



title: Phosphorite Research and Development
Geological Society Special Publication ; No. 52

author: Notholt, Arthur John George.

publisher: Geological Society of London

isbn10 | asin: 0903317532

print isbn13: 9780903317535

ebook isbn13: 9780585233796

language: English

subject Phosphate rock--Congresses.

publication date: 1990

lcc: QE471.15.P48P47 1990eb

ddc: 553.6/4

subject: Phosphate rock--Congresses.

GEOLOGICAL SOCIETY SPECIAL PUBLICATION NO. 52

Phosphorite Research and Development

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1990
Published by
The Geological Society
London

Geological Society Special Publications
Series Editor K. COE

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Published by the Geological Society from:
The Geological Society Publishing House
Unit 7
Brassmill Enterprise Centre
Brassmill Lane
Bath
Avon BA1 3JN
UK
(Orders: Tel. 0225 445046)

First published 1990

Distributor USA:
AAPG Bookstore
PO Box 979
Tulsa
Oklahoma 74101-0979

USA

(Orders: Tel. 918-584-2555)

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British Library Cataloguing in Publication Data

Phosphorite research and development.

1. Phosphate deposits

I. Notholt, A. J. G. (Arthur John George)

II. Jarvis, I. (Ian) III. Geological Society of London IV. Series 553.64

ISBN 0-903317-53-2

Printed in Great Britain at the Alden Press, Oxford

Contents

Preface	v
Phosphorite research: a historical overview <i>Cook, P. J., Shergold, J. H., Burnett, W. C. & Riggs S. R.</i>	1
Mineralogy of sedimentary apatites <i>McClellan, G. H. & Van Kauwengergh, S. J.</i>	23
Experimental study of the substitution of Ca by Sr and Ba in synthetic apatites <i>Lucas, J., El Faleh, E. M. & Prevot, L.</i>	33
Humic substances in phosphorites: occurrence, characterization and significance <i>Nathan, Y.</i>	49
Sedimentation dynamics and redox iron-cycling: controlling factors for the apatite-glaucconite association on the East Australian continental margin <i>O'Brien, G. W., Milnes, A. R., Veeh, H. H., Heggie, D. T., Riggs, S. R., Cullen, D. J., Marshall, J. F. & Cook, P. J.</i>	61
Organic carbon cycling and modern phosphorite formation on the East Australian continental margin: an overview <i>Heggie, D. T., Skyring, G. W., O'Brien, G. W., Reimers, C., Herczeg, A., Moriarty, D. J. W., Burnett, W. C., & Milnes, A. R.</i>	87
Diagenetic stability of the isotopic composition of phosphate-oxygen: palaeoenvironmental implications <i>McArthur, J. M., & Herczeg, A.</i>	119
Episodes of phosphogenesis and phosphorite concretion formation in the North Sea Tertiary <i>Balson, P. C.</i>	125
Comparative geology and mineralogy of the southeastern United States and Togo phosphorites <i>Van Kauwenbergh, S. J. & McClellan, G. H.</i>	139

Microbial mediation in phosphatogenesis: new data from the Cretaceous phosphatic chalks of northern France <i>Lambooy, M.</i>	157
Pebbly phosphate and granular phosphorite (Late Cretaceous, southern Israel) and their bearing on phosphatization processes <i>Lewy, Z.</i>	169
Geological significance of carbonate substitution in apatites: Israeli phosphorites as an example <i>Nathan, Y., Soudry, D. & Avigour, A.</i>	179
Role of microbial processes in the genesis of Jordanian Upper Cretaceous phosphorites <i>Abed, A. M. & Fakhouri, K.</i>	193
Depositional sequences of the Duwi, Sibaiya and Phosphate Formations, Egypt: phosphogenesis and glauconitization in a Late Cretaceous epeiric sea <i>Glenn, C. R.</i>	205
Clay minerals and phosphorite genesis in the Upper Cretaceous of the northern Siberian Platform <i>Zanin, Yu. N., Zverev, K. V. & Solotchina, E. P.</i>	223
Condensation and phosphogenesis: example of the Helvetic mid-Cretaceous (northern Tethyan margin) <i>Föllmi, K. B.</i>	237
Early Ordovician shelly phosphorites of the Baltic Basin <i>Ilyin, A. V. & Heinsalu, H. N.</i>	253
The distribution of phosphatic facies in the Georgia, Wiso and Daly River Basins, Northern Australia <i>Howard, P. F.</i>	261
Events leading to global phosphogenesis around the Proterozoic/Cambrian boundary <i>Donnelly, T. H., Shergold, J. H., Southgate, P. N. & Barnes, C. J.</i>	273
Phosphogenic events and skeletal preservation across the Precambrian-Cambrian boundary interval <i>Braiser, M. D.</i>	289

