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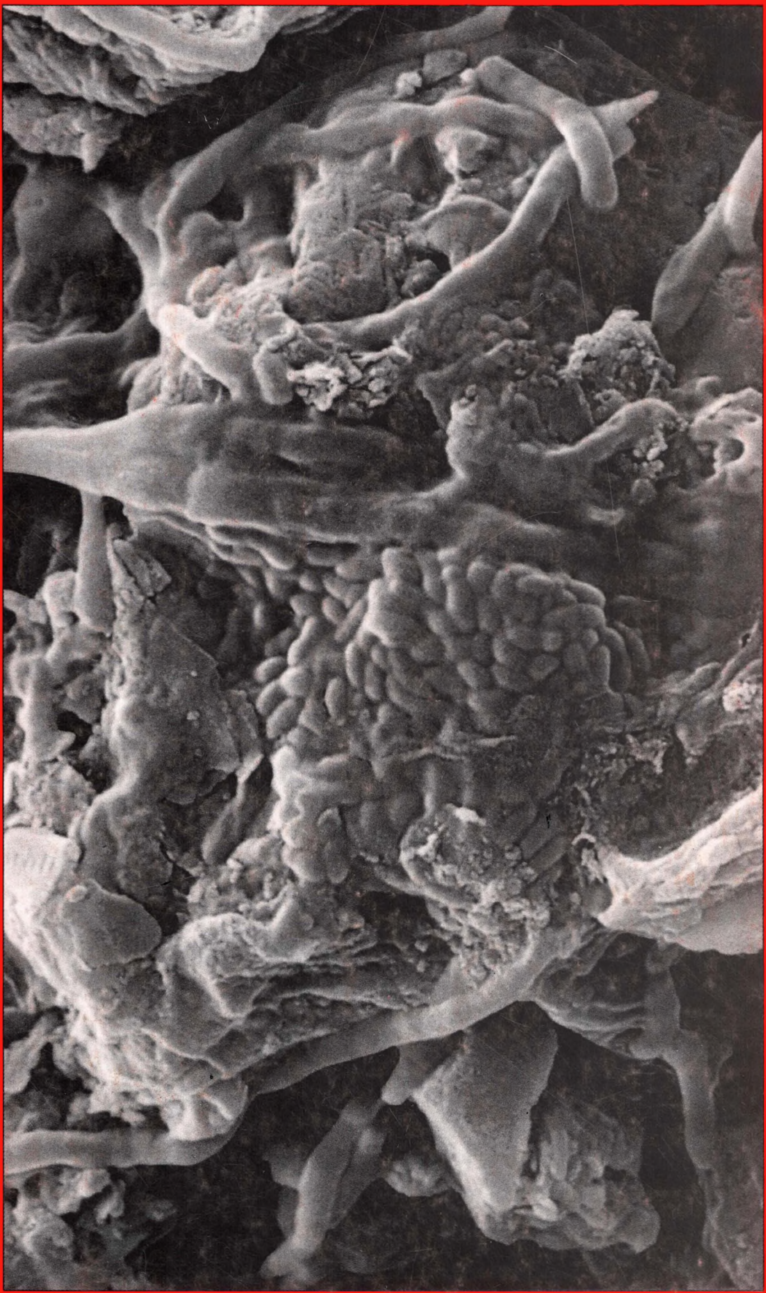

Michael Schmitz &
Karin Ernst (Eds)

Microorganisms, Facies Analysis and Fossil Diagenesis

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Aptian and Albian Phosphorites of Northwestern Germany (With Emphasis on the Biogenic Aspects of Phosphorite Formation)

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Zusammenfassung

Phosphate und Phosphorit-Vorkommen im Ober-Apt und Alb des Niedersächsischen Beckens (Raum Hannover-Braunschweig-Goslar-Alfeld) wurden durch Beobachtungen im Gelände und mikropaläontologische Analysen sowie mit Hilfe von Dünnschliffen (z.T. im Phasenkontrast), Autoradiographien, Rasterelektronenmikroskopie, Röntgenfluoreszenz und Röntgendiffraktometrie untersucht. Man kann zwischen Beckenphosphoriten (Vöhrum, Mittellandkanal Mehrum-Schwicheldt, Stedum und Sarstedt) und Marginalphosphoriten (Morgenstern und Georg Friedrich Tagebaue, Alfeld) unterscheiden. Die Marginalphosphorite zeigen höhere Sand- und beachtliche Glaukonitgehalte. Die beiden häufigsten Endglieder der Phosphorite sind: (1) weiche, hellfarbene, erdige phosphatreiche Knollen und (2) harte, dunklerfarbene, meist konzentrisch gebaute karbonat- und phosphatführende Konkretionen. Untergeordnet tritt Phosphorit auch als Steinkern in Wohnkammern von Ammoniten und als faust- und stabförmige Konkretionen auf. Meist sind Tone und Mergel das Nebengestein.

Hauptminerale der Phosphorite sind zu wechselnden Anteilen: Karbonat-Fluor-Apatit, Siderit und Mangankarbonate; nur untergeordnet treten Calcit und silikatische Minerale (Quarz, Feldspat und Tonminerale) hinzu. Der Kristallisationsgrad von Apatit ist gering. Globularstruktur der winzigen Phosphatpartikel (1-3 µm) – vermutlich unter biogener Mitwirkung entstanden – ist verbreitet in den weichen erdigen phosphatreichen Knollen. Die meisten Phosphorite zeigen intensive Durchwühlung. Vielfach führen sie auch Kotpillen unterschiedlicher Korngröße. Biogene Komponenten sind vor allem Mikrofossilien (Kleinforaminiferen und Radiolarien) sowie kieselige Schwammrelikte zu wechselnden Anteilen. Chemische Analysen auf Haupt- und Spurenelemente von ausgesuchten Phosphoritproben werden diskutiert. Die autochthonen Beckenphosphorite entstanden „in situ". Mechanisch aufgearbeitete allochthone Phosphorite, wie sie später in der Oberkreide des Niedersächsischen Beckens verbreitet sind, finden sich nur an der südlichen Peripherie des Beckens.

Apt und Alb waren eine Zeit tektonischer Unruhe. Sedimentationsunterbrechungen sind häufig. Es fehlt aber an Hinweisen, daß die autochthonen Phosphoritkonkretionen mit Sedimentationsunterbrechungen in Zusammenhang stehen oder nur auf anoxische „Schwarzschiefer" beschränkt sind. Vielmehr scheint eine Zunahme des "seafloor spreading" der übergeordnete Kontrollfaktor auch bei der Bildung der Phosphoritkonkretionen zu sein. "Seafloor spreading" war begleitet von aktiver Tektonik, einer Zunahme von Vulkanismus und bedeutenden Änderungen der orographischen Systeme. In diesem Zusammenhang muß auch die früher vorgetragene Hypothese der Phosphoritbildung durch Auftrieb von kaltem Tiefenwasser (upwelling) aus dem N, die durch die Assoziation mit SiO_2-reichen Sedimenten und Kaltwasserfaunen gestützt wird, gesehen werden.

Abstract

Phosphate and phosphorite, mainly of Upper Aptian and Albian age, from the Lower Saxony Basin (Hannover-Braunschweig-Goslar-Alfeld area) were investigated. The analytical work included megascopic inspection of the sediments in the field, micropaleontological analysis, thin-section examination (in some cases using phase-contrast microscopy), autoradiographs, scanning electron microscopy (SEM), X-ray fluorescence analysis (XRF), and X-ray diffractometry (XRD). Phosphorites from the central part of the basin (Vöhrum, Mittelland Canal, Stedum, and Sarstedt) contrast with phosphorites at the southern margin of the basin (Morgenstern and Georg Friedrich open-pit mines, Alfeld). The marginal phosphorites have a higher content of sand and a considerable proportion of glauconite. The two most common types of phosphorite are characterized as follows: soft, pale-colored, earthy nodules rich in phosphate, and hard, dark-colored, mostly concentric carbonate and phosphate-bearing concretions. Phosphorite also occurs as internal casts of ammonite chambers and as fist- and rod-shaped concretions. The host sediments are mainly clays and marls, and rarely sandstones.

The primary minerals of the phosphorites in varying proportions are: carbonate-fluorine apatite, siderite, manganese carbonate, calcite and silicate minerals (quartz, feldspar and clay minerals). The apatite is poorly crystallized. Tiny phosphate particles with globular structure (1-3 µm), presumably formed by biogenic activity, are common in the earthy nodules. The phosphorites show intense bioturbation and are often composed of fecal pellets of differing size. The biogenic components are mainly microfossils (foraminifera and radiolarians) and sponge remains in varying proportions. The major and trace element compositions of selected samples are discussed. The phosphorites in the central part of the basin are autochthonous. Allochthonous reworked phosphorites, which become common in the Upper Cretaceous of the Lower Saxony Basin, are only found at the southern periphery of the basin.

The Aptian / Albian was a time of tectonic unrest. Breaks in sedimentation are numerous. There is no evidence that the autochthonous phosphorite concretions are associated with breaks in sedimentation or with anoxic black shales only.

Mid-Cretaceous phosphorite deposition – a climax of autochthonous phosphorite formation in earth history – is explained by increased seafloor spreading as the main controlling factor. The seafloor spreading has been associated with active tectonism, increase in volcanic activity, and changes of orographic systems. In this context the hypothesis of cold-deep-water upwelling from the north has to be seen. The upwelling hypothesis is supported by the association of the phosphorites with sediments rich in SiO_2 and with sediments containing cold-water faunas.

Contents

1. Introduction

Phosphate precipitation and phosphorite formation have been investigated in many countries during the past two decades. The Cretaceous phosphorites in northwestern Germany, however, remained unknown in international English literature, because most of the work was published in German (ZIMMERLE 1982; ZIMMERLE & EMEIS 1983; KELLER et al. 1989). Brief summaries in English on the phosphorite occurrence in Germany exist though (PAPROTH & ZIMMERLE 1980). Thus, this compilation is aimed at presenting a condensed English version of previous work and current observations.

The study of sedimentary phosphate and phosphorites deserves renewed attention for the following reasons:

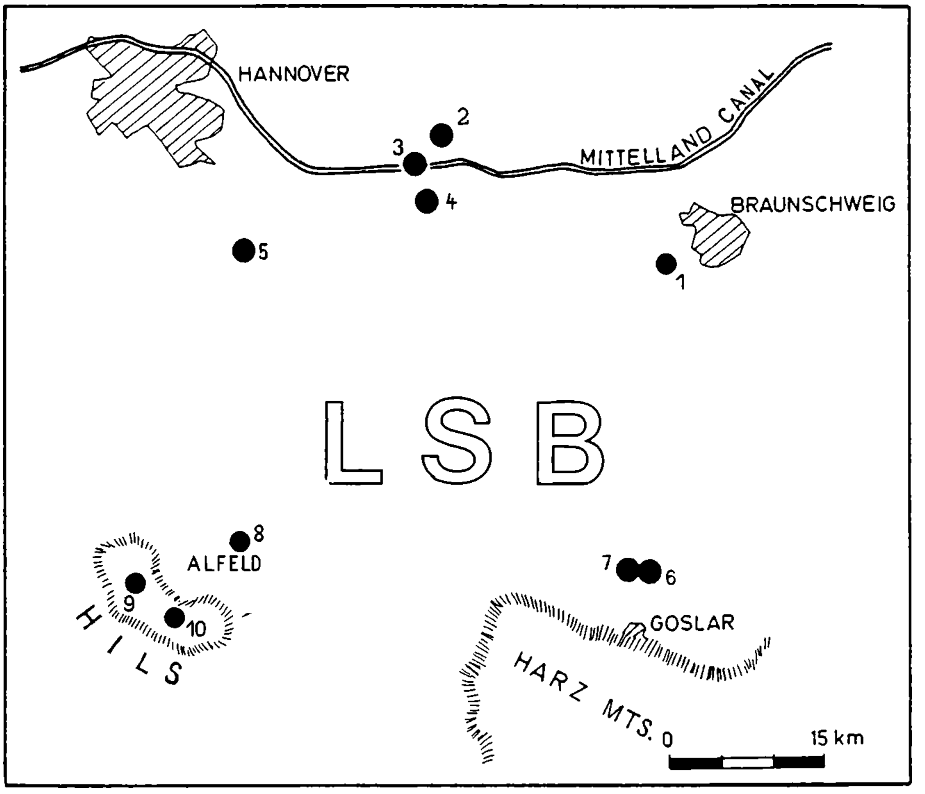
- The knowledge of the occurrence and distribution of sedimentary phosphate and phosphorite supplements environmental analysis (e.g. BENTOR 1980; BATURIN 1982) and studies of early diagenesis (e.g. NÖLTNER 1988).
- Phosphate gains increasing importance as fossilizing agent preserving every detail of fossils, in faunas as old as Cambrian (ALLISON 1988; MAISEY 1991; DONOVAN 1991; MÜLLER & WALOSSEK 1991). Some extraordinary fossils are a source of preserved biomolecules.
- Accumulations of phosphorites will also be of economic interest not only as fertilizers but also as source for exotic elements, e.g. rare earth elements which are concentrated in phosphorites (WOLF & CHILINGARIAN 1988: 335), likely to various extents according to the age, type and diagenesis of phosphorites.
- The factors controlling phosphorite formation are being intensely studied, but still not completely known. Monocausal explanations, such as the concentration of sedimentary phosphorus by upwelling only, stand against polycausal explanations. In the past years, new models of phosphorite formation were searched for and proposed (BÜHMANN et al. 1989; BALSON 1990; FÖLLMI & GARRISON 1991).

