

# MARINE AUTHIGENESIS, A HOLISTIC APPROACH

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## HISTORICAL PERSPECTIVE

This book is a collection of papers focusing on various aspects of authigenic and diagenetic marine minerals and related elemental cycling. In essence, it belongs to a line of specialized volumes marking major steps of continued international cooperation. Closely following the establishment of UNESCO International Geological Correlation Programme (IGCP) Project 156 (Phosphorites) in 1978, *SEPM Special Publication 29* (Marine Phosphorites, edited by Y. K. Bendor) was published in 1980 as a collection of stimulating papers stemming from a symposium on marine phosphorites held at the Xth International Congress on Sedimentology in Jerusalem in July 1978. Nearly simultaneously, a thematic set of special papers on “Phosphatic and Glauconitic Sediments” was published by the *Journal of the Geological Society* (Volume 137, 1980) following a meeting of the Geological Society on the same subject earlier that year. Led by P. J. Cook and J. H. Shergold (1978-1984) and later by W. C. Burnett and S. R. Riggs (1984-1988), IGCP Project 156 conducted 29 international and regional field workshops and symposia.

Over the next two decades, a flourishing of international research on phosphorites and their related facies ensued, with many workers attempting to solve the many “Unsolved Problems” outlined by Bendor (1980) in his seminal introduction to *SEPM Special Publication 29*. A great deal of this research was submitted for Special Publication 52 of the *Journal of the Geological Society of London*, published in 1990, and edited by A. Notholt and I. Jarvis, who organized the final International Symposium of UNESCO Project 156 in Oxford in 1988. In 1991, a successor UNESCO IGCP Project 325 titled “Correlation of Paleogeography with Phosphorites and Associated Authigenic Minerals” was initiated by J. Lucas and L. Prévôt. The title of this research group clearly illustrates the increasing desire of its researchers at that time to expand the scope of the project to the study of the origin and occurrence of other authigenic minerals. In addition to a myriad of independent publications, a number of other important books were published in association with the IGCP Projects during this period. These included a three-volume set of 151 papers published by Cambridge University Press titled “Phosphate Deposits of the World,” including *Vol. 1 — Proterozoic and Cambrian Phosphorites* (Cook and Shergold, 1986), *Vol. 2 — Phosphate Rock Resources* (Notholt et al., 1989), and *Vol. 3 — Neogene to Modern Phosphorites* (Burnett and Riggs, 1990). Also published during this time frame were special thematic publications of *Sciences Géologiques* (Lucas and Prévôt, 1979, 1985; Lucas et al.,

1989). Later, *Siliceous, Phosphatic and Glauconitic Sediments of the Tertiary and Mesozoic* (Iijima et al., 1994) was published following a symposium of the International Geological Congress in Japan in 1992. In 1993, members of IGCP Project 325 met in Interlaken for a meeting and workshop to discuss concepts and controversies that continued to surround the origin of marine phosphorites and this resulted in a multi-authored set of papers published in *Eclogae geologicae Helveticae* (Föllmi, 1994).

The present volume contains many papers which were either presented at the final symposium and workshop of UNESCO Project IGCP 325 (led by J. Lucas and L. Prévôt-Lucas) titled “Deposystems of Phosphorites and Related Authigenic Minerals: Processes, Pathways and Products” in Strasbourg (October, 1996), or at the first symposium of its successor, the SEPM Research Group on Marine Authigenesis (convened by C. R. Glenn & W. C. Burnett) titled “Formation of Authigenic Marine Minerals,” in Kona, Hawaii (May 1997). As with related predecessor volumes, this special publication contains a number of papers still searching for answers relating to the origin of marine phosphorites, including several papers relating to the biogeochemical cycling of phosphorus, yet it also contains a number of papers that discuss many other aspects of marine authigenic mineralization. The commingling of the various studies of authigenic minerals is partly the result of the increasing awareness that there are many overlaps, even direct associations, between different authigenic minerals, both in time and space. In compiling this volume we have taken the “holistic” attitude towards marine authigenesis, which considers the integrated whole to be more than the simple sum of its parts.

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Many marine authigenic minerals are more or less directly tied to marine biological activity, both benthic and pelagic. This implies a strong dependence on the chemical characteristics of the environment and on nutrients, which are conducive not only to high biological productivity, but also to variations of predominant species and hence to variation of their chemical composition. In addition, all authigenic minerals may play significant roles in the long-term biogeochemical cycling of elements in the oceans, and many may have been overlooked in terms of their relative importance with regard to providing a sink for reverse weathering reactions. Among nutrients, phosphorus is one of the most important so-called limiting nutrients, which explains and justifies the special interest in the P-cycle during the last decade. *Compton et al.* explore the modern P cycle and its possible variations in the geologic past. These authors gain in