Two decades of phosphorite investigations in India <i>Choudhuri, R.</i>	305
The influence of magnesium ions during the formation of stromatolitic phosphorites of Udaipur, Rajasthan, India <i>Sisodia, M. S. & Chauhan, D. S.</i>	313
Index	321

Preface

This book contains a selection of the papers contributed to the 11th and Final International Field Workshop and Symposium of International Geological Correlation Programme (IGCP) Project 156: Phosphorites, which was held at Hertford College, Oxford, England, 58 September, 1988. The main aim of the meeting, which attracted over 70 delegates and speakers representing 14 countries (Notholt & Jarvis 1989), and the aim of this volume, is to present the scientific results and ideas that have arisen from research carried out in recent years by geological surveys, universities and other establishments in many parts of the world. Phosphorites provide the basis for the world's fertilizer industry, the backbone of modern intensive agriculture; their occurrence in a sedimentary succession is almost certainly indicative of dramatic changes in palaeoenvironment and sedimentation. Few naturally-occurring raw materials offer such a combination of great socio-economic importance and fundamental scientific significance.

During its ten-year existence, Project 156: Phosphorites became known as one of the largest and most successful of the long-term interdisciplinary geological research projects supported by the IGCP. It owes its creation in 1977 to Peter J. Cook, of the Bureau of Mineral Resources, Geology and Geophysics, Canberra, who hypothesized that a major Proterozoic-Cambrian phosphogenic province extends throughout the Asian and Australian region, one that was perhaps comparable in size (and therefore economic importance) with the Late Cretaceous-Eocene Tethyan province of northern Africa and the Middle East. Project 156 was established, therefore, as a research programme on Proterozoic-Cambrian phosphorites of Asia and Australia, but the international interest that the Project generated led rapidly to the formation of three other Working Groups, devoted respectively to an International Phosphate Resource Data Base; Young Phosphogenic Systems; and Cretaceous-Eocene Phosphorites. Much of the research carried out under the aegis of these working groups has to date formed the basis of three major publications on phosphorites (Cook & Shergold 1986; Notholt, Sheldon & Davidson 1989; Burnett & Riggs 1990).

The present volume starts with a comprehensive review of phosphorite research by Cook *et al.*, the former leaders of Project 156, emphasizing the

considerable value to phosphate exploration of Kazakov's 'Upwelling Hypothesis' which came into prominence in the 1930s, followed by the 'Phosphoria Model', developed as a result of extensive studies by the US Geological Survey, which involves upwelling on the flanks of open ocean basins at water depths of 200-300 m. These models remain fundamental to much modern thinking on phosphogenesis. The importance of global factors such as sea-level changes and plate tectonics, and their interaction with the processes of phosphate formation has become better understood in recent years, and links between periods of phosphogenesis and major evolutionary changes have also been established.

The following contribution by McClellan & van Kauwenberg on the mineralogy of sedimentary carbonate fluorapatites (francolite) emphasizes the importance of CO₃²⁻ substitution for PO₄³⁻, variations in francolite composition with stratigraphical position and particle size as possibly indicators of the extent and type of post-depositional alteration. Geochemical composition may provide additional evidence of depositional, early diagenetic and post-burial history. It is well known that numerous elements may be incorporated into the francolite structure, including the substitution of Sr for Ca, and the experiments described by Lucas *et al.* support the conclusion that Sr may be a valuable indicator of the genetic environment of apatite, although variations in the Sr/ Ca ratio also may reflect differences in post-depositional history. Studies of carbonate substitution in apatite (francolite) from phosphorites of Santonian (Late Cretaceous) to Eocene age in Israel, reveal a significant decrease in CO₂ concentrations in samples that have been subjected to epigenetic alteration and/or weathering (Nathan *et al.*). Carbon, oxygen and sulphur isotopes have also been used to study the diagenetic history of phosphorites, and have made possible differentiation between those formed in oxic/suboxic and anoxic conditions. However, again, the effects of diagenetic alteration need to be taken into account if sound palaeoenvironmental interpretations are to be made based on analysis of the isotopic composition of the phosphate-oxygen bond (McArthur & Herczeg). The organic geochemistry of phosphorites has also attracted considerable interest. Notably significant is the recognition that humic substances form a significant component of organic matter in many phosphorites of various ages. The humic material may be primary, as in