2. The geological setting of the Lower Saxony Basin

The relatively small Lower Saxony Basin (length 280 km, average width 80 km) was separated from the Cretaceous North Sea by the mainly submarine Pompeckian Rise. During the Aptian and Albian, however, it did not act as a barrier. Thus, the basin can be regarded as the southern part of the epicontinental North Sea. The Lower Saxony Basin, a marginal trough north of the Rheno-Bohemian landmass, had been subjected to strong subsidence. The water depth is estimated to have been several hundred meters. This trough is characterized by high to abnormally high sedimentation rates (particularly thick sequences). The thickness of the Clansayesian, for example, is 150 m. The Upper Aptian/Lower Albian (especially Clansayesian) is composed of dark clays and marls in the eastern part of the Lower Saxony Basin. Recently, two sections have been examined in detail (Text Fig. 1): (1) a section along the Mittelland Canal between Mehrum and Schwicheldt (basin center) = No. 3 in text Fig. 1 and (2) that of the Sarstedt clay pit (southern margin of the central basin) (KEMPER 1982). Plenty of material has been supplied from the landmass to the south. Most of the organic matter is of terrigenous origin (mainly type III kerogen), too.

Three facies belts (Text Fig. 9) can be observed (KEMPER 1982; KEMPER & ZIMMERLE 1983): Belt 1 near the edge of the basin with glauconitic pelites containing phosphorite nodules and giant ammonites.

Fig. 1: Location of Upper Aptian/Lower Albian phosphorites studied (based on and modified from GEORGI 1976; KEMPER 1982; ZIMMERLE 1982; KOLBE et al. 1985; KELLER et al. 1989).
LSB = Lower Saxony Basin
Legend:
1 = Konrad 1 Mine shaft,
2 = Vöhrum clay pit,
3 = Mittelland Canal (Mehrum-Schwicheldt),
4 = Stedum clay pit,
5 = Sarstedt clay pit (Otto Gott),
6 = Morgenstern open-pit mine (abandoned),
7 = Georg-Friedrich open-pit mine (abandoned) (Revier Eisenkuhle),
8 = Alfeld section,
9 = Grünenplan,
10 = Kaierde.



Belt 2 with a biosiliceous facies. Two subtypes can be distinguished: firstly, black smectitic clays rich in diatoms and radiolarians, containing elevated amounts of organic material and lacking ammonites and the bivalve genus *Aucellina* and secondly, a variegated marl facies comparable with the "Flammenmergel" facies. This marl facies is characterized by siliceous sponges and authigenic clinoptilolite. In belt 3, precipitation of phosphorite in the form of internal moulds of comparatively small mother-of-pearl ammonites and carbonate phosphorite nodules occur. Kutnahorite is a characteristic mineral component. Epibiontic suspension feeders are abundant in the macrofauna and agglutinated foraminifera and the calcareous genus *Epistomina* in the microfauna. The plankton, especially radiolarians, diatoms, calcareous dinoflagellate cysts, and coccoliths, were important for the analysis of the environment. Other fossil groups include ostracods, foraminifera, porifers, gastropods, ammonites, and bivalves of the genus *Aucellina*.

The facies distribution in narrow belts indicates that deposition took place under cold coastal upwelling conditions. Diagnostic features are the appearance of abundant diatoms combined with elevated C_{org} values in belt 2, in addition to other phenomena such as partial solution of coccoliths etc. The upwelling of nutrient-rich deep water into the euphotic zone led to an enormous production of microorganisms. A specific model of cold-water upwelling was established: a cool epicontinental sea in a humid climatic zone with a rich supply of terrigenous material. The deep water was most probably supplied from the north through the Central Graben of the North Sea. North of the Rheno-Bohemian landmass, a greensand belt developed extending from southern England to Poland. The widespread Aptian and Albian dark pelites represent the basinward equivalent of the greensand. Cold water masses are indicated by the occurrence of diatoms, calcareous dinoflagellate cysts, coccoliths, and arenaceous foraminifera. The profuse appearance and diversification of diatoms and planktonic foraminifera point to pelagic conditions at the beginning of the Aptian (extensive epicontinental seas).

The Aptian/Albian was a time of tectonic unrest. Breaks in sedimentation are numerous. A new era of earth history – the oceanic era – commenced. This fundamental "modernization" of the marine biosphere was associated with catastrophic breaks in the faunal sequence. The Aptian and Albian represent a decisive epoch for the phylogeny of marine organisms. Many faunal groups received a "modern" imprint due to the appearance of new forms. The following endogenetic and exogenetic factors were active (ZIMMERLE 1985): increased rate of seafloor spreading, epeirogenic and tectonic movements accompanied by paroxysmal plutonism and volcanism, change in volume of the ocean basins and in climatic conditions. The complex interplay of environmental factors was the cause of the abnormal bursts of evolution of the marine organisms during this period. Fluctuations of the climate and transgressions played a significant role. Evolution of the fossil groups took place "in bursts induced by environmental influences". Transgressions match with phases of appearance of new species.

Phosphorite formation was common in northwestern Germany during Upper Aptian and Albian times. These phosphorites - and older ones (Jurassic) - were later reworked in the nearby younger Santonian transgression conglomerates. Thus, the gross paleogeographic framework of phosphorite formation is fairly well known. The phosphorites occur in an environment of variegated, occasionally dark-colored pyritic clays and marls which only locally represent incipient anoxic conditions of deposition. The Albian clays and marls show Cu, Zn, and Ni contents characteristic of a shallow marine environment (BROCKAMP 1978). The fauna of the phosphorites is composed of calcareous foraminifera, arenaceous foraminifera, and radiolarians. Bioturbation is common in the nodules as well as in the enclosing clays.

3. The phosphates and phosphorites

Small-scale phosphate mineralization and large-scale phosphorite formation are observed in the dark gray marine clays and marls. Phosphorites have been studied in the Hannover-Braunschweig-Goslar-Alfeld area in detail during the past decades (VINKEN 1977; PAPROTH & ZIMMERLE 1980; ZIMMERLE 1982; ZIMMERLE & EMEIS 1983; KEMPER & ZIMMERLE 1983; PAPROTH et al. 1978; KELLER et al. 1989). The analytical work included megascopic inspection of the sediments in the field, micropaleontological analysis, thin-section examination (in some cases using phase-contrast microscopy), autoradiographs, scanning electron microscopy (SEM), X-ray fluorescence analysis (XRF), and X-ray diffractometry (XRD). The locations of Upper Aptian/Lower Albian phosphorites studied or mentioned in the text are shown in Figure 1.

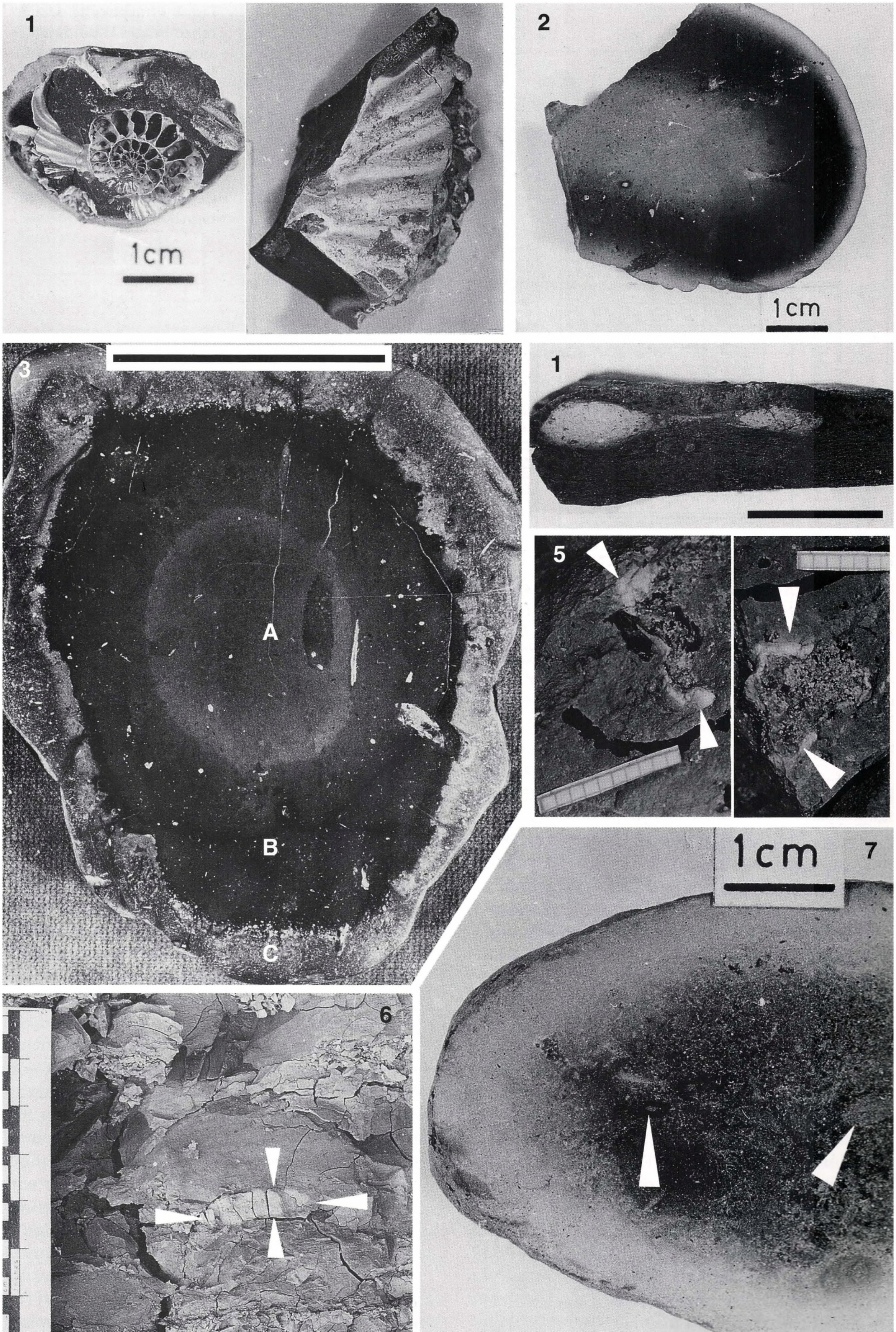
3.1 The macroscopic appearance

Precipitation of phosphates is found in form of diffuse phosphate concentrations, earthy phosphorites, nodular and tubular phosphorites, and elongate phosphorite lenses in variegated, mainly grey clays as well as in form of phosphate cement in nearshore sandstones.

In outcrops, phosphate precipitation is found in thin crusts on sedimentary breaks, e.g. in the Konrad 1 Mine (Text Fig. 3). Phosphate forms internal casts of ammonite chambers at Vöhrum clay pit (Plate 1, Fig. 1) and oval concretions in the Mittelland Canal profile between Mehrum and Schwicheldt (Pl. 1, Fig. 2). Hard zonal carbonate-phosphate concretions of complex composition (Pl. 1, Fig. 3) and soft lenticular kutnahorite nodules coexist in the Stedum clay pit. Diffuse light-colored banding (Pl. 1, Fig. 5) occurs in the basal marl at Sarstedt clay pit as well as in form of soft, friable, pure phosphorite nodules (Pl. 1, Fig. 6). Phosphatization and sideritization of tubular *Thalassinoides*-type burrows and fist-size dwelling cavities (Text Fig. 6 + 7) took place locally (e.g. Vöhrum clay pit).

