

Composition, Morphology, and Origin of Phosphate Pellets: Evidence from Phosphorites of the Lesser Karatau

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Abstract—The global Vendian–Cambrian epoch of phosphate accumulation is marked by the virtually synchronous appearance of giant sedimentary basins, where the largest phosphate-bearing provinces were formed in a relatively short time span. The paper is devoted to one of the main problems in phosphate geology, namely the origin of phosphate pellets. They are observed as microscopic particles in the stratified microgranular phosphorites formed during the Vendian–Cambrian epoch. Different forms of pellets from the productive formation of the Lesser Karatau were studied with the scanning electron microscope. The morphogenetic comparison of phosphate particles and microbiota found in the Vendian–Cambrian or older rocks was carried out. The distribution of major chemical elements in different pellets was studied for the first time. Based on the results obtained, regularities of the vertical and lateral distribution of phosphate pellets in the Lesser Karatau and the issue of their origin is discussed.

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INTRODUCTION

Phosphorites of the world's largest Vendian–Cambrian phosphate provinces and the Permian Phosphoria paleobasin are usually combined into the group of stratified fine-grained phosphorites (Yanshin, 1983; Sokolov et al., 2001). Many geologists noted the similarity of geological structure and sedimentation conditions in the phosphorite-bearing regions of Asia, such as Yangtze–Lao Cai, Lesser Karatau, Okino–Khubsugul, and others (Eganov and Sovetov, 1979; Il'in, 1972, 1990), and the Permian Phosphoria basin (Eganov et al., 2000). Since the Lesser Karatau is easily accessible, well exposed, and characterized by block-type structure, it was repeatedly considered as the model of phosphorite formation. Therefore, phosphorite deposits and occurrences in this region have been studied in detail.

It was believed for a long time that the stratified phosphorites are chemogenic formations, because they are composed of microscopic grains and oolites. However, the genesis of these rocks is as yet unclear. Therefore, following (Kholodov and Paul, 1999), genetically more neutral terms 'pellets' and 'microparticles' are used in the present communication.

Phosphorites of the Lesser Karatau were also considered typical chemogenic rocks for a long time. According to the hypothesis of Kazakov (1939), which dominated for several decades, phosphates are delivered to the oceanic shelf due to the upwelling of deep waters, and phosphorus is precipitated during the decrease in CO₂ partial pressure. The fine-grained oolitic structure of phosphorites was considered to support the chemogenic hypothesis. Oolites were consid-

ered either as a form of colloid coagulation (Rozhkova and Solov'ev, 1937; Chukhrov, 1955) or as a special type of crystalline matter precipitating from true solutions in a very mobile environment (Zavaritskii, 1929). It was also suggested that phosphorites could be formed by both ways (Tushina, 1960). An alternative viewpoint assumed that pellets are products of the vital activity of different organisms, mainly bacteria and algae (Vologdin and Korde, 1945; Sokolov and Mashkara, 1938), or coprolites (Bushinskii, 1966).

It was later confirmed that bios played a significant role in the formation of recent oceanic phosphorites (Baturin, 1978). The detection of a great number of biomorphogenic structures and microstructures in the Lesser Karatau (Eganov, 1988; Litvinova, 1990) changed the concepts of the purely chemogenic nature of ancient stratified phosphorites. Further study of microstructures in this area showed that oolites, i.e., pellets with several rounded shells of similar thickness, account for no more than 1–2.5% of the total number of pellets (Litvinova, 1991). This fact also contradicts the assumption of chemogenic precipitation of phosphorus.

Several morphological types of phosphate pellets were distinguished by Kholodov and Paul (1993, 1995, 1999) based on the study of microstructures of phosphorites in rock sections of the Lesser Karatau. They identified oval, lenslike, rhombic, spherical, droplike, prismatic, dumbbell-shaped, hemispherical, and complex pellets. Proportional variations in size in each type were also revealed. Morphometric studies showed that dimensions of the most abundant particle type often

coincide even in different sections (Kholodov and Paul, 1999, p. 365). Reproduction of their shapes was attributed to the biological growth of particles. Therefore, Kholodov and Paul refuted the assumption that oolites are micronodules (Tushina, 1960), intraclastites (Eganov, 1988), or coprolites (Bushinskii, 1966). Instead, they suggested that pellets represent bacterial–algal colonies.

Application of electron microscopy provided new insights into the morphology of phosphate particles. In particular, evolution of bacterial forms was first established in the phosphorites of Khubsugul (Rozanov and Zhegallo, 1989), Siberia (Zanin et al., 1987), and China (Tan Tianfu et al., 1994, 1997; Zeng Yunfu et al., 1994). Subsequent electron microscopic studies allowed many researchers to consider phosphorites as biogenic formations (Shkol'nik et al., 1999). The electron microscopic study showed that phosphate pellets of the Lesser Karatau can be fragments of phosphatized microbial mats with sponge remains (Eganov et al., 1997; Litvinova, 1998, 1999).