the Tunisian phosphorites, or appear to be secondary, as in phosphorites from the western United States, where it has probably formed by degradation of kerogen (Nathan.) It seems generally agreed that humic substances and phosphorites are closely associated genetically.

The East Australian continental margin is one of only four areas where modern (Neogene to Holocene) marine phosphorite nodules are known to be forming at present. These phosphorites were the subject of a detailed, multidisciplinary study mounted in 1987 by the Australian Bureau of Mineral Resources, which included an examination of the processes controlling the cycling of such elements as organic carbon, nitrogen, phosphorus, sulphur and iron, and also of the role of these processes in the formation of modern phosphorites. Sediment data from samples collected between 29° and 32° S indicate that organic carbon oxidation by oxygen and sulphate reduction, iron and phosphorus recycling between oxic and anoxic sediments, and sediment mixing by bioturbation are three key processes in their formation (Heggie *et al.*). Ultimately, the compositions of the phosphorites reflect this interaction between redox-driven diagenetic processes and multiple periods of reworking (O'Brien *et al.*). Ferruginous Neogene phosphorites occur within glauconitic, foraminiferal sands and are concentrated within depths of 200-300 m, where they form discrete nodules and massive hardground units; Quaternary phosphorite nodules occur in deeper water (250-460 m), in sands of similar composition, but notably they exhibit lower goethite contents.

The development of phosphorite concretions in the marine, clastic sequence of the southern North Sea Tertiary Basin displays a clear cyclicity which corresponds to sea-level 'highstands' (Balson). In particular, the concretions distributed sparsely in Early Eocene mudstones occur just above levels which indicate initiation of more open connection between the Atlantic Ocean and the relatively enclosed North Sea Basin. Thus, the development of phosphorite concretions appears to be linked to large-scale, possibly global, cycles in addition to changes in the local diagenetic environment.

Several major phosphogenic episodes of global extent are now known to occur, together containing deposits with resources estimated to be at least 133000 Mt of all grades and varieties of phosphate rock. Among the largest and economically the most important deposits in the world are those contained in the Neogene succession of the southeastern USA. There the Miocene Pungo River and Miocene-Pliocene Hawthorn Formations together

represent a major phosphogenic episode which also coincided with an extensive global rise in sea level associated with the Miocene transgression. Cores penetrating phosphatic sediments of the Hawthorn Formation in southcentral Florida record multiple phosphogenic episodes separated by quartz-rich sands and indurated carbonates. Comparison of these deposits with those of Eocene age in southern Togo, confirm that both have been produced by a combination of primary depositional and secondary diagenetic processes (van Kauwenbergh & McClellan). The latter account for the removal primarily of carbonates and the decarbonatization of francolite (carbonate-fluorapatite), as well as the development of Fe-Al phosphate minerals and clay mineral alteration profiles. The North Carolina deposits appear to be relatively unaltered or merely in the early stages of alteration.

The Late Cretaceous-Eocene Tethyan Phosphogenic Province is also one of the most extensive in the world, with major deposits situated throughout north Africa and the Middle East. Those of Late Cretaceous age in Egypt are associated with porcellanites, cherts, dark-coloured shales, glauconitic sandstones and bioclastic fine-grained carbonate of the Duwi Group. Although oceanic upwelling is usually advocated as the source of the phosphorus in most phosphorite deposits, at least some Tethyan occurrences may have been strongly influenced by an input of local fluvially-derived phosphorus (Glenn). These Egyptian occurrences are believed to be the result of current winnowing and reconcentration of authigenic grains initially precipitated in reducing shales and biosiliceous sediments. Studies of Upper Cretaceous (Turonian-Maastrichtian) nodular phosphorites in the Yenisei Mouth Depression of northern Siberia (Zanin *et al.*) demonstrate that these phosphate-bearing strata contain a consistent and distinctive clay mineral assemblage of kaolinite and chlorite, with a small but constant admixture of gibbsite, and in some cases montmorillonite. The mineralogical assemblage indicates that, in these deposits at least, phosphogenesis accompanied periods of intense weathering of the adjacent continental landmass under warm and humid climatic conditions, a process which provided a local, possibly fluvially-derived, source of phosphorus. The development of many massive phosphorite deposits appear to be caused by condensation. Very low accumulation rates (210 m Ma⁻¹) are indicated, for example, by the occurrence, on the Alpine Helvetic Shelf, of condensed phosphatic beds of Aptian to early Cenomanian age, formed within a stable westward-flowing current system along the northern Tethyan margin (Föllmi). These beds are thin, generally less than 50 cm, and consist of closely