The most common types of phosphorite accumulations are (1) soft, pale-colored earthy nodules (up to 5 cm in size) that are enriched in phosphorus, and (2) hard, dark-colored carbonate-phosphate concretions (up to 1 m in size), either with concentric structure or with bioturbated internal structure. Transitions between carbonate-phosphate concretions and siderite concretions occur. The host rocks of the phosphorites are clays and marls. Most of the phosphorites preserve bioturbation; they also include fecal pellets of various size. Main biogenic components comprise fragments of macro-

Plate 1: Macroscopic appearance of autochthonous phosphorites.
Fig. 1: Infilled ammonite chambers as phosphorite concretions.
Fig. 2: Oval, zonal phosphorite concretion (F-apatite > 90%, quartz 2%, traces of calcite).
Fig. 1 + 2 Mittelland Canal (Mehrum-Schwicheldt).
Fig. 3: Hard, fist-size carbonate-phosphorite concretion without noticeable bioturbation. XRD mineral composition: nucleus (A): Mn-siderite, siderite, calcite, Mn-calcite, F-apatite, quartz-intermediate zone (B): Calcite, Mn-calcite, F-apatite-siderite clay crust (C): Quartz, F-apatite, traces of siderite and clay. The amount of apatite increases from the nucleus to the crust, that of the carbonate vice versa. Stedum clay pit, coarse concretion horizon. Scale bar 4.5 cm.
Fig. 4: Soft, lenticular earthy kutnahorite nodule. Stedum clay pit. Scale bar 1 cm.
Fig. 5: Pale-colored phosphate clusters (arrows) lining erosional depressions containing coarse-grained sediment (= incipient phosphate concretion?) in the transgressive dark brownish clay at the base of the Middle Aptian (see Text Fig. 2). Black marks from felt-tipped pen. Scales with millimeter division.
Fig. 6: Soft, earthy phosphorite nodule (arrows) enclosed in clay. Scale on left in centimeters, on right in inches. Sarstedt clay pit.
Fig. 7: Compact, oval phosphorite concretion (cut and polished section) displaying coarse pellet structure (arrows) in the dark center. The pale-colored phosphatic crust (± 1 cm thick) contains siliceous sponge spicules and clinoptilolite. The undeformed fecal pellets demonstrate that the synsedimentary to early diagenetic sediment fabric is well preserved in the concretions. Sarstedt clay pit (Sa 10).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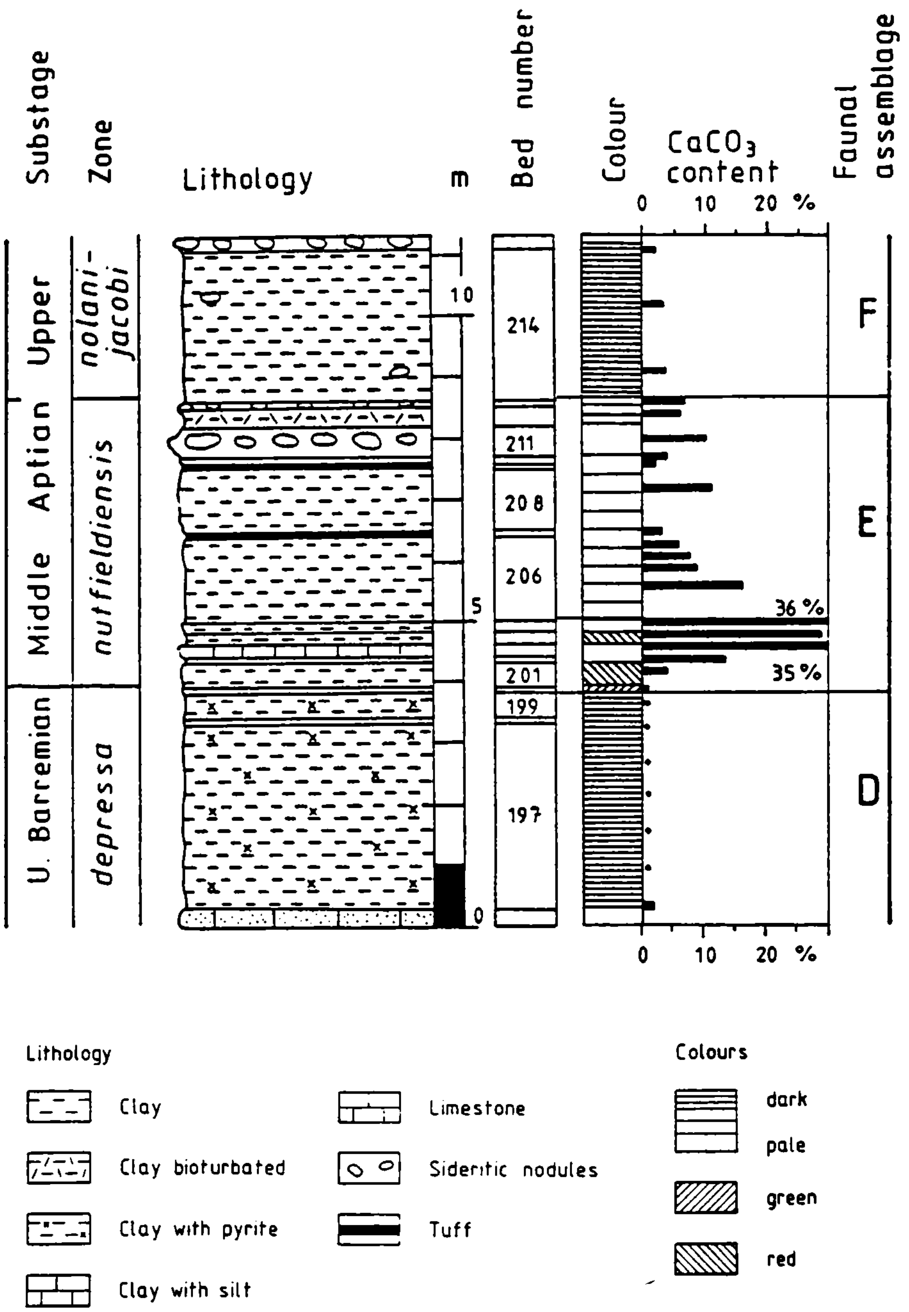


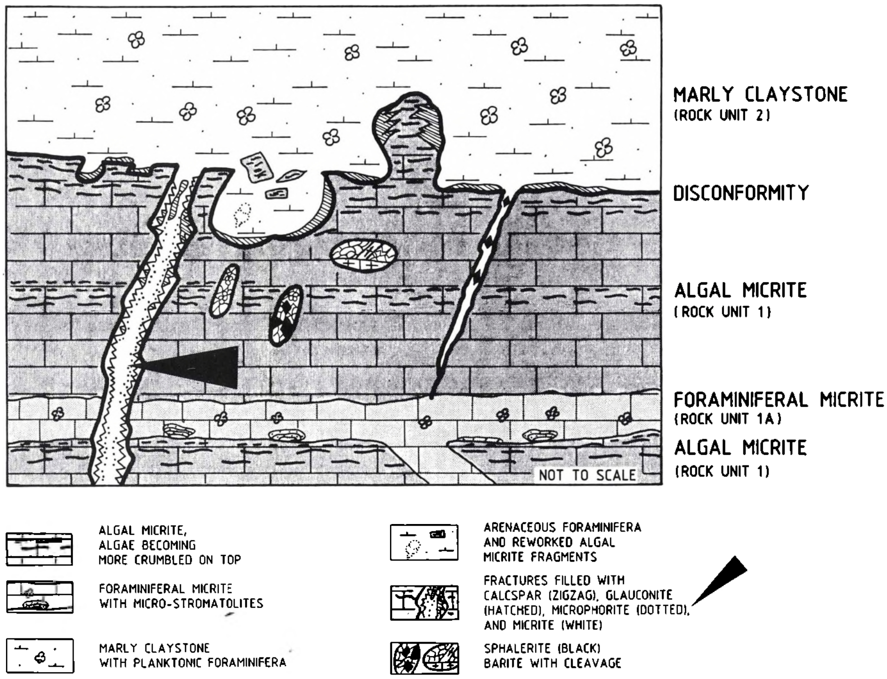
Fig. 2: Phosphorite occurrence in and lithological association of Upper Barremian and Middle to Upper Aptian clays and marls with bed number, color, $CaCO_3$ content and faunal assemblages, Sarstedt clay pit (simplified after MUTTERLOSE 1987: Fig. 2).

fossils, microfossils (planktonic and arenaceous foraminifera and radiolarians) and siliceous sponge particles in varying proportions.

In the basal marl at the Sarstedt clay pit (Text Fig. 2) and in the Konrad 1 Mine (Text Fig. 3) very thin phosphate crusts and patches formed on the ancient seafloor. In the Konrad 1 Mine greenish plastic marls, thin crusts with glauconitization and pyritization as well as with kaolinite, sphalerite, and barite are associated with the syngenetic to early diagenetic phosphate. The phosphorites from the central part of the Lower Saxony Basin (Vöhrum, Mittelland Canal, Stedum, Sarstedt) contrast with those at the southern margin (Morgenstern, Georg Friedrich, Alfeld). The marginal phosphorites are characterized by a higher sand and glauconite content. In the more sandy clay and in the nearshore sandstone facies structureless, cryptocrystalline or colloform phosphate cement occurs together with abundant glauconite (glauconitic phosphorites). All phosphorite concretions in the central portion of the basin have been formed "in situ" (autochthonous phosphorites). At the southern periphery of the basin reworked allochthonous phosphorites (Text Fig. 4) are locally accumulated (Alfeld, Grünenplan).

The various morphological types of small-scale

Fig. 3: Upper Barremian/Upper Aptian disconformity in the Konrad 1 Mine shaft (at 546.40 m) (after KOLBE et al. 1985). Upper Aptian marly claystone overlying Upper Barremian algal micrite. Notice thin microphorite = microcrystalline phosphate coating on left-side fracture (arrow).



phosphate concentrations as well as of large-scale phosphorite concretions are found in the following areas (Text Fig. 1):

Basinal portion
Konrad 1 Mine: thin phosphate coatings on a hardground (Barremian-Aptian disconformity) (Fig. 2).

Vöhrum clay pit: soft, pale-colored earthy phosphorite nodules, hard fist- and rod-shaped carbonate phosphorites (burrows of decapods), and internal casts of ammonite chambers.

Mittelland Canal (Mehrum-Schwicheldt): soft, pale-colored earthy phosphorites, hard carbonate phosphorites, internal casts of ammonite chambers, and diffuse phosphate bands.

Stedum clay pit: soft, pale-colored earthy kutnahorite phosphorite of varying size and shape and hard carbonate phosphorite concretions.

Sarstedt clay pit: soft, pale-colored earthy phosphorite nodules, hard carbonate phosphorites, and diffuse, soft, earthy phosphorite concentrations.

Periphery of the basin
Morgenstern and Georg Friedrich open-pit mines: soft pale-colored phosphorite nodules, rich in glauconite and sand admixture.

Southern shelf area
Alfeld, Grünenplan and Kaierde: autochthonous phosphorite concretions as well as allochthonous, glauconitic phosphorite conglomerates.

In summary, the Aptian and Albian strata of the Lower Saxony Basin contain a wide spectrum of small-scale phosphate and large-scale phosphorite accumulations, with respect to composition, concentration, and shape. Colloform structures and phosphate ooids, however, have not been observed.

3.2 X-ray diffractometer analysis

The first step of analyzing crypto- to microcrystalline phosphates and phosphorites is that by X-ray diffractometry. Main mineral components of the phosphorites are in varying proportions: apatite and siderite. Manganese kutnahorite, siderite, manganous calcite, calcite and dolomite as well as varying minor amounts of silicate minerals (quartz, feldspar) and clay minerals (smectite, kaolinite/chlorite and illite/muscovite) and soft unstable rock fragments are subordinate. Glauconite is sparse in carbonate phosphorites. The apatite is poorly crystallized. The major portion of the primary minerals is crypto- to microcrystalline.