Thus, numerous studies of ancient phosphorites seemed to confirm convincingly a significant role of bios in their formation. At the same time, many unclear and problematic issues remain in the nature of phosphate pellets. This work is aimed at the further morphological study of phosphate pellets of the Lesser Karatau and their comparison with the Vendian–Cambrian microbiota. Regularities in the distribution of major elements revealed for the first time using scanning electron microscope can make it possible to understand the nature of not only pellets but also stratified microgranular phosphorites.

GEOLOGY OF THE LESSER KARATAU

Geology of the Lesser Karatau, Kazakhstan was described in detail in many works (Ankinovich, 1969; Bezrukov, 1954; Bushinskii, 1966; Gimmel'farb, 1965; Eganov and Sovetov, 1979; Smirnov, 1972; Kholodov, 1973, and others). It should be noted that the Lesser Karatau anticlinorium is a part of the Baikal–Caledonian Talas–Karatau lithostructural zone. It extends from the southeast to the northwest over 120 km at a width of 30 km and consists of Riphean, Vendian, Cambrian, and Ordovician rocks (Fig. 1a). The Lower Cambrian rocks compose the base of the transgressive Tamdy Group, which overlies the older volcanosedimentary rocks. They include Kyrshabakty and Chulaktau (productive) formations and lower parts of the Shabakty Formation (Missarzhevskii and Mambetov, 1981).

The Chulaktau Formation includes gently dipping phosphorite-bearing deposits crosscut by oblique faults into separate phosphorite-bearing occurrences extended mainly from the southeast to northwest (Fig. 1). This formation is dated by numerous faunal remains as the Lower Cambrian Tommotian (Missarzhevskii and

Mambetov, 1981). The thickness of productive sequence is no more than 120 m. It is overlain by thick sequences (3–4.5 km) composed of dolomites and limestones of the Shabakty Formation. According to different finds of microbiota, the Shabakty Formation is dated back to the Upper Atdabanian–Lenan (Korolev and Maksumova, 1976; Missarzhevskii and Mambetov, 1981).

STRUCTURE OF THE PRODUCTIVE FORMATION OF THE LESSER KARATAU

The Chulaktau Formation of the Lesser Karatau is subdivided into four (lower dolomite, siliceous, phosphate, and ferromanganese) units. The lower dolomites (Berkuta Horizon) are rocks with coarse-wavy-laminated structure (Eganov and Sovetov, 1979). Under microscope, they look like a thin alternation of carbonate–crystalline interlayers with carbonate–clayey pelitomorphic mass. The Berkuta dolomites are assigned to the Vendian or Lower Cambrian based on trilobites (Ergaliev and Pokrovskaya, 1977) or chiolites (Missarzhevskii and Mambetov, 1981).

The lower dolomites are overlain by siliceous horizon with the basal phosphorite bed 0.1–0.6 m thick (Eganov and Sovetov, 1979). The bed characterized by bacterial–algal structure (Figs. 2a, 2b) is considered biostromes (Eganov, 1988; Litvinova, 1990). The basal phosphorite is made up of thinly alternating layers of converged pellets and spongolites, pelitomorphic phosphorite, and silica. Microscopic study under great magnification revealed reticulate or lacy aggregates of white phosphate pellets and siliceous material (Fig. 2c). In the lower part of the section, the siliceous horizon is composed of spongolitic chalcedony rocks with phtanites and carbonate–siliceous shales in the upper part (Dzhumaliev and Kholodov, 1970). The first variety represents an organic-rich chalcedony–quartz–clayey rock, while the second variety represents weathered phtanites (Kholodov, 1973). The horizon includes stratified, nodular, and columnar stromatolitic buildups (Eganov, 1988; Litvinova, 1990). The total thickness of the siliceous horizon is 20 m.

The phosphate horizon consists of one to three phosphorite units separated by carbonate–siliceous shales. The upper part universally includes phosphate gravelstone layer up to 2–2.5 m thick. The total thickness of the horizon is no more than 80 m.