packed phosphatic particles and crudely laminated crusts embedded in glauconitic sands, marls, and pelagic micrites.

In spite of a considerable increase in data, divergent views continue to be expressed on the precise mechanism of phosphate precipitation. Some petrographic and SEM studies have emphasized the significant role played by microbial communities in phosphogenesis. For example, the Upper Cretaceous (Santonian-Campanian) phosphatic chalks of northern France are now shown to consist essentially of mineralized microbial remains (Lamboley). In the Negev Desert of Israel, the phosphate nodules found at specific levels in the chalky, locally bituminous, Ghareb Formation of Campanian-Maastrichtian age are also believed to have been microbially generated, the globular microstructures commonly found in the phosphate cements being regarded as mineralized cells of endobenthic microorganisms (Lewy). Similarly, cyanobacterial sheaths have been identified within the laminae of phosphorites of Maastrichtian age in Jordan. These phosphorites are interpreted as having formed as algal mats in shallow-water, subtidal to intertidal environments (Abed & Fakhouri).

Palaeozoic phosphorite deposits and occurrences have been identified in recent years from several parts of the world. Major resources have been delineated within the Baltic Phosphorite Basin where, for example, the predominantly lower Tremadoc (basal Ordovician) Rakvere deposits in Estonia contain the equivalent of 400 Mt P (Ilyin & Heinsalu). The Cambrian phosphorites of the Georgina Basin in western Queensland and eastern Northern Territory, Australia, are among the most intensely studied deposits of their type in the world. These have been assigned collectively to the Beetle Creek Formation, which is of Ordian and/or Templetonian (earliest middle Cambrian) age. The carbonate-siltstone-chert phosphatic facies bordering the Georgina, as well as the Wiso and Daly River basins is similarly mainly of Ordian age (Howard). In addition to the 18 or so deposits delineated within the Georgina Basin over a distance of approximately 1000 km, borehole logging together with modelling of aeromagnetic data has led to the discovery of two new phosphorite areas: the Lady Judith in the Wiso Basin, which rests on volcanics and interdigitates with members of the Montejinni Limestone; and the Ammaroo deposit, in the southwestern part of the Georgina Basin, which occurs within a depression bounded by limestones of the Arthur Creek Formation.

Among the most notable achievements of Project 156 is the recognition of the Proterozoic-Cambrian as a major phosphogenic episode of global extent, particularly in central and southern Asia. It is noteworthy also that the Precambrian-Cambrian boundary provides the strongest evidence for a close link between major phosphogenic events and important evolutionary changes (Cook *et al.*). In this context, it has been suggested (Brasier) that the phosphogenic events were themselves related to the first widespread appearance of small shell spaces and faecal/dead organic substrates which provided suitable environments for the formation of authigenic phosphate (and glauconite) minerals. Interactions between early Cambrian ecosystems and phosphogenesis are well preserved in South China, where preservation reaches a climax in the Zhongyicun Member (lower Meishucunian Stage, basal Cambrian). In India, Proterozoic basins offer the most important phosphate exploration potential and several outstanding phosphate discoveries have been made since the mid-1960s (Choudhuri). The Proterozoic phosphorite-bearing sequences of the three main areas around Udaipur, Jhabua, and Hirapur-Lalitpur all lie on Archaean basement and comprise essentially a basal quartzite member succeeded by phosphorite-carbonate sequences. The Jhamarkotra deposit near Udaipur, in Rajasthan, is now a major source of phosphate rock in India.

