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Jean-Pierre Cuif, Yannicke Dauphin and James E. Sorauf

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## BIOMINERALS AND FOSSILS THROUGH TIME

Fossils are essential to the reconstruction of the evolution of life and episodes in Earth history. Fossil skeletal material serves as the repository of chemical data widely used in the reconstruction of the Earth's climate-ocean system at various time scales. Knowledge of biomineralization – the processes associated with the formation of mineralized biological structures – is essential to properly evaluate data derived from fossils. Additionally, knowledge of biomineralization is critical to the understanding of major events in the evolution of faunas, such as the original appearance of skeletons and some major extinction events.

This is the first book to concentrate on aspects of biomineralization through Earth history. The book emphasizes skeletal formation and fossilization in a geologic framework in order to understand evolution, relationships between fossil groups, and the use of biomineral materials as geochemical proxies for understanding ancient oceans and climates. Approaching the subject from this viewpoint allows the authors to link the biotic, physical, and chemical realms. The focus is on shells and skeletons of calcareous organisms, although the broader impacts of these processes on other elements are also addressed, especially their roles in the global chemical cycles of carbon and silicon. The book explores the fine structures and mode of growth of the characteristic crystalline units, taking advantage of the most recent physical methodological advances. It is richly illustrated and will be of great interest to advanced students and researchers in paleontology, Earth history, evolution, sedimentary geology, geochemistry, and materials science.

JEAN-PIERRE CUIF was appointed professor of paleontology at the Université de Paris-Sud, Orsay, in 1980, after obtaining a doctoral thesis at the Museum National d'Histoire Naturelle (Paris). As a part of the Geology Department, the paleontological research team has developed a specialized approach to the mineralized units that built the calcareous skeletons of the invertebrates. In addition to basic research on distributions and compositions of the organic compounds associated with the mineral phases, this approach has led to participation of the team in multiple collaborative programs dealing with invertebrate evolutionary history and biomineralization disturbances in economically important molluscs.

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extended her research to the structure and composition of modern and fossil molluscs, corals, and vertebrate skeletons.

JIM SORAUF taught sedimentology and paleontology at the State University of New York at Binghamton from 1962 until becoming emeritus in 2001. He has published approximately 70 papers in peer-reviewed journals on skeletal structures of modern corals, and on systematics and paleobiology of fossil corals ranging in age from Cambrian to Pleistocene. He is a former co-editor of *Fossil Cnidaria and Porifera*. He was a Trustee of the Paleontological Research Institution in Ithaca, New York, for many years, serving as President of their Board of Trustees from 1988 to 1990.

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BY

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## Preface

During the last few decades, research on climate change and threats to biodiversity have drawn public attention to present-day modifications of the world environment. Thus the public is now receptive to the concept of a *changing Earth*, a vision familiar to paleontologists for roughly two centuries, as investigations into fossilized life-forms began a few decades before the nineteenth century. A method for establishing the chronological distribution of the fossil record was rapidly developed and continuously improved, thereby providing access to Earth history for the first time. From a very restricted number of research centers, convergent information resulted in a completely new view of the Earth that outlines progressive changes in geography, and reconstructs environmental and faunal modifications through time. Also, up through the first half of the twentieth century, improving our description of the fossil record was an essential activity. It was the golden age of great paleontological monographs, in which the compositions of fossil faunas were compared in minute detail.

In the middle part of the twentieth century new physical methods were developed that led to innovative uses of fossils, many of which were based on study of the chemical record preserved in biogenic calcium carbonate of shells, reflecting environments in which the fossilized organisms lived. The first application of such a new method is precisely known: the reconstruction of annual variations in water temperature in Jurassic seas (about 150 million years before present), as a result of the study of variations in oxygen isotope ratios. These were recorded from within the calcified layers of a belemnite rostrum (a fossil cephalopod). For the first time, numerical values with astonishing precision were provided for an important environmental parameter. This spectacular result was obtained by H. C. Urey and his collaborators and reported in 1951. Thus, at the start of the second half of the twentieth century, it could legitimately be expected that improvement of instrumental techniques would furnish data of increasing precision and rigor that had been lacking in geological and paleontological reconstructions up to that time. Consequently, identification of fossils which was demanding of expertise and frequently uncertain as a result, was to be replaced by interpretations based on numerical values directly obtained from the fossil carbonate. This was precisely what did occur, with the result that paleontology declined in its role as part of university training for Earth scientists.