The apatite-group minerals and the carbonate-group minerals, analyzed by X-ray diffractometry, were termed differently by different authors in the course of work and time (K.-H. GAIDA in VINKEN 1977; K.-H. GAIDA & H. RÖSCH in ZIMMERLE 1982; P. STOFFERS in KELLER et al. 1989). In most cases apatite was not specified. Moreover, the manganese carbonates: kutnahorite, manganese siderite and manganous calcite are presumably handled as synonyms or used interchangeably. This has to be kept in mind.

3.3 Microscopic aspects

The wide spectrum of phosphorite morphotypes, briefly reviewed in chapter 3.1, is also reflected in microscopic dimensions when studied in thin sections. Under the polarizing microscope the various kinds of phosphatic material and the admixture of muddy carbonate are mostly crypto- to microcrystalline (< 10 µm). On the other hand, siliciclastic admixtures (quartz, feldspar, and rock fragments), glauconite grains, fecal pellets, and biogenic constituents reach 200 µm in size. Thus, the crypto- to microcrystalline matrix contrasts markedly with the siliciclastic silt and fine-sand admixture as well as the biogenic constituents of siliceous and/or calcareous composition (rarely of phosphatic composition as fish bones and scale).

The matrix is composed either of cryptocrystalline apatite which characteristically appears under crossed nicols almost isotropic, i.e. black, (Pl. 2, Fig. 1) or of a mixture of crypto- to microcrystalline carbonate minerals of varying composition and fluctuating amount. Minor amounts of concealed clay minerals are dispersed. These clay minerals are the only synsedimentary mineral component in the concretions, beside the autochthonous biogenic calcareous constituents. They form the primary framework for the subsequent, penecontemporaneous and early diagenetic neoformation of replacive apatite and carbonate minerals. Fossils such as shell fragments, gastropods, and siliceous sponge spicules rarely occur in the nodules. The microfauna consists of planktonic foraminifera, arenaceous foraminifera, and radiolarians. Coccoliths and nannofossils of uncertain derivation can be recognized under the microscope likewise. Part of the original clay matrix, some of the calcareous microfossils, and larger fossil fragments of siliceous or calcareous composition are partially or completely replaced by phosphatic matter; in the hard carbonate phosphorites by microcrystalline siderite, especially the bacteria (Pl. 2, Fig. 2; Pl. 3, Fig. 5) and by other carbonate phases. Detrital quartz and feldspar grains are replaced by cryptocrystalline phosphate only locally.

The carbonate minerals are the main lithifying component which lead to the consolidation and compact appearance of the carbonate phosphorites. The carbonate minerals – according to XRD analysis: siderite, kutnahorite, other manganese carbonate minerals, dolomite and calcite – are characterized by different crystal habits (skalenohedral, rhomb-shaped and anhedral), which were not examined in further detail yet. In contrast to the basinal phosphorites, the marginal phosphorites are characterized by replacive sparry calcite, not by siderite or manganous calcite.

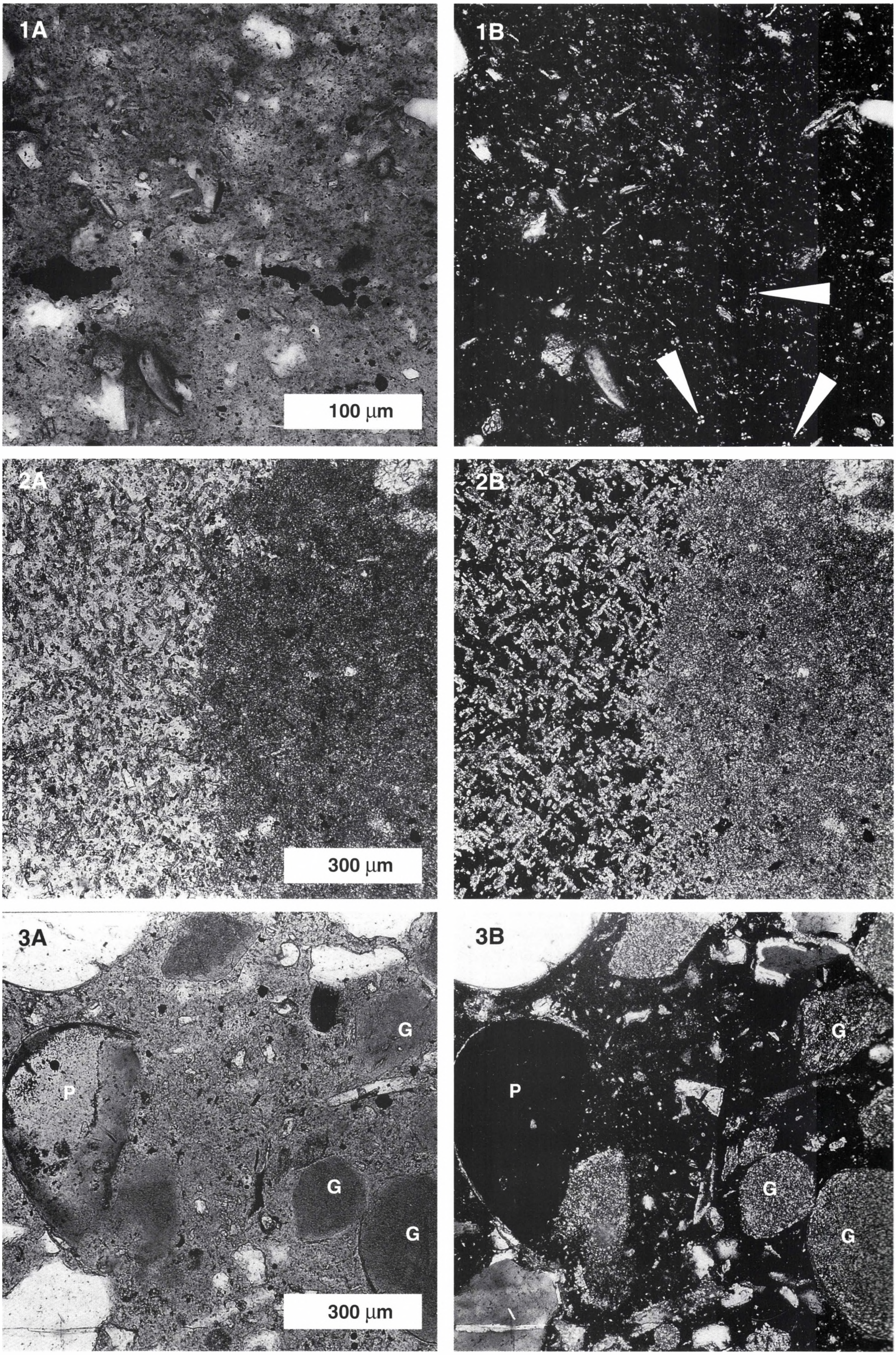
The internal structure of the nodules is either concentric with several layers or very heterogenous. Phosphorus is concentrated either in the crust or in the middle layer. Bioturbation and pelletoid cores are common. Glauconite is sparse in the earthy and carbonate phosphorites of the basin center as compared to the very glauconitic sandy facies equivalents in the south.

Plate 2 depicts three representative examples of characteristic thin sections under parallel and crossed nicols. The view under crossed nicols facilitates recognition of the phosphatic component which then appears almost isotropic (dark gray to black). Plate 2 (Fig. 1) shows the thin section of an earthy phosphorite, rich in phosphatic substance. Plate 2 (Fig. 2) depicts a microscopic cross-section of a tubular carbonate phosphorite. Plate 2 (Fig. 3) demonstrates a highly glauconitic sandy phosphorite from the southern periphery of the basin.

Phase-contrast microscopy facilitates the study of phosphorite in thin sections by bringing out details in structure and composition (compare Zimmerle 1982).

The scanning electron microscope (SEM) is another tool to examine phosphates and phosphorites, especially if combined with integrated X-ray fluorescence analysis (Nöltner 1988). Colleagues operating different types of scanning electron microscopes assisted in the present study. There is no other way to determine size, shape, sorting, and composition of individual phosphate particles (Zimmerle 1982, Plates). Microstructural features

Plate 2: Thin-section characteristics of representative autochthonous phosphorites.
Fig. 1: Cryptocrystalline matrix of pale-colored earthy phosphorite (close-up) with admixture of silt and with a layer of authigenic pyrite. Note microcrystalline flaky clay minerals and isotropic appearance of the cryptocrystalline apatite under crossed nicols. Angular siliciclastic and carbonate silt admixture amounts to less than 5 vol.-%. Arrows mark coccoliths. Glauconite and authigenic carbonate are absent. A = parallel nicols, B = crossed nicols, Sarstedt clay pit.
Fig. 2: Cross-section of a zonal rod-shaped siderite phosphorite (close-up). On the right dense, slightly pelletai, microcrystalline siderite matrix. On the left rod-shaped siderite crystals replacing bacteria within a pale-colored phosphatic matrix. A = parallel nicols, B = crossed nicols, Vöhrum clay pit.
Fig. 3: Glauconitic and arenaceous phosphorite (close-up). The cryptocrystalline phosphatic matrix remains isotropic under crossed nicols. Oval glauconite grains (G) amount up to 50 vol.-%; they display the characeristic aggregate polarization under crossed nicols. The siliciclastic sand grains are angular to rounded. The detrital high-grade phosphate grain (P) signals the beginning of reworking of phosphoritic components at the southern periphery of the basin. A = parallel nicols, B = crossed nicols, Georg Friedrich open-pit mine (abandoned).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300 µm
3B
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such as the uniform and minute particle size (less than 3 µm) and globular particle shape of the soft earthy phosphorites can be demonstrated best by scanning electron micrographs (Pl. 3, Figs. 1-3).

3.4 Diagenetic alteration processes

Partial or complete, penecontemporaneous and early diagenetic replacement of the original clay matrix and of biogenic constituents such as siliceous sponge spicules, radiolarians, diatoms either by calcite, siderite and/or kutnahorite, and/or by phosphate is widespread and common. The extremely fine particle size of the original smectitic clays favors the precipitation of carbonate minerals and phosphate. Tuffaceous clays and marls, that are frequently characterized by admixtures of minute angular mineral splinters (<10 µm), are preferentially phosphatized. Fragments or concretions of such a cryptocrystalline groundmass, mainly composed of apatite and rich in minute mineral splinters, are an additional hint at the genetic interrelation between tuffaceous deposits and subsequent phosphatization. The association of phosphate and glauconite which is also common worldwide and the occasional occurrence of clinoptilolite is also of genetic relevance.

Phosphatic substances can replace clay minerals, biogenic calcite and opaline silica of sponge fragments. Some of the calcareous microfossils and fossil debris are completely replaced by phosphate. Locally, neoformation of pyrite, clinoptilolite and various carbonate-group minerals is observed.

The diagenesis of the Aptian/Albian phosphorites from the Lower Saxony Basin is characterized by the lack of recrystallization phenomena of apatite and by the lack of conspicuous neoformation of other mineral phases such as quartz or feldspar. Thus, heat fronts of potential Upper Cretaceous intrusions (see Zimmerle 1989: 962) did not induce high-rank diagenetic effects into the phosphorites in the Hannover-Braunschweig-Alfeld-Goslar area as they occur close to the Massif of Vlotho (Rose 1984 and own observations).

The various carbonate-group minerals such as siderite, kutnahorite, manganous calcite, dolomite and calcite seem to have been precipitated in a certain diagenetic order.

Radioactive zonation within some of the phosphorite concretions, shown by autoradiography (Zimmerle 1982: pl. 2, figs. 7 + 8), reflects primary differences in element composition and/or secondary diagenetic processes.

3.5 Inorganic-chemical composition

The P_2O_5 content of the Lower Cretaceous phosphorite nodules of the wider Subhercynian Basin fluctuates much from 4 to 25 per cent as previously described by Heberle (1914). The enclosing clays and marls contain up to 3 per cent, rarely even 12 per cent of P_2O_5. Data on trace element composition (in ppm) of Albian phosphorites from the Lower Saxony Basin was given by Benda et al. (1962):

U	Zn	Cu	Pb	RE
5-54	50-340	8-55	8-340	Y, Yb, La, Dy, Gd

Chemical and X-ray diffractometric analyses (Vinken 1977: tabs. 10, 11) of Lower Albian siderite phosphorites (i.e. grobkonzentrische Ca-Fe-Mn-Karbonat-Phosphat-Konkretionen) from the Vöh-

Table 1: Chemical and X-ray diffractometric analysis of Lower Albian siderite-phosphorites (grobkonzentrische Ca-Fe-Mn-Karbonat-Phosphat-Konkretionen) (after Vinken 1977: Tab. 11) Analysts: Lodziak/ Requard, BGR and Gaida, RWE-DEA; Vöhrum clay pit.