Major palaeoceanographic changes occurred during the Late Proterozoic, with the temporary development of a stagnant oceanic regime (Donnelly *et al.*). Enhanced burial of organic matter must have caused significant increases in atmospheric oxygen, which may have stimulated the evolution of new metazoan groups. Increased rates of oceanic turnover during the earliest Cambrian would have caused the influx of P-rich, deep-ocean waters into epicontinental seas, thereby promoting a phosphogenic event. Oxidation associated with the development of better mixed oceans would have caused an increase in atmospheric CO₂, which may have been an additional factor in promoting the appearance of mineralized skeletons in many fossil groups.

Important insights into prevailing depositional conditions during the formation of Proterozoic phosphorites are provided by their almost ubiquitous association with stromatolites. Probably the best known examples of stromatolitic phosphorites in the world are those found near Udaipur, where they exhibit both carbonate (mainly dolomite) and phosphate (francolite) mineralogies. It has been proposed (Sisodia & Chauhan) that the differences in mineralogy were caused by

differences in the Mg contents of the primary sediments, which reflected varying depositional environments. The high Mg content of intertidal stromatolites may have prevented extensive phosphatization in this facies.

It may be concluded that our understanding of the origin, nature, and distribution of phosphorites has progressed considerably in recent years. Nevertheless, it is evident also that many problems remain unresolved and that phosphorites will continue to provide a fascinating and fruitful field of scientific research for many years to come.

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Acknowledgements

We would like to acknowledge the generous support of the Geological Society of London and the Royal Society, and also of Albright & Wilson Ltd, the British Sulphur Corporation Ltd, and the International Fertilizer Industry Association, Paris. Following four days of plenary sessions at Oxford, there were two three-day field trips: to the Cretaceous phosphorites of southern England, led by Dr Ian Jarvis, Kingston Polytechnic, and to the Cretaceous phosphorites of northern France and Belgium, led by Drs Francis Robaszynski, Faculté Polytechnique de Mons, and Gérard Sustrac, Bureau de Recherches Géologiques et Minières, Orleans. In this context, the logistical support of these three research establishments is also gratefully acknowledged.

We are greatly indebted to the 43 contributors for their collaboration, and to the following for their assistance in producing this volume: Shimshon Axelrod, James B. Cathcart, Robert E. Garrison, Christopher V. Jeans, Hugh C. Jenkyns, William J. Kennedy, James R. Lehr, James F. Marshall, H. Martyn Pedley, Terence G. Powell, Liliane Prévôt, Adrian W. A. Rushton, Mark W. Sandstrom, Richard P. Sheldon, Graham B. Shimmiel, Maurice Slansky, John Thomson, and Jean Trichet. Finally, the considerable efforts of Angharad Hills and other staff of the Geological Society Publishing House, Bath, are much appreciated.

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London
January 1990

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Phosphorite research: a historical overview

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Abstract: The nature and origin of phosphorites have been a matter of much speculation since were they first discovered more than 150 years ago. They are also of wide scientific interest in that they provide evidence of past changes in the biology and chemistry of the world's oceans.

In the past ten years or so, due to a considerable extent to the efforts of the many participants in IGCP Project 156, our knowledge and understanding of phosphorites has increased enormously: it is now evident that there were times in earth history when phosphorites were preferentially deposited in many parts of the world. This probably was the consequence of the interaction of a number of factors including oceanography, changes of sea-level, and plate tectonics. Perhaps one of the most intriguing features to have become apparent in recent years is the link between times of phosphogenesis and periods of major evolutionary change. Not only has our knowledge of ancient deposits increased but much information now exists on present-day deposits, such as those off Chile-Peru and the more enigmatic deposits off southern Australia. In addition, there are better data and a greater understanding of some of the details of phosphorite formation and phosphate hardgrounds, on the role of bacteria in phosphogenesis, and on the petrology, mineralogy, geochemistry and biology of phosphorites.

Whilst a great deal has been achieved in the past 10 years, there still remains much to be done: there is scope for grass-root phosphate exploration in countries presently lacking their own sources of phosphate; the nature of the relationship between phosphate and some diagenetic minerals such as zeolites has yet to be elucidated; similarly the link between phosphogenesis and the formation of petroleum source rocks needs to be better understood and much more work is required on Precambrian phosphorites.