In an interesting turn of history, this continuous improvement of measurement methods – truly amazing during the past three decades – has forced researchers to pay new attention to



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specific characteristics of biologically produced calcareous structures, the dominant material of fossils. Early in the development of chemical and isotopic studies, the properties of these Ca-carbonate shells were seen to be closely tied to the taxonomy of the producer organisms, that is to say, their position in the overall phylogenetic scheme. Moreover, in comparing Ca-carbonate structures from different species living in the same environment and simultaneously exposed to its variations, it was noted that environmental changes were effectively registered by each species, *but with values that are unique to each of them*. Therefore, long before understanding the biological processes responsible for shell formation, it was suspected that biocrystallization involves different mechanisms than simple chemical precipitation does as it occurs in saturated solutions. In his pioneering publication, H. C. Urey predicted that such a phenomenon may exist, and named it the “vital effect.”

During the two last decades, the spatial resolution of instruments used for chemical or isotopic measurement has been increased to the micrometer range, providing possibilities for obtaining data recorded from different parts within a single shell. Resulting data clearly show that the specific controls exerted on crystallization by each of the specialized areas of the mineralizing organ lead to the recording of distinct and differing signals within each shell layer. Physical and chemical measurements now demonstrate that within a shell, several “vital effects” actively influence the formation of the distinct shell layers they contain. This provided unexpected support of early studies of Bowerbank (1844) and Carpenter (1845, 1847), who first showed that calcareous shells are built by superposed layers of differing sizes, shapes, and spatial arrangements of skeletal units.

Multiple physical and chemical methods now produce convincing evidence that not only taxonomy must be considered when studying biogenic Ca-carbonate structures as potential sources of environmental data. In addition, the precision of these measurements requires that close attention is paid to distinct shell layers and their species-specific spatial arrangement. More fundamentally, evidence of these layer-specific structural and chemical properties leads us to a re-examination of the biocrystallization process itself. Improved analytical instruments now provide convergent evidence indicating that the former concept of crystallization by saturation within a fluid that more or less resembled seawater does not account for the detailed properties of the skeletal units that make up shells.

Therefore, most of this book is dedicated to an in-depth examination of the structural and chemical properties of the crystal-like units which are found forming shells and other calcareous skeletons. Morphological diversity of shells is familiar to everyone and is still emphasized by the very precise species-specific three-dimensional arrangements of their skeletal components, described at the microscopic level since the middle of the nineteenth century. Here their mode of growth is described at the micrometer and nanometer scales, providing information and examples for developing more accurate methods of microstructural analysis. Beyond the variety of sizes, shapes, spatial organizations, and growth modes of skeletal units, modern instruments also reveal striking similarities in these parameters when seen at submicrometer scales. Subunits with dimensions in the range of 10 nm can be recognized within all of these Ca-carbonate structures. Their internal structures observed at still higher resolutions provide the first direct evidence regarding the sequence of events

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leading to the crystallization process itself, where organic molecules are involved. When compared to equivalent data concerning phosphatic and siliceous biominerals, the specificity of the calcareous biocarbonates is still more instructive.

It is of great importance to improve our understanding of this biochemically driven crystallization process characterized by a permanent interplay between organic and mineral components. This is apparent, not only because of multiple applications, but, more essentially, to gain an increasingly profound understanding of the process of shell calcification. Recently, the genomic approach to the mineralizing process has established an amazing complexity to this aspect of biology. Most surprisingly, it is now clear that, in contrast to the rather low mineralogical diversity of shell carbonates, the calcification processes developed within major biological groups involve very different groups of genes. Therefore, the question now arises as to how genomic diversity active in the cellular mechanism of calcification is transferred to the hierarchical organization of these calcareous units in such a specific form. It is this form that allows characterization of even the most common shell. Fundamentally, deciphering the structure and mode of growth of biocrystals contributes to creating a consistent scheme that coordinates the intracellular preparative processes of calcification and the following step, the still largely unexplored organomineral interplay that drives Ca-carbonate crystallization. Remember that this is operating outside of the cell membrane. Here lies the origin of the “vital effect.”

Thus, just a short time after the decline of paleontological studies due to an oversimplified application of physical methods to fossils, there is a touch of irony in the observation that, both in basic research and in its application, the understanding of shell structures and the biological mechanisms controlling shell crystallization have become a prerequisite for rational use of these newer methodologies. In addition, when applying these methods to fossil materials, relevant structural and chemical comparisons with their extant representatives now can be carried out at the micrometer scale, allowing unprecedented accuracy in research on the fossilization process, thus improving the reliability of the multiple categories of information brought to us by the fossil record.

Therefore it is noteworthy that, transferred to a new base in advanced analytical methods, the continuing dialog between the ancient and the modern worlds that has been, since its beginning, the essence of paleontology, is today no less important than it was two centuries ago.