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Organic-inorganic interactions during phosphogenesis in the Western Central Paratethys (Late Eocene, Austrian Molasse basin)

Organisch-Anorganische Wechselwirkungen während der Phosphogenese in der westlichen Zentral-Paratethys (spätes Eozän, österreichisches Molassebecken)

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Abstract

Distinct intervals of phosphate rock occur in the lower part of the organic-rich Schöneck Formation (Late Eocene to Early Oligocene) in the Austrian Molasse Basin. These intervals were studied in four wells which represent an upper paleo-slope position at the northern basin margin. It is the aim to study the textural appearance of the phosphate rocks, and to retrace the influence of organic matter and organic-inorganic interactions during diagenesis on the formation of sedimentary apatite.

Dysoxia, primary productivity and bioturbation favoured phosphate formation in the form of predominantly authochthonous nodules and layers (microsphorite), and reworking by bottom water currents occurred to a minor degree. Phosphogenesis was controlled by intense bacterial consumption of marine, consumable organic material, and favoured by less intense sulphate reduction. Intervals with phosphates containing low amounts of pyrite were subsequently overprinted by intense precipitation of authigenic calcite and Fe-dolomite during methanogenesis. This diagenetic process was coupled to a significant conversion of marine organic material. An increase in bottom water anoxia and carbonate sedimentation rate inhibited further phosphogenesis.

$\delta^{13}C_{org}$ values as low as –26.4 ‰ and $\delta^{15}N_{org}$ values as low as –0.1 ‰ in phosphate-bearing intervals are evidence for the presence of refractory terrigenous organic material. Furthermore, the exclusive presence of retenes and arborenes, biomarkers for terrigenous organic matter, within a phosphate nodule indicates that predominantly labile marine organic matter was consumed by bacteria. Conversion of organic matter led to the release of reactive dissolved phosphor species and subsequent precipitation of apatite. Moreover, the predominance of terrigenous organic matter in phosphate-bearing rock may have limited the crystallization process which resulted in small and cryptocrystalline apatite aggregates.

Zusammenfassung

Im österreichischen Molassebecken treten in der organisch-reichen Schöneck Formation (spates Eozän bis unteres Oligozän) Horizonte mit Phosphatkonkretionen und –lagen auf. Die phosphatführenden und zwischengeschalteten Lagen wurden in vier Bohrungen untersucht, deren Lage paläogeographisch dem oberen Nordhang zuzuordnen sind. Es ist das Ziel der vorliegenden Arbeit, die Texturen der phosphathaltigen Gesteine zu untersuchen und den Einfluss des organischen Materials, seiner Umwandlung und gekoppelte organisch-anorganische Wechselwirkungen während der abgelaufenen Diagenese aufzulösen, die zur Fällung des sedimentären Apatits führten.

Die sedimentären Phosphate (petrogr. „Microsphorit“) treten vorwiegend als autochthone Konkretionen und Lagen auf; Aufarbeitung wurde selten beobachtet. Die Phosphatfällung wurde durch dysoxisches Bodenwasser, hohe Primärproduktion, und geringe Bioturbation ermöglicht. Ein wichtiger Steuerungsmechanismus für die Intensität der Phosphogenese war der Grad der bakteriellen Umsetzung von metabolisierbarem, marinen organischen Material, der durch verminderte Sulfatreduktion gefördert wurde. Phosphat-haltige Intervalle führen wenig Pyrit, erfuhren aber eine markante Fällung von authigenem Calcit und Fe-Dolomit während der Methanogenese. Während dieser Diageneseprozesse wurde metabolisierbares, marines organisches Material intensiv abgebaut. Die

Fällung sedimentären Apatits wurde durch die Entwicklung eines anoxischen Bodenwassers und zunehmende Karbonatsedimentation beendet.

Niedrige $\delta^{13}C$- Werte von bis –26,4 ‰ und $\delta^{15}N$-Werte von bis zu –0,1 ‰ des organischen Materials der Umgebungssedimente zeigen charakteristische Signaturen terrigenen organischen Materials und belegen, dass dieser Teil des organischen Materials weniger stark metabolisiert wurde. Im Unterschied zu den Zwischenlagen konnten Retene und Arborene ausschliesslich in einer Phosphatkonkretion nachgewiesen werden. Deren ausschließliches Auftreten in der Phosphatkonkretion belegt, daß terrigenes organisches Material im Rahmen organisch-anorganischer Wechselwirkungen wenig abgebaut wurde und daß das Auftreten des terrigenen organischen Materials möglicherweise die Fällungsprozesse nur sehr kleiner und kryptokristalliner Apatitaggregate steuerte.