	Nodular Siderite-phosphorite	Tubular Siderite-phosphorite
SiO_2	4.45	5.77
Al_2O_3	1.98	2.45
Fe_2O_3	15.50	7.61
TiO_2	0.156	0.180
MnO	6.60	11.18
CaO	31.08	31.76
MgO	1.27	1.07
Na_2O	0.48	0.40
K_2O	0.26	0.34
P_2O_5	10.55	9.98
LOI	25.88	24.26
Total	98.21	95.00
U	13 ppm	16 ppm

Chemical analysis of siderite-phosphorite, Voehrum claypit.

	Nodular Siderite-phosphorite	Tubular Siderite-phosphorite
Apatite	24.4	23.1
$MnCO_3$	10.6	18.2
$FeCo_3$	22.6	11.0
$CaMg(CO_3)_2$	5.8	4.9
$CaCO_3$	23.9	24.6
Muscovite	4.8	6.1
Quartz	2.1	2.9
CaO (rest)	2.1	3.4
Total	96.3	94.2

Normative mineral composition of siderite-phosphorite, Voehrum claypit.

Table 2: Major element analysis of Middle Aptian earthy phosphorites (compare Fig. 2)
Legend: Horizon A = bed no. 206 lower part, horizon B = 206 middle part, horizon C = 206 upper part, horizon D = 211 and horizon E = 214 base; Sarstedt clay pit.

Horizon	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5
E	8.03	2.66	8.07	0.15	5.93	32.97	1.02	n.d.	0.43	16.19
D	27.37	8.55	2.55	0.40	0.07	27.90	1.04	n.d.	1.52	14.08
C	23.38	6.60	4.70	0.32	4.19	25.91	0.96	n.d.	1.20	14.37
B	27.49	8.32	2.54	0.40	0.09	27.89	1.02	n.d.	1.50	15.27
A	31.59	10.20	8.16	0.49	0.22	20.49	1.71	n.d.	1.85	3.96

n.d. = not determined
(courtesy P. STOFFERS)

Table 3: Trace element analysis of Middle Aptian earthy phosphorites (compare Fig. 2)
Legend: Horizon A = bed no. 206 lower part, horizon B = 206 middle part, horizon C = 206 upper part, horizon D = 211 and horizon E = 214 base; Sarstedt clay pit.

Horizon	Ba	Sr	V	Cr	Rb	Ni	Zn	Cu	Co	Pb
E	163	1523	53	23	12	48	585	n.d.	18	16
D	172	1195	77	48	62	54	83	183	<10	21
C	162	1216	75	36	52	435	1013	34	28	47
B	184	1333	75	50	63	93	207	60	<10	22
A	220	531	106	71	85	59	50	25	18	25

n.d. = not determined
(courtesy P. STOFFERS)

rum clay pit are shown in Table 1. Additional inorganic-chemical analyses of phosphorites were compiled by ZIMMERLE (1982) and by KELLER et al. (1989). Finally, five horizons of pale-colored earthy phosphorites: namely beds no. 206, 211 and 214 from the Vöhrum clay pit (Text Fig. 2) which resemble each other in size of the concretion, microscopic and submicroscopic aspects were analyzed for major and trace elements (Tab. 2 + 3). An element analysis of an earthy phosphorite nodule (Horizon C) is shown in Text Fig. 5. H. PIETZNER (Krefeld) analyzed the basal Middle Aptian beds (MUTTERLOSE 1987) by means of the microprobe and confirmed the occurrence of disperse phosphate and incipient phosphorite (Pl. 1, Fig. 5).

Autoradiographs demonstrate that radioactive elements are unevenly distributed within the nodules.

For a long time, field geologists generally called most concretions from the Mid-Cretaceous interval "phosphorites", especially the hard ones. The hard concretions and the rod-shaped accumulations are composed of various kinds of carbonate minerals and of apatite. They have been termed Ca-Mn-Fe carbonate phosphate concretions first (VINKEN 1977). Later (ZIMMERLE 1982), the other type, the soft earthy accumulations, high in phosphorus and without a remarkable carbonate content, has been recognized in various outcrops and in boreholes of the Lower Saxony Basin. The present chemical analyses (Tab. 2 + 3) and previous analytical data (ZIMMERLE 1982: tabs 4.7-1/4.7-5) document this marked contrast in composition.

The P_2O_5 content of the soft earthy phosphorites ranges between 20-30%, that of the carbonate phosphorites between 10-20%.

Major Elements – The major element distribution shows the following characteristics: Conspicuous is the presence of manganese carbonate and the marked manganese content in the carbonate-phosphate concretions (compare also BROCKAMP 1978: 244). The unusual manganese content might indicate an exhalative source of the manganese (compare GRUSS 1958). The Al_2O_3, TiO_2, and K_2O contents are normally low; they characterize the amount of clay admixture. Na_2O is low and presumably associated with apatite. The magnitude of detrital input is also marked by Si, Al, Ti, Na and K. The high Fe_2O_3 and MnO values are found in carbonate phosphorites.

The CaO and P_2O_5 content in the five earthy phosphorite samples from Sarstedt increases, gradually and with recurrences, from the base to the top of the section (Text Fig. 2); the SiO_2, Al_2O_3, and TiO_2 content shows an opposite trend (Tab. 2).

Fig. 4: Conglomerate of allochthonous phosphorite concretions (arrows) with glauconite-rich matrix marking a stratigraphic break (dashed line). Outcrop at Grünenplan (Hils).

Trace Elements – Previous analyses show the following trends: The Ba content corresponds to the Ba content of other phosphorite occurrences worldwide. Rb, Th, and Zr contents are slightly higher in phosphorites from tuff-bearing and tuffaceous clay sections (Sarstedt, Vöhrum). Ce, Co, La, Ni, and Y contents are higher than those in other phosphorites world-wide. The high Ce content indicates increased terrestrial input. The amounts of Cr, Mo, Pb, Sc, V, and Zn are low as compared with the world-wide standards, except for some values from the Sarstedt clay pit. U is below the world-wide standard.

The trace element content of the five earthy phosphorite samples from Sarstedt fluctuates considerably (Tab. 3), especially Zn and Ni. Zn is presumably derived from sphalerite which can be seen under the microscope. The horizon C is characterized by the highest values of Pb, Zn, Ni, and Co.

Trace element composition of phosphorites from the basin center and the southern margin does not differ.

ISRAILI & KHAN (1980), TAMBIYEV & BATURIN (1981), and TAMBIYEV & BATURIN (1982) studied the trace elements in phosphorites from other occurrences. Many metallic and non-metallic elements have been reported as concentrations in phosphate minerals or particles (e.g., pellets or oolites).

The C_{org} content of enclosing sediments and phosphorites is moderate (WEHNER 1982).

ICP-MS and isotope analysis were not carried out yet on the phosphorite examined. In this respect AHARON & VEEH (1984) and SHEMESH et al. (1983) commented that isotopes must be used with great caution in environmental and genetic interpretations of phosphorites.

The heterogeneous composition of the Aptian/Albian phosphorites shows that the controlling factors for the chemical composition of the various kinds of phosphorite concretions are complex.

4. Biogenic aspects of phosphorite formation

Biochemical processes as an essential factor for phosphorite formation were assumed and postulated early in phosphorite research (cit. ZIMMERLE 1982: 198). In the past decades, research on the microbic aspects of phosphorite genesis intensified. O'BRIEN et al. (1981), SOUDRY & CHAMPETIER (1983), BREHERET (1988) and LAMBOY (1988) referred to bacterial origin of continental margin phosphorites and microbic processes in ancient phosphate accumulations. FERRIS et al. (1991) treated in general bacteria as nucleation site for authigenic minerals. Based on observations of the Messel Oil Shale SCHMITZ-MÜNKER & FRANZEN (1988) and SCHMITZ (1992) stressed the importance of coprolites as substratum for bacteria enrichment and nuclei for subsequent phosphatization.

Which observations are taken as hints of potential microbic activities in the Lower Saxony Basin phosphate and phosphorites?

Inorganic factors

- extremely minute particle size of the clay minerals with smectites predominating. Such a substrate facilitates chemical reactions
- globular shape of the phosphatic "building stones"

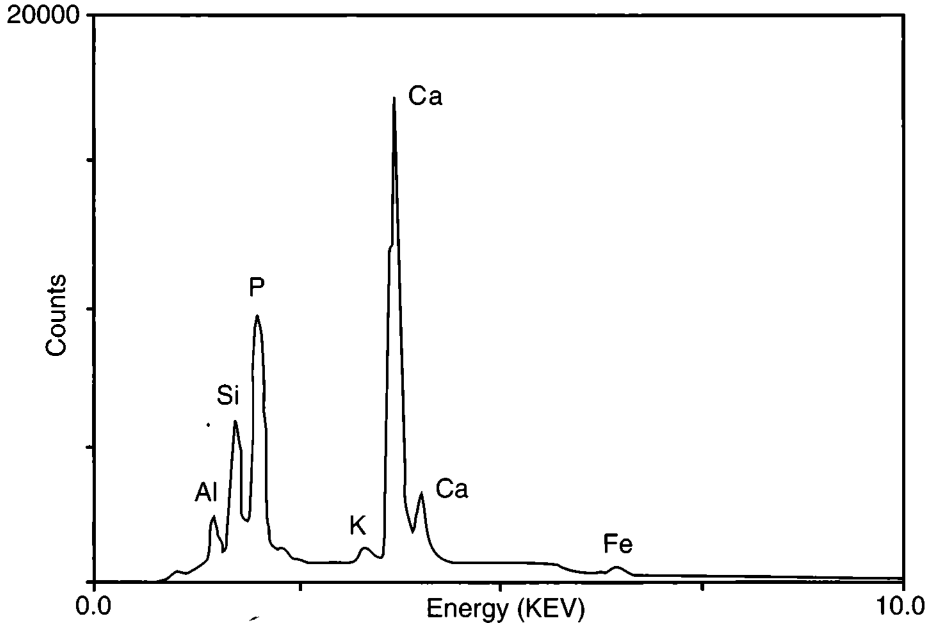


Fig. 5: Element analysis of an earthy phosphorite nodule (Phosphorite horizon C = bed No. 206 in Text Fig. 2). Scanning electron micrographs of this phosphorite are shown in Plate 3 (Fig. 1 + 2). Sarstedt clay pit.

Organic components

- presence of minute coccoliths
- presence of fungal hyphae in biogenic phosphate particles, e.g. fish scales
- organic pyrite "chains"
- abundance of fecal pellets (up to a few millimeter in size), rather undeformed in phosphorite concretions and deformed and, thus, mostly concealed in clays and marls. Fecal pellets are always accompanied by a rich microbic life.

Some fecal pellets (Pillen) in the Ca-Fe-Mn carbonate phosphorite concretions from the Vöhrum clay pit are preferentially phosphatized (Vinken 1977: Tab. 10). This indicates the chemical affinity between fecal pellets, rich in organic substances of various kinds, and penecontemporaneous to early diagenetic phosphatization. Such a phosphatization is a phenomenon of interstitial water and not of seawater.

Spectacular fossil preservation as in the concretions of the Lower Cretaceous Santana Formation (Brazil), however, or replacement of delicate soft tissues by phosphate (e.g. Müller & Walossek 1991) were not observed yet.

4.1 The globular microstructure of phosphorites

In the pale-colored phosphorite nodules globular microstructure of minute and uniform phosphate particles (1-3 µm in diameter) is commonly observed, for instance in Vöhrum, Stedum, and Sarstedt. It seems that the earthy phosphorites throughout the Lower Saxony Basin display this particular microstructure. The origin of such globular microstructures, whether inorganic or organic, is still being debated.

The stratigraphic section of the Sarstedt clay pit in which most of the globular microstructures were observed in phosphorites is well exposed (Text Fig. 2). Middle/Upper Aptian clays and marls with several horizons of autochthonous phosphorites rest unconformably on Upper Barremian black clays without phosphorites. The phosphorite formation begins at the unconformity with unconspicuous, thin, whitish crusts walling erosional pockets in the clayey transgression horizon. Between the unconformity and the Lower Tuff horizon friable pale-colored earthy phosphorites predominate; they form several horizons (A-C). Above the Upper Tuff horizon layers with friable earthy phosphorites and with hard siderite-phosphorite concretions alternate. In this section there is a definite paragenetic association between tuffs, phosphorite and siderite concretions. Moreover, Aptian/Albian phosphorite formation in the Lower Saxony Basin is associated with an increase of the smectite content in the clay, with the occurrence of thin tuff layers, with the presence of manganous carbonates, and with increased production of SiO_2 (siliceous marls with radiolarians).

