by prescriptive methods of teaching and practical experience, then perhaps we can get a hold of a little of its ephemeral quality by the process of inspiration. Nearly every scientist has encountered individuals that are worthy mentors, who express fun, excitement, and joy through their work, who take great delight in the unveiling of the unknown, and who are generous in sharing this knowledge and privilege. But do these fine attributes alone solve deep problems or uncover great secrets? Clearly, inspiration must also be stirred up at some fundamental practical level, where the sublime world of ideas and concepts slams hard against the prosaic experience of technical pragmatism demanded of scientific endeavour. Over many centuries, a tried and tested way of pump-priming this hard-wired type of inspiration is to look to Nature as a revelation not only with regard to the optimisation of solutions to specific functional problems, but as a treasure-trove of novel process, most of which are so unusual and strange that they fall outside the mind's imagination and have to be retained by fascination.

This book is another significant testament to the importance of inspiration as an engine of creativity in science. In this case, the primary archetype is the biological process of biomineralization, in which inorganic-based materials (calcium

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carbonate, calcium phosphate, iron oxides, silica etc) are deposited in elaborate forms and structures for functional use. Each chapter illustrates striking advances in materials chemistry that have been inspired by a knowledge and understanding of biomineralization. This *biomimetic* (or *bioinspired*) approach involves a multitude of strategies that together illustrate the richness and fascination to be gained by studying a natural process within the context of a tangential field. As a natural phenomenon, biomineralization has been studied for many centuries, and whilst the importance of biomineral structure and hierarchy were recognised relatively early on as models for the design of materials with enhanced mechanical properties, the translation of molecular-based principles into synthetic strategies (chemistry) is very recent. In particular, biomineralization teaches that there are deep principles residing at the organic-inorganic interface – supramolecular preorganization, interfacial molecular recognition, vectorial regulation and multilevel processing for example – that exemplify new chemistry strategies based on confinement, template-directed nucleation, morphosynthesis, and crystal tectonics, respectively. Thus, we have chapters that highlight new model systems, novel concepts, innovative synthetic methods and applications, and in each case it is evident that there is a lot of fun and excitement going on in these research groups. Indeed, what is so clearly seen in this book is the remarkable inventiveness and creativity that scientists bubble with once a source of inspiration (biomineralization) has been identified.

I warmly congratulate the editors for bringing together such an outstanding group of scientists, and the authors themselves for their remarkable contributions to the advancement of this new and exciting field.

Bristol, March 2007 *Professor Stephen Mann FRS*

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