1. Introduction

Phosphorites have been found worldwide in numerous geological formations, but their formation is rather a rare phenomenon than an abundant process. On the other hand, phosphogenesis is an ubiquitous process and known from sediments in many aquatic systems. Besides frequent descriptions from upwelling areas (e.g. Garrison & Kastner, 1990; Purnachandra Rao & Lamboy, 1995), this early diagenetic process also occurs in deltaic settings (Ruttenberg & Berner, 1993), on shallow continental margins (Kim et al., 1999) and along continental slopes underlying low productivity areas (Ruttenberg & Berner, 1993), in the deep-sea (Bernoulli & Gunzenhauser, 2001) as well as in lacustrine environments (Stamatakis & Koukouzas, 2001).

The term *phosphogenesis* summarizes all processes of precipitation/mineralization of sedimentary apatite which leads to the development of pristine (orthochemical, in-situ) phosphate fabrics. On the other hand, the term phosphorite genesis is referred to all subsequent sedimentary processes which result in the formation of allochemical phosphorites (e.g. winnowing, reworking and sediment transport; Trappe, 1998).

Single factors controlling the multi-parameter process phosphogenesis in aquatic systems have been resolved. Very low sedimentation rates and/or current activities as external factors play important roles in phosphogenesis prolongating phosphate precipitation at critical shallow burial levels (Glenn et al., 1994). In the sedimentary column phosphate concentrations in the porewater can increase significantly by conversion of organic matter, dissolution of biogenic apatite in fish debris, and reduction of Fe-oxyhydroxides (Froelich et al., 1988; Suess, 1981; Van Cappellen & Berner, 1988). The later "iron-pumping model" (summarized in Jarvis et al., 1994) offers an explanation for the complex genetic relationship between Fe and P. However, the processes and mechanisms initiating these events may widely vary in different environments.

The stratigraphical and facies association of phosphorus and organic carbon-rich rocks is widely recognized in the geological column (Krajewski et al., 1994). However, the quality not the quantity of the organic material plays the dominant role in phosphogenesis in the marine realm (Trappe, 1998 and references herein). The type and reactivity of organic matter that reaches the bottom sediments control the phosphorus removal from biological recycling and, thus, storage and concentration in porewater or water layers, and finally apatite precipitation. Thus, the efficiency of bacterial utilization of sedimentary organic matter controls phosphogenesis (Föllmi, 1996; Glenn et al., 1994) and is highlighted by the occurrence of sedimentary phosphates in young organic-lean sediments off the coast of East Australia (Heggie et al, 1990; O'Brien et al, 1990). Moreover, dissolved sea-water phosphate represents an additional source which may become important in the formation of phosphatic hardgrounds (Föllmi, 1996).

Multi-proxy data of organic material (e.g. organic carbon content, hydrogen index, etc.) in modern to subrecent phosphates and the host sediments highlight the role of early diagenesis of organic matter during phosphogenesis (e.g. Schuffert et al., 1998). Studies on the organic matter of ancient phosphorites and host sediments from marine environments show benthic microbial degradation and oxidation as prominent processes which affect the organic material during phosphogenesis. These processes prevail intensely in highly condensed horizons. The organic material was identified as being derived from planktonic algae, to a lesser degree from land plant material, but significantly again from bacterial communities (sulphate reducing, anaerobic photosynthesizing or methanogenic bacteria). Furthermore, humified organic matter seems to favour the formation of organo-mineral aggregates by adsorption on the surface of minute preexisting apatite particles. On the other hand, humic acids inhibit mineral crystallization leading to poorly crystalline organo-mineral aggregates (summarized in Krajewski et al, 1994 and references herein).

The Schöneck Formation is a proven hydrocarbon source rock for oil and gas fields in Bavaria and Upper Austria. The sediments were deposited on the northern slope of the Austrian Molasse Basin during the Eocene-Oligocene transition. In the framework of a paleoceanographic study about the Schöneck Formation phosphates