Plate 3 (Figs. 1 + 2) shows a typical example of such a globular microstructure in an earthy phosphorite nodule (Bed no. 206 upper part) from the Sarstedt clay pit, as seen under the SEM. The "sorting" of the globules is excellent. Their submicroscopical internal structure still remains unknown.

The phosphorite nodule examined, 1.3 cm in diameter, occurs in laminated clay and displays rather sharp contacts. Under the polarizing microscope the nodule appears to consist of a yellowish brown, rather uniform phosphate-clay matrix. Detrital silt and fine-sand admixture comprise angular grains of quartz (partly also of rather bizarre shape), muscovite with rutile microlites, degraded micas, phyllite, and chlorite. Solitary grains of green glauconite and "chains" of framboidal pyrite are sparse. Opaline silica is enclosed in this phosphatic micro-environment. Solitary vermicular kaolinite crystals are of diagenetic formation. Notable are large authigenic crystals of euhedral pyrite and sphalerite and cloudy leucoxene pigment. The microfauna comprises thin-shelled calcareous foraminifera, arenaceous foraminifera, ghosts of opaline sponge spicules, funnel-shaped radiolarians, and sporadic coccoliths. Also translucent, brown plant fragments are dispersed. The enclosing clay is characterized by microcrystalline clay with leucoxene and some pyrite "schlieren", microfossils, fossil fragments, and slight sand admixtures (quartz, muscovite, and green biotite).

In contrast to the above thin-section characterization stands the rather uniform view under the scanning electron microscope (Pl. 3, Fig. 1 + 2). Dominating component are the well round phosphate globules, 1-2 μm in diameter and of a rough surface. Interspersed are minute flakes of clay. Both, phosphate globules and minute clay flakes seem to be of penecontemporaneous to early diagenetic formation.

Other examples of globular microstructure, e.g. from the Vöhrum clay pit, were demonstrated by means of the phase-contrast microscope (Zimmerle 1982: Pl. 4.7-5, Fig. 3-6) and under the scanning electron microscope (Pl. 3, Fig. 3 A + B).

Plate 3 (Fig. 3 A + B) documents how globular phosphate replaced opaline radiolarians preserving the fossil structure of the tests in detail. This exemplifies the penecontemporaneous to early diagenetic replacement not only of an inorganic mineral matrix, but also of microfossil tests by phosphate.

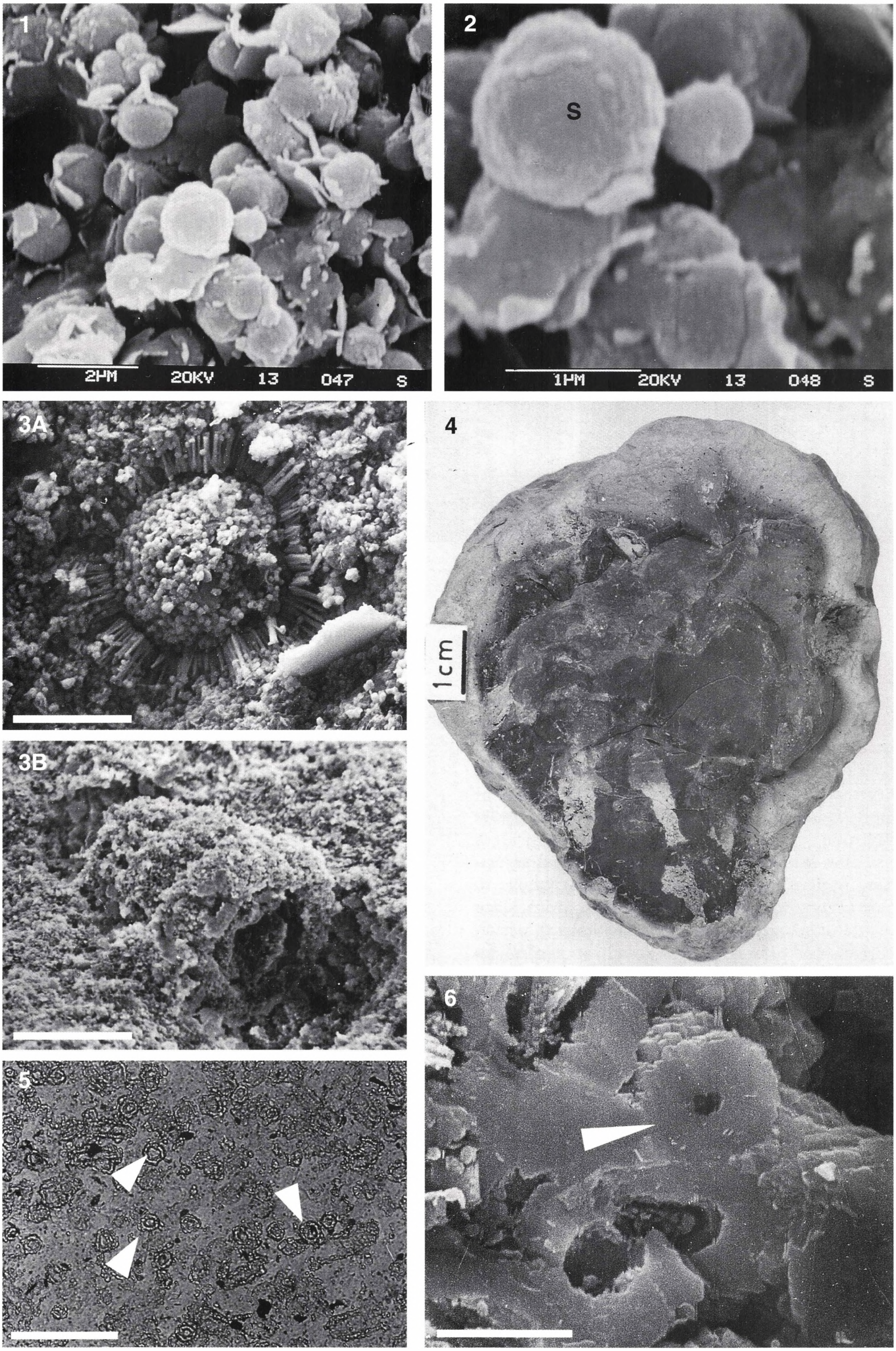
According to the author's observation scanning electron micrographs of poorly crystallized matrix of Middle Jurassic phosphorites reveal minute apatite globules (less than 5 μm in size), too.

In phosphatized soft-bodied squids from the Upper Jurassic Oxford Clay Allison (1988: Fig. 5 D + E) showed "microspherical apatite" (about 3 μm in diameter) pseudomorphing muscle tissues. Similar microstructures of globular apatite were depicted by Burnett et al. (1980, Fig. 6) from Recent phosphate nodules off Peru. However, this kind of globular apatite aggregates displaying rough surfaces was interpreted to be "the effects of solution" of euhedral apatite crystals.

4.2 Branching system of decapod burrows

Fossil decapod burrows associated with microbic activities from the lower Albian are observed in the Vöhrum clay pit (Zimmerle & Emeis 1983). Hard, fist-size carbonate phosphate concretions which are highly bioturbated (Pl. 3, Fig. 4) form a burrow system together with rod-shaped carbonate-phosphorite concretions, occasionally with hollow central channels, in the dark gray clays (Text Fig. 6). The fist-size concretions are considered to be dwelling cavities of decapods (Domichnia), the rod-shaped concretions to be interconnecting burrows between the dwelling cavities. The latter, a few millimeters to several centimeters in diameter, mostly lie in the bedding plane. In cross-sections they are concentric, often with dark nuclei rich in carbonate minerals and pale-colored crusts rich in phosphate, occasionally also with pyrite encrustation (Text fig. 7). The round cross-sections of the rod-shaped concretions, the hollow central channels in the concretions, and the good preservation of the originally coarse-grain fabric (mainly fecal pellets) prove an early diagenetic mineralization prior to mechanical compaction, mainly associated with commonly horizontal, occasionally branching burrows of the *Thalassinoides* type. Sideritic spherules (5-25 μm in diameter and up to a maxi-

Pl 3: Biogenic aspects of phosphorite formation.
Fig. 1: Globular microstructure of an earthy phosphorite as seen under the SEM, mainly composed of apatite spherules. Minute clay flakes are interspersed. Sarstedt clay pit (Phosphorite horizon C), Bed no. 206 (upper part).
Fig. 2: Apatite spherules (S), less than 2 μm in diameter, in an earthy phosphorite as seen under the SEM. Note the rough surface of the spherules with vague indications of crystal faces. Sarstedt clay pit (Phosphorite horizon C), Bed no. 206 (upper part).
Fig. 3: Radiolarians in phosphorite nodules, completely replaced by apatite. A = spherical, B = conical. Sarstedt clay pit. Scale bar 20 μm (A), 100 μm (B).
Fig. 4: Hard, fist-size carbonate-phosphate concretion (overview), highly bioturbated and with a pale-colored crust rich in phosphate (2-12 mm thick). This concretion type represents the dwelling cavity of a decapod (Domichnia). Vöhrum clay pit.
Fig. 5: Siderite spherules (arrows) which were formed by post-mortem sideritization of bacteria (thin section). The bacteria lived preferentially in the slimes of burrow walls (compare Text figs. 6 + 7). Subsequently the hard, rod-shaped carbonate-phosphorites formed. Vöhrum clay pit. Scale bar 40 μm.
Fig. 6: Siderite spherules (arrow) as in Fig. 5, but seen under the SEM. Vöhrum clay pit. Scale bar 5 μm.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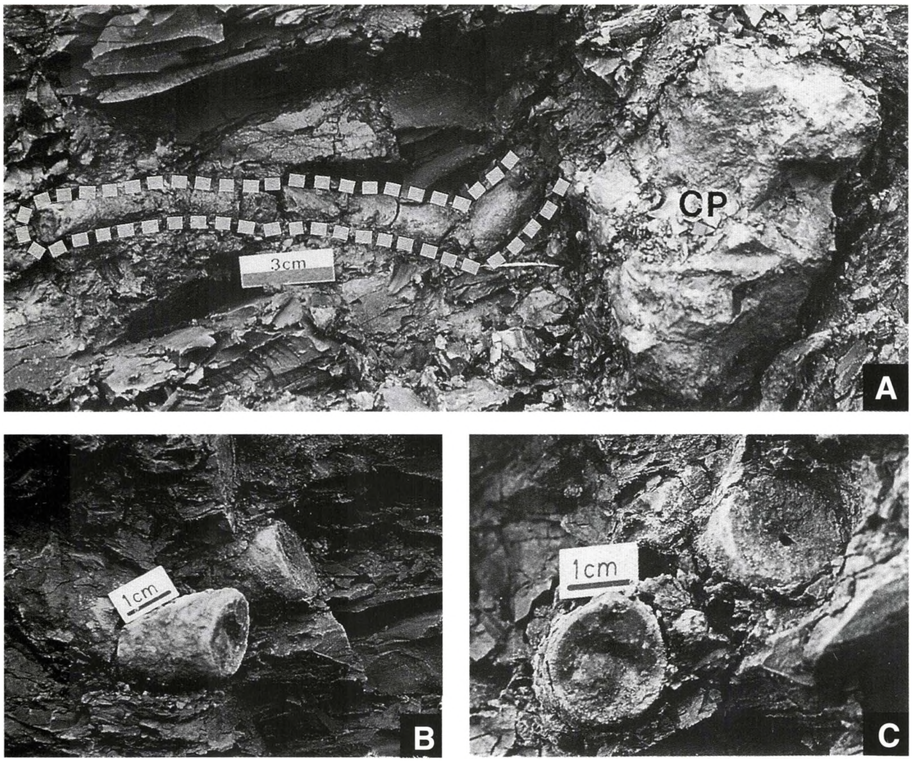

Fig. 6: Branching system of decapod burrows (after ZIMMERLE & EMEIS 1983, Fig. 2), A = horizontal, rod-shaped burrow (dotted line) and fist-size carbonate-phosphorite concretion (CP), B = two hard rod-shaped burrows leaving the soft clay wall, C = two hard rod-shaped concentric burrows leaving soft clay. Note central hole in the right burrow. Vöhrum clay pit.

mum length of 80 μm) are concentrated in the phosphate-rich crusts of the rod-shaped carbonate-phosphorite concretions (Pl. 3, Fig. 5 + 6). In their present form the spherules are interpreted as being diagenetic post-mortem incrustations of bacteria by siderite which have been concentrated in the zone of the original walling of the burrows. Occasionally also post-mortem incrustations by pyrite occur.