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refinement on earlier established general principles which interweave climate, weathering of continents, tectonics, rate of oceanic spreading and accompanying mid-oceanic ridge hydrothermal fluxes, etc. *Subramanian* suggests in this volume that the importance of modern Asian riverine P inputs may have been overlooked in some past P-cycle models. Uncertainties in past global P cycle budgets are then further emphasized as *Colman and Holland* provide special attention to the fate of the marine P of which the return flux from its sink in seafloor muds to overlying seawater is higher than the riverine input. These authors emphasize the strong coupling between the redox state of marine sediments and the return flux of P to seawater (increasing with more reducing conditions). As P is a limiting nutrient that plays a dominant control on organic C production, and as organic C burial is a major control on atmospheric O<sub>2</sub> production, *Colman and Holland* also show how the marine P cycle plays an important role in stabilizing atmospheric O<sub>2</sub>. *Guidry et al.* further discuss how global tectonics may also play an important role in the removal of phosphate from seawater by carrying a non-negligible part of P into tectonically subducted sediments. In addition, *Rasmussen* suggests that aluminophosphate minerals may be an important underestimated sink for oceanic phosphate.

Sedimentary phosphorite formation, a major global P sink, has occurred episodically over geologic time, and *Shields et al.* discuss what can be discerned regarding the origin of two of the largest groupings of these occurrences using combined sedimentary isotopic modeling (Sr, Nd, S, and C), contrasting results obtained for the Precambrian-Cambrian episode with those for the Late Cretaceous to Recent. A causal connection is put forward between metazoan evolution and widespread phosphogenesis. *Van Houten* re-examines the episodocity of phosphorite formation through time, and contrasts this with new data on the temporal variability of ooidal ironstones. He finds that many ooidal ironstones and phosphorites have many similarities, developing in similar shallow water environments experiencing slow sedimentation rates, being influenced by oceanic upwelling, and exhibiting marked evidence reworking, transport, and condensation. For about 75% of the Phanerozoic, however, these two authigenic facies are dissimilar in their temporal distribution; ironstones appear to correlate with greenhouse phases of global climate, increased continents, and subaerial weathering. Greenhouse conditions thus appear to play a perhaps subordinate control on the timing of major phosphogenesis.

The amount of available nutrients determines the rate of productivity, which utilizes various elements depending on the dominant species, delivering to sediments organic matter, carbonates, and silica in various amounts. *Fonseca* looks at the early diagenetic evolution of this material and how it depends on the ambient redox conditions or on the redox conditions induced by the sediment itself (type, sedimentation rate, etc.). *Lucas and Prévôt-Lucas* find the causes of switching between carbonate-dominated sedimentation and phosphorite-dominated sedimentation are established before deposition. They discuss the role of relative N/P nutrient ratios in determining carbonate-producing phytoplankton versus organic matter-producing

naked phytoplankton. They believe when the local morphology of the shelf is favorable, the major cause of the formation of giant phosphate deposits is the type of productivity rather than an episodically enhanced global P-input. *Soudry* explains how micritic limestones built by calcification of bacterial mats and phosphorites may occur closely together in some phosphorite suites, while *Benaliouhaj et al.* conclude that, in the relationship between phosphorites and black shales, the disassociation of the two facies may occur during early diagenesis through differential preservation of organic matter on the shelf; the availability of inorganic clays is one factor favorable to the preservation of organic matter.

Comparative studies of formation and accumulation of phosphorites in various settings provide better knowledge of the required environmental conditions and prove in this volume that it is not reasonable to try to elaborate one single model. Several scenarios are proposed, including phosphatized microbial mats in the shallow water cases studied by *Schwennicke et al.*, or diatomaceous, weakly-consolidated organic-rich muds developing phosphatic grains and nodules through a process of progressive phosphatization that involves compaction, crystallization of phosphatic matter along with the dissolution and expulsion of nonphosphatic components, as explained by *Baturin*. *Baturin* convincingly interprets most of the common varieties of carbonate fluorapatite mineral morphologies, including colloform masses, globules, globular aggregates with pronounced radial crystallization, rods, spindles, and dumb-bell shapes, as shown by SEM, to be diagenetic crystallites and not phosphatized (or phosphatizing) bacteria, as previously suggested by other workers. The different scenarios are even further complicated when, as pointed out by *Fountain and McClellan*, originally authigenic pristine minerals change through repeated diagenetic events, from cryptocrystalline carbonate fluorapatite rich in structural CO<sub>3</sub>, to hexagonal apatite crystals depleted in CO<sub>3</sub>, or to ferruginous CO<sub>3</sub>-depleted nodules. Ultimately, more or less intense reworking is able to totally change the character of the primary sediment in which grains, nodules and other types of solid phosphate particles and associated authigenic minerals undergo sorting, displacement (transport), and sedimentological stacking. Phosphate and other authigenic mineral deposits are also subjected to allostratigraphic and sequence stratigraphic controls. As *Grimm* points out, much of the attention paid to phosphorites derives from their hybrid character, including their genesis as biogeochemical precipitates, and the puzzling array of processes that govern their stratigraphic distribution and various facies associations. Utilizing sequence stratigraphy, *Hendrix and Byers* re-examine the processes and products leading to the generation of a heterogeneous collection of sedimentary facies of the "world-class" Permian Phosphoria Formation, which contains about six times the amount of elemental P present in today's oceans. *Riggs et al.* use refined age assessments in interpreting the sea level history and paleoceanographic implications of cyclical phosphogenic events associated with yet another phosphorite giant in the Miocene sections of southeast North America. *Taylor and Macquaker* stress the importance of the variability of accommodation availability as they tackle how early authigenic/diagenetic assemblages (including

calcites, siderite, dolomite, berthierine, chamosite, glauconite, and phosphates) vary spatially and temporally across various mudstone-dominated successions.

