

# Discussions and conclusions

Objektyp: **Chapter**

Zeitschrift: **Eclogae Geologicae Helvetiae**

Band (Jahr): **87 (1994)**

Heft 3: **Concepts and controversies in phosphogenesis : proceedings of the symposium and workshop held on 6-10 September 1993**

PDF erstellt am: **18.09.2024**

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## Discussion and conclusions

As a broad generalisation, there is a correspondence between those trace elements which are enriched in seawater and/or marine organic matter (Tooms et al. 1969; Prévôt & Lucas 1979; Piper 1994), and those occurring at high levels in phosphorites. This relationship is not unexpected given the open-marine depositional setting of most deposits, and the inherent involvement of organic matter and bacterial processes in their formation. Levels of enrichments are controlled not only by the crystallographic properties of francolite and kinetic factors, but also by ambient geochemical conditions (Eh, pH, alkalinity) during precipitation, and may be modified substantially by late diagenetic, metamorphic and weathering effects. Moreover, phosphorites contain complex admixtures of other inorganic and organic constituents, and these may additionally host high proportions of trace elements. Consequently, there is commonly no simple correlation between the most enriched elements and P even within a single deposit, and different deposits will have different characteristics that relate to their unique geological histories.

Difficulties in apportioning trace-elements to particular phases are partly a consequence of sampling constraints. Phosphorites are by their very nature highly inhomogeneous at all scales, from the dissemination of phosphatic grains or nodules in a bed of siliciclastic and/or carbonate sediment, through the intimate association of  $\mu\text{m}$ -scale francolite crystallites with other authigenic and detrital particles and organic matter, down to geochemical variation on the surfaces of and within individual crystals. Most of our current knowledge concerning trace-element distributions in phosphorites originates from a relatively limited range of bulk-rock analyses. Only a few deposits, such as the Middle Cambrian Georgina Basin deposits of northern Australia (Cook 1972; Howard & Hough 1979), Permian Phosphoria Formation of the US (Gulbrandsen 1966, 1975; McKelvey et al. 1986; Piper & Medrano 1994), and Cretaceous-Eocene deposits of Morocco (Prévôt & Lucas 1985; Prévôt 1990) are well characterised. Additional high quality multi-element data sets for geologically and stratigraphically well-constrained sample sets are needed to complement these data, while the greater use of physical and chemical separation techniques would add significantly to our knowledge of trace-element partitioning in different sediment components.

Major advances require new approaches. The use of high resolution imaging techniques, including backscattered scanning electron microscopy, combined with sensitive microanalytical methods (see Potts et al. 1993a for a recent review) such as the ion microprobe, synchrotron X-ray fluorescence microprobe, laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS), particle-induced X-ray emission or LA-gas source-MS analysis, have enormous potential to determine inter-elemental and isotopic relationships on a single-crystal scale. Such work is in its infancy, but is already having an impact on the field (Grandjean & Albarède 1989; Jarvis & Jarvis 1991; Grandjean-Lécuyer et al. 1993). An ability to determine the geochemical composition of separate phases and to study compositional variation within individual grains and crystals is essential to improve our understanding of the processes which lead to the incorporation of trace elements in phosphorites. It should be stressed that this work must be integrated with established field, petrographic and geochemical techniques if interpretations of the information obtained are to be soundly based.

Experimental data concerning the kinetics and thermodynamics of trace-element incorporation by francolites is a prerequisite for quantitative modelling. Further experimental work, together with mathematical modelling of natural and artificial systems, are essential if the transition is to be made from empirical to theoretical studies of phosphogenesis. However, the complexities of natural phosphogenic environments should not be underestimated. It is also important to make the point that there remains a limit to which present-day phosphorites may be used as analogues for the genesis of ancient deposits. The most notable difference is that most major phosphorites are granular while modern phosphorites are dominantly nodular. Recent studies have demonstrated that granular phosphorites are forming in modern settings and that phosphorite hardgrounds are more widespread in both the modern and ancient than previously realised (Glenn et al. 1994a, b). Nonetheless, there remains no known exact analogue for the phosphorite 'giants' of the geological record. The basic physical-chemical processes which control the precipitation of francolite and the genesis of phosphorites must have been the same in the past as they are at the present day, and there is no doubt that we have learnt much about these from our studies of modern sediments. Nonetheless, there remains the fundamental questions as to why ancient deposits are so different and what are the environmental factors that these differences reflect?

Over the last two decades, geochemical and particularly isotopic studies have led to major advances in our understanding of the genesis and diagenesis of phosphorites, but many problems remain unsolved. What is the precursor mineral to francolite in modern environments? When and how are specific trace elements incorporated in phosphorites, where are they located and what was their source? Are humic compounds or other organic complexes instrumental in these processes? To what extent do kinetic and thermodynamic factors control trace-element contents? Are trace-elements good redox indicators? Are weathering and metamorphic effects kinetically controlled; is long term-burial at modest depths equivalent to short periods of deep burial?

To answer these questions, traditional geological analyses of ancient and modern phosphorites will have to be complemented by: (1) new analytical methods to empirically determine the distribution and behaviour of trace elements and isotopes in phosphorites; (2) better integration of inorganic and organic geochemical studies; (3) multi-element and multi-phase studies to examine the relationship between francolite geochemistry and those of associated mineral phases; (4) more extensive data on the porewater and solid-phase geochemistry of modern phosphogenic and associated non-phosphogenic environments; (5) experimental work to determine the kinetic and thermodynamic factors which control apatite precipitation and the incorporation of trace elements in francolite; (6) more refined modelling of natural and experimentally derived data.

Results from these geochemical studies will continue to provide one of the best means of refining models of phosphogenesis. An understanding of geochemical processes is essential to assessing and ameliorating the environmental impact of phosphate rock extraction and processing and the use of phosphate fertilisers.

### Acknowledgements

This paper is based partly on presentations made at the IGCP 325 International Symposium & Workshop, *Concepts and Controversies in Phosphogenesis*, held in Matten, Switzerland, 6–10 September 1993. The authors wish to thank Karl Föllmi (ETH Zurich), other members of the organising committee, and the sponsors, for their