FERRIS et al. (1991) showed that bacterial-associated mineralization, especially by amorphous to microcrystalline metal sulfides, iron oxides, silica crystallites, and limonitic clays, facilitates the structural preservation and, thus, fossilization of bacteria.

Consequently, biogenic processes and the formation of the concretions are intimately linked, in macroscopic as well as in microscopic dimensions.

Coeval *Thalassinoides/Ophiomorpha* burrows, however filled with coarse pebbles derived from an overlying conglomerate, were observed by GROETZNER (1968) in the Hils Sandstone at the southern sandy margin of the Lower Saxony Basin (in the abandoned Morgenstern open-pit mine). In sands the *Thalassinoides* tubes are deformed to oval cross-sections. But in carbonate-cemented portions round undeformed cross-sections prevail (GROETZNER 1968: 160). Petrographic details in respect to possible mineralization associated, however, were not given by the author.

Architecture and size of the burrows in the Lower Cretaceous from the Vocontian Basin, SE France, described by GAILLARD (1984: Pl. 1), are similar to the above rod-shaped siderite-phosphorite concretions. However, no petrographic investigations from this occurrence are known.

LAMBOY (1988) and BREHERET (1988) believe that microbic phosphatization is one of the most important processes, also in the economic phosphate deposits of N and W Africa as well as the Mid-Cretaceous of the Vocontian Basin.

In summary, the presence of microscopic organic particles, fecal pellets of varying size, shape and derivation, and larger coprolitic residue, all rich in microbes (bacteria), favors their post-mortem replacement by phosphate and/or siderite. The globules, which are the elementary "building stone" of the earthy phosphorites, are considered being of early diagenetic formation and the result of biogenic activity. An organic origin is also postulated for sideritized bacteria which presumably formed in a narrow zone in the wall of burrows, especially rich in organic slimes. Further work, submicroscopic as well as geochemical, however, is needed to further substantiate this claim of microbic involvement.

Chemical methods for phosphate removal such as precipitation and flocculation by means of Fe, Al, and Ca compounds as well as biological phosphate removal from waste water by "Belebt-Schlamm-Organismen" or algae as applied in industrial processes furnish helpful models for phosphatization.

5. Conclusions and model

The phosphorites occur in a marine environment which is composed of variegated, occasionally dark-colored pyritic clays and marls which only locally represent incipient anoxic conditions of deposition. They are of penecontemporaneous to early diagenetic origin. Phosphorite formation is a phenomenon of interstitial water and not of seawater. Previously, the widespread abundance of autochthonous phosphorites in the Aptian/Albian from the Lower Saxony Basin has been explained solely by coastal upwelling of cold deep-waters rich in nutrients coming from the north (Zimmerle 1982; Kemper & Zimmerle 1983). The Late Early Cretaceous of northwestern Germany is considered to be an example of sedimentation in a rather cool boreal-sea under humid climatic conditions. The basin was strongly subsiding from Late Jurassic to Late Early Cretaceous. The three depositional belts distinguished (compare p. 2/3) display a remarkable facies asymmetry. This pronounced asymmetry means that certain rocks are confined to one side of the basin only. Correlations are impossible, even over short distances. Such asymmetrical facies patterns are frequently the result of coastal upwelling. Typical features are: (1) abundance of siliceous sediments (radiolarians, diatoms) in a nearshore belt, (2) presence of phosphorite accumulations, and (3) a rather high supply of organic matter causing oxygen deficiency in the environment of the second belt. A schematic north-south cross section (Kemper 1979) through the Lower Saxony Basin shows this asymmetric facies distribution (Text Fig. 9).

A detailed facies analysis of Upper Aptian and Lower Albian sedimentary rocks from the Lower Saxony Basin in northwestern Germany was published in a special volume (Kemper 1982). This volume contains contributions on the micro- and macropaleontology, sedimentology, thin-section and X-ray analysis, inorganic and organic geochemistry of the above interval.

The upwelling system as such was essentially controlled by (1) the physiography of the marginal sea and (2) by the paleocirculation system nurtured by cool waters coming from the north. A drop of temperature caused influx of cool Arctic waters in the Late Aptian. The paleolatitude was around 47°N; it corresponded to a boreal region with a preponderantly humid climate. This climate was somewhat beyond the optimum conditions for phosphorite formation. Influx of terrigenous material in suspension from the adjacent southern continent was considerable.

Noteworthy is the rather sudden appearance and widespread occurrence of smectite (Brockamp 1976; Kull 1979; Gaida et al. 1981; Keller et al. 1989) at the beginning of the Aptian. In the thin tuff layers of the Aptian and Albian (Zimmerle 1979, 1989),

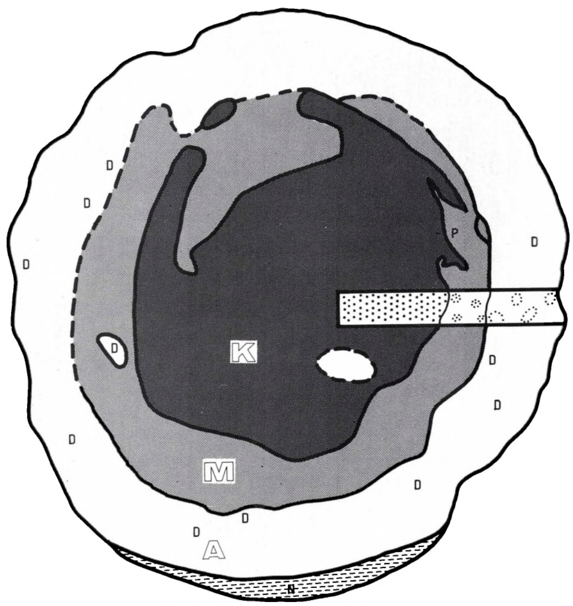

Fig. 7: Cross-section of a hard, rod-shaped carbonate-phosphorite concretion (23 mm in diameter). The following zones can be distinguished: K = core, M = middle zone, A = pale-colored crust, N = adherent clay, D = drusy porous areas with slightly larger spherules, P = area rich in phosphate. The insert displays schematically the microscopic texture: K = uniform siderite matrix, M = isometric siderite clusters, A = siderite spherules.

smectite is derived from early diagenetic alteration of volcanic glass and volcanic lithoclasts.

The organic carbon content (C_{org}) is low to moderate (0.5-1.5%). Glauconite is abundant on the southern margin of the basin.

Phosphorite concretions are common and widespread except for their sporadic occurrence in the dark-colored clays of belt 2 with elevated C_{org} values. The association of phosphate, manganese carbonate, and siderite, a so-called remineralization assemblage, might well indicate, in accordance with observations in the Baltic Sea by Suess (1979), a terrestrially influenced marginal-sea environment. But the environment of the Aptian/Albian is not as poorly oxygenated as that in the Landsort Deep of the central Baltic Sea.

The synsedimentary to early diagenetic mineral assemblage manganese carbonate, siderite, phosphate, smectite, and glauconite – together with the organic carbon and low calcite content – reflect specific pH and Eh conditions (Text Fig. 8). The particular faunal and floral assemblages, i.e. arenaceous foraminifera, siliceous microplankton, siliceous sponges in belts 1 and 2, and abundant suspension feeder communities in belt 3, are mainly controlled by nutrient supply, but presumably also

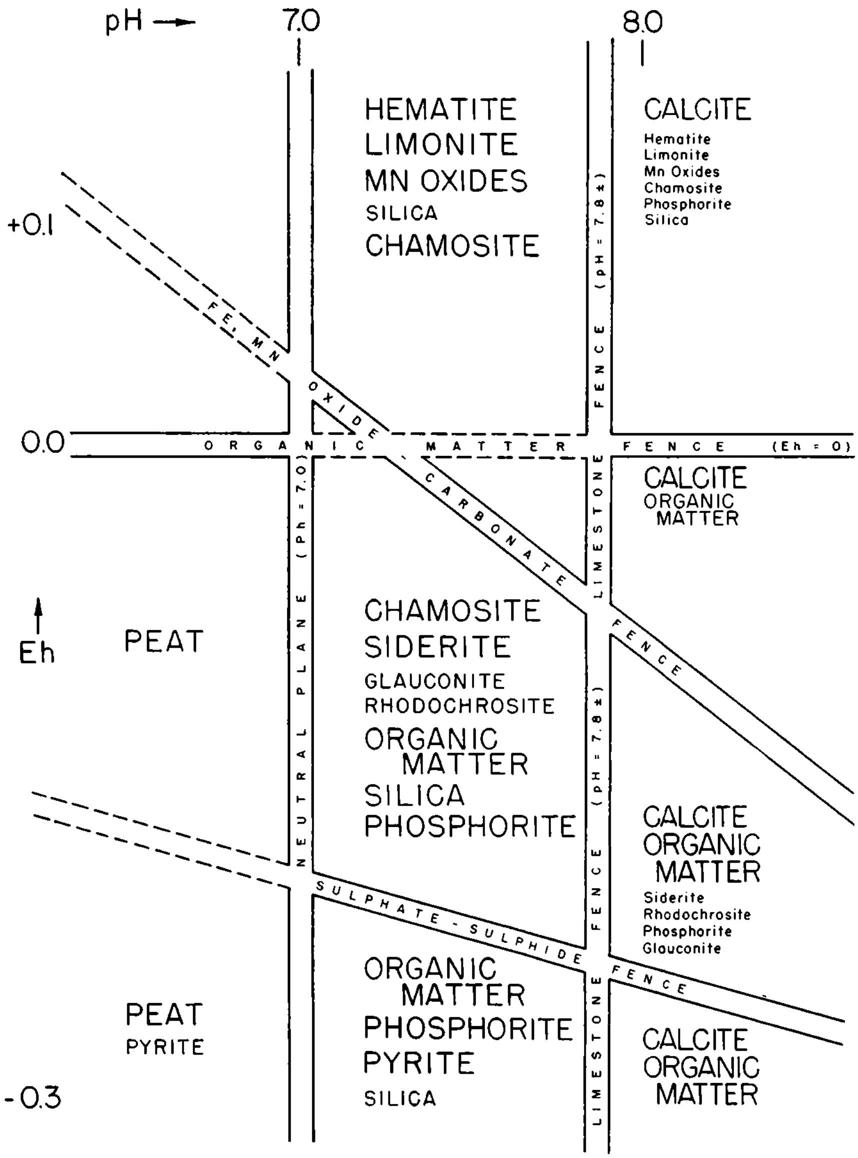

Fig. 8: Phosphorite formation as function of pH and Eh in the frame of sedimentary chemical end-member association (after Krumbein & Garrels 1952).

by pH and Eh. Also these patterns are indicative of upwelling conditions (Diester-Haass 1978).

Comparable sedimentary rock and mineral associations (Sokolowski 1976) as well as faunal and floral fossil assemblages, appeared in most European basins in Late Aptian and Albian times as a consequence of increasing current activity triggered by cooling. These associations extend from Great Britain and France in the west to as far as the Caucasus, Caspian Sea, and even Iran in the east. Also, glauconite is widespread and abundant in the Aptian/Albian interval throughout Europe. Presumably, the presence of smectite favored the neoformation of glauconite (Jeans et al. 1982). Upwelling intensity and distribution of this unique rock and mineral assemblage varies depending upon the local orography and the paleocurrent systems. Future geochemical studies should help to support these interpretations.