Authigenic minerals are usually found in periods and places starved of background sedimentation, such as hardgrounds and seamounts, where they accumulate in crusts and various nodules. Millimeter by millimeter isotope studies by *Burnett et al.* of "protocrusts" from the Peru margin upwelling zone indicate an extremely young age for gelatinous phosphatic to phosphoritic crusts, for which a model of authigenic growth from the diffusion of the interstitial P of muds at the sediment-water interface is proposed. Seamounts are favorable settings for phosphorite crusts (*Benninger and Hein*) and/or ferromanganese crusts (*Bertram and Cowen*), which are of similar diagenetic origin, and some of these are associated with iron-manganese and other authigenic mineral associations, including palagonite, smectite, phillipsite, and barite. An experimental investigation *in situ*, on Cross Seamount, suggests that the deposition of organic matter within microenvironments may contribute to the formation of the narrow bands of Mn- and Fe-oxides observed within crusts and nodules. As for other low-productivity phosphorite deposits, the close association between carbonate fluorapatite and Fe-Mn oxyhydroxides suggests that seamount phosphatization is facilitated by Fe-oxyhydroxide redox reactions whereby P adsorbed to Fe-oxyhydroxides is released to bottom waters or pore waters upon encountering reducing conditions. Phosphatization is characterized by mineralization fronts. Its frequent association with Fe-Mn oxy-hydroxides indicates oxic to sub-oxic conditions of genesis.

The importance of microbial activity in marine authigenesis is emphasized by *Konhauser* for a very different reason. He relates the long-debated occurrence and origin of the enigmatic Precambrian Banded Iron Formations (BIFs), one of the most abundant sedimentary deposits of the Precambrian, to bacterial biomineralization associated with hydrothermal processes. The comparison with phosphate deposits is intriguing. The results of REE studies are provided for various authigenic associations: REE in Upper Carboniferous phosphate of Mid-Continent North America by *Cruse et al.*, REE and U in modern phosphatic sediment off Goa, India, by *Nath et al.*, and REE in P-Fe-Mn crusts by *De Carlo et al.* All these results, and even those on Pt in Pacific Fe-Mn crusts by *VonderHaar et al.*, show an obvious diagenetic relationship. *Martín-Algarra and Sánchez-Navas* report on the origin of other examples of crusts in Mesozoic sediments, which they do not consider diagenetic, but biosedimentary microbial accretions (pelagic stromatolites). These pelagic stromatolitic beds, composed of phosphate and iron-manganese nodules, also contain other authigenic minerals such as barite and glauconite, which require similar conditions for formation. These minerals are minor constituents in the previous case but these become the major minerals in other facies, including the bedded barite facies as reviewed by *Jewell*, and the green clay minerals, verdine and glauconite reviewed by *Thamban and Purnachandra Rao*. Both record essential genetic characters revealing their close relationship with phosphatic facies. Hence, the authigenic green clay minerals explored by *Amorosi and Centineo* in the Lowermost Cenomanian of Cape Blanc Nez

(Northern France) and by *Kronen & Glenn* in mixed carbonate-siliciclastic foreereef sediments (Great Barrier Reef, Australia) play significant sedimentologic, stratigraphic, and sequence-stratigraphic roles.

Dolomite, which plays an important part in ocean-atmosphere interaction, is another authigenic mineral, the genetic conditions of which may seem far different from those of the other authigenic minerals considered above. *Arvidson et al.* revisit the "Dolomite Problem" combining a modified geochemical model of atmospheric CO<sub>2</sub> fluctuations over the past 100 million years with new experimental precipitation rate data for dolomite and calcite. They conclude that the decrease in the dolomite to calcite ratio observed over time is largely a result of changes in the saturation state of the oceans with respect to these minerals and global surface temperature. *Wright* addresses another aspect of the "dolomite problem," the apparent inability to synthesize dolomite in physio-laboratory experiments, and suggests that the lack of convincing hydrologic models requires new exploration of the role of benthic microbial communities in the formation of dolomite, not just in association with the now well-documented "organodolomites," but also linking the role of organic diagenesis played by the interaction between cyanobacteria and sulfate-reducing bacteria in association with the formation of the large platform dolomites of the Proterozoic and Paleozoic. However, the model of microbial dolomite proposed brings this mineral within the fold of the "phosphate family" and supports the idea of a close genetic relationship suggested by the frequent occurrence of dolomite in many phosphate deposits of the world.

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