The monocausal explanation of phosphorite deposition by upwelling alone (Kemper & Zimmerle 1983), however, seems to be too simple for explaining phosphorite formation in the Mid-Cretaceous of the Lower Saxony Basin. Other factors, such as tectonic framework with changing orography, increasing volcanism and fluctuating biogenic activities, appear to interfer with phosphorite formation. In the present case, for instance, changing orography triggered renewed phosphorite formation above the stratigraphic break Upper Barremian/Upper Aptian (Kolbe et al. 1985) and in the condensed section of the Calcareous Alps (Föllmi 1989). The interference with volcanic activity – and presumably with hydrothermal processes (compare Feely

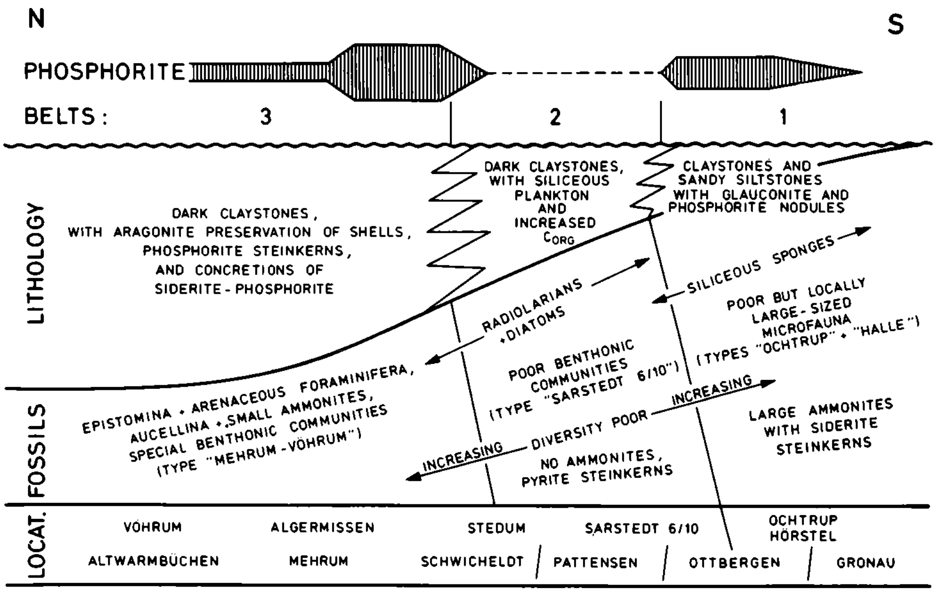

Fig. 9: Schematic facies distribution (N-S cross-section) in the Aptian/Albian of Lower Saxony Basin with phosphorite distribution, lithology, fossil assemblages, and locations within the facies belts 1-3 (after Kemper & Zimmerle 1983).

et al. 1990) – is indicated by the close paragenesis and spatial association of volcanic tracers in the sediments such as detrital volcanic rock fragments, the presence of siliceous fossils such as radiolarians, diatom pseudomorphs, and siliceous sponge spicules, and of authigenic clinoptilolite.

A genetic association of phosphorites with volcanic rocks was considered repeatedly. For instance, volcanic influence on the formation of phosphorites in the Dinantian was advocated by Rösler (1961), Krylatov (1964), Brodskaya (1974) and Timmermann (1976). Submarine volcanism has been suggested as a local source of the fluorine, phosphorus, and/or silica of some marine phosphorites in the stratigraphic columns of various areas (Taliaferro 1933; Mansfield 1940; Salvan 1952; Bidaut 1953; Miller 1964; Gibson 1967; McKelvey 1967; Krasil'nikova 1967; Brodskaya 1974; Timmermann 1976; Chaudhri 1977; Giresse 1978; Sokolov et al. 1978). An endogenic iron supply for the clay ironstones associated with the phosphorites was advocated by Brockamp (1978) for the Lower Cretaceous.

The detrital particle size, already previously claimed to be characteristic of phosphorite occurrences (Paproth & Zimmerle 1980: 92) might have facilitated phosphorite as well as glauconite neoformation. The common presence of phosphorite and glauconite seems to be quite symptomatic in this respect.

Extremely fine particle size of the enclosing clays and marls favor penecontemporaneous to early diagenetic nucleation and precipitation of phosphorus out from the concentrated pore water and/or most likely through an intermediate colloidal stage. Golterman (1978) emphasized that clay adsorption has been often underestimated in models describing the relationship between phosphorus concentrations and phosphorus loading. The genetic interrelation postulated between minute particle size and phosphorite formation is strongly supported by observations in Recent sediments. Rao & Krishna Murti (1987) pointed to the high phosphate adsorption capacity of noncrystalline aluminosilicate gels in kaolin and bentonite clays.

Finally, microbic activity was strong in minute phosphate clusters and larger phosphorite concretions as well as in slimes. It favored precipitation of penecontemporaneous and early diagenetic phosphate. Reflections by Watson (1978) suggest that bacteria play an important role in the realm of upwelling.

The new model presented by Föllmi & Garrison (1991), however, cannot be applied directly and unmodified to the Mid-Cretaceous phosphorite formation in the Lower Saxony Basin. There is no evidence that all horizons with autochthonous phosphorites are associated with breaks in sedimentation or with anoxic black shales.

In summary, the autochthonous phosphorites of the Lower Saxony Basin Aptian/Albian are characterized as follows. Concretions of varying shape predominate; layered phosphatization is of minor importance. The concretions formed penecontemporaneously to early diagenetically. The particle size of the enclosing clays and marls is extremely fine. Siliceous microfossils are common. The environment of deposition was mostly shallow marine. The stratigraphic interval investigated represents a time of tectonic disturbance and paleogeographic change (transgressions). The phosphorites are associated with tuffs or reworked volcanogenic clays and marls. The heterogeneous phosphorites

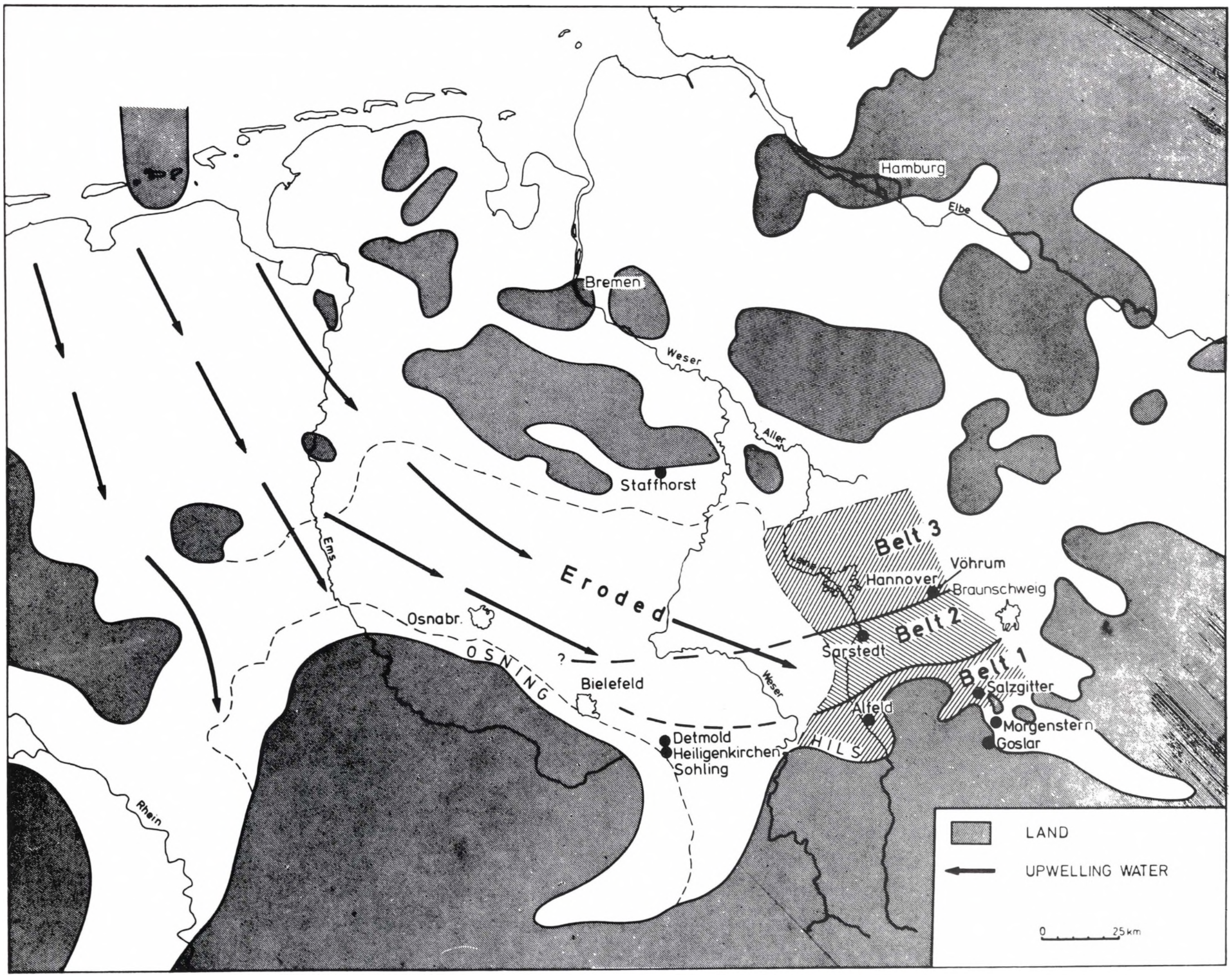

Fig. 10: Paleogeography, ocean currents, and NW-SE directed upwelling system during the Late Aptian and Albian in the Lower Saxony Basin (after KEMPER & ZIMMERLE 1983). Arrows show the general direction of the inferred upwelling. The three depositional belts are marked. The Rheno-Bohemian land mass separates the boreal region in the north from the Tethys in the south. Phosphorite and glauconite formation predominate at the southern margin of the boreal ocean, north of the Armorican and Rheno-Bohemian land mass (NSB = Lower Saxony Basin).

range between rather pure phosphorite nodules and siderite nodules. The internal structure of the nodules is concentric and/or very heterogeneous. Bioturbation is common in the clays; it is present even in some of the phosphorite nodules. Phosphorites in the clays and marls contain only sparse glauconite; however, in the more sandy nearshore environment they occur in close association with glauconite (greensands). The content of pyrite and organic carbon fluctuates. The colors of the enclosing clays and marls vary markedly. The clays are variegated and less dark-colored with grey and greenish hues.

The following model of phosphogenesis in the Lower Saxony Basin during Mid-Cretaceous time is advocated. Geological distribution of phosphorites and their physical chemistry indicate that the formation of phosphorite (i.e. the precipitation of apatite) is restricted to a rather specific environment. Favorable conditions for the accumulation and precipitation of phosphorite, in general, include negative eH, pH around 7.8 (Fig. 8), increased salinity, moderate water depth (50-300 m), warm basinal waters, low oxygen concentrations, supersaturation of phosphates and calcium in sea waters, warm and humid climate, prolific growth of organisms, high content of organic matter, shallow seas, stable tectonic conditions, and "non-depositional sedimentation environment". Phosphate precipitation takes place directly below the sediment-water interface in association with local suboxic to slightly anoxic microbial degradation of organic matter.

The pale-colored earthy phosphorites display a globular microstructure of minute and uniform phosphate particles (1-3 µm in diameter). The globules, which are the elementary "building stone" of the phosphorites, are considered being the result of biogenic activity. An organic origin is also demonstrated for sideritized bacteria, associated with organic slimes of branching decapod burrows.

Because the Aptian/Albian was a time of tectonic unrest, breaks in sedimentation are numerous. There is no evidence yet that the autochthonous phosphorite concretions are associated with breaks in sedimentation or with anoxic "black shales" only. On the other hand, allochthonous conglomeratic phosphorite accumulations at the southern margin of the Lower Saxony Basin mark sedimentary breaks. The Mid-Cretaceous phosphorite formation – one of the climaxes of autochthonous phosphorite formation in earth history – is explained by increased seafloor spreading as the main controlling factor. The seafloor spreading has been associated with active tectonism, changes in the ruling orographic system and, thus, of upwelling conditions, and increase in volcanic and hydrothermal activity.

FÖLLMI (1989) reached a similar conclusion for the Mid-Cretaceous phosphogenesis along the eastern Helvetic Shelf at the northern Tethys margin. Phosphorite formation, however, most likely proceeded along various routes (compare CHAUDHRI 1977, SOKOLOV et al. 1978). The question of phosphorite origin is still controversial, much more than claimed by the advocates of monocausal phosphogenesis.

Further research on phosphorites and their capacity to attract and incorporate exotic elements such as the rare-earth elements (REE), is necessary because there is an increasing need of REE such as samarium, neodymium, lanthanum, europium, and yttrium in industry (metallurgy, glass and ceramics, catalysts in petrochemistry). Some experts even claim the REE to become the "raw materials of the 21st century".

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