Rocks of the Lesser Karatau are so variable that one can see the simultaneous presence of siliceous, carbonate, and monomineral phosphorites even within a single thin section. Microscopic study showed that phosphorites are composed of phosphate pellets and siliceous–carbonate–phosphate material, which usually contains separate grains of detrital quartz, scarce biotite flakes, pyrite crystals, and some other heavy minerals (Bushinskii, 1966; Smirnov, 1972; Litvinova, 2004; and others), admixture of organic matter, as well as interbeds,

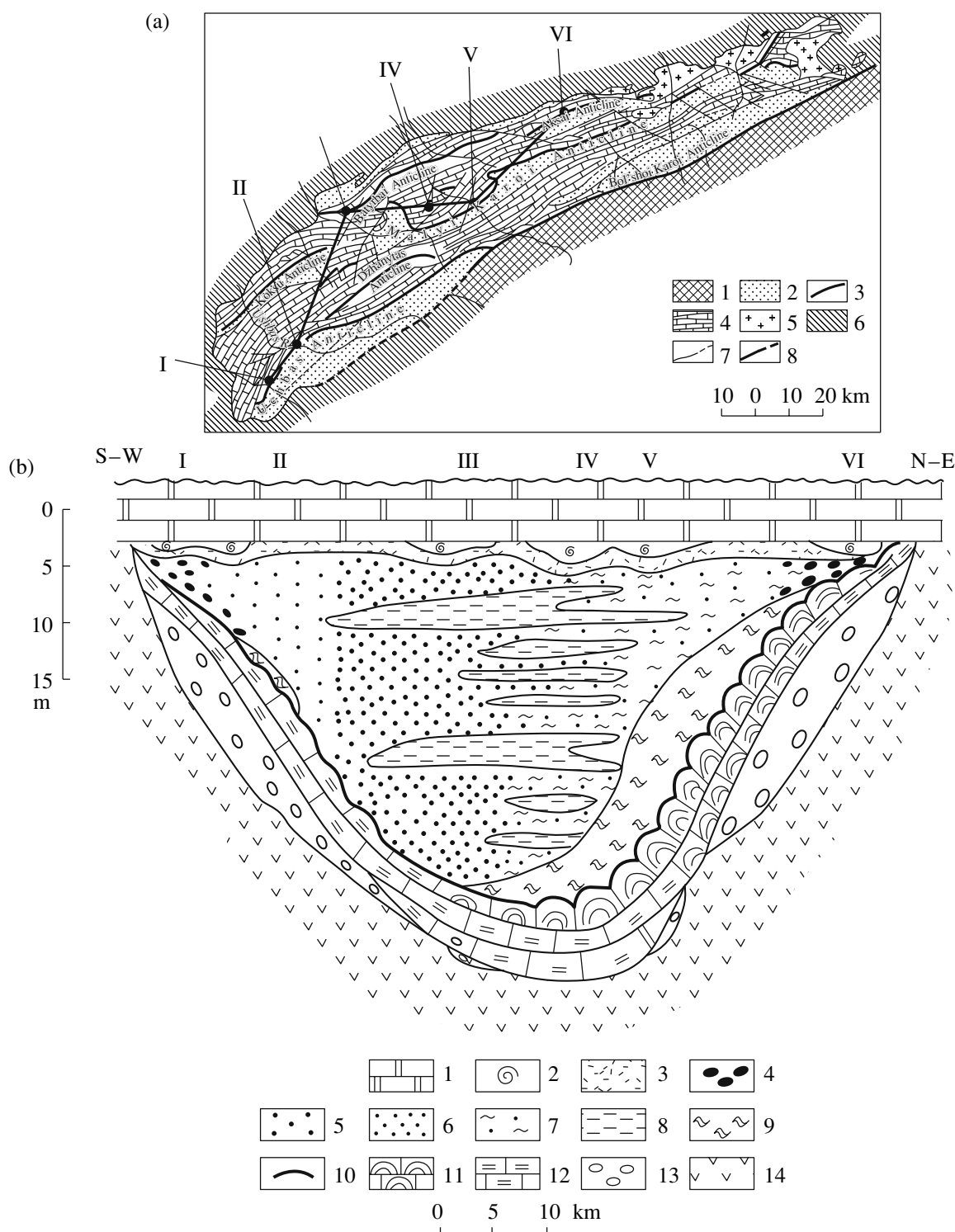


Fig. 1. Geological structure of the Lesser Karatau. (a) Schematic geological map of the Lesser Karatau. (I–VI) Sections: (I) Baba-ata, (II) Geres River, (III) Koksui River, (IV) Akdzhaz River, (V) Dzhihan River, (VI) Kyrshabakty River. (1) Kokdzhot Group (Riphean); (2) Bol'shoi Karoi, Koksui, Toguzbas, Aktugai, Chichkan, and Kurgan formations (Vendian); (3) Kyrshabakty and Chulaktau (phosphorite-bearing) formations of the Tamdy Group (Vendian–Cambrian); (4) Shabakty Formation of the Tamdy Group (Lower Cambrian–Ordovician); (5) granitoid intrusions; (6) Middle Paleozoic and younger deposits; (7) faults; (8) Main Karatau Fault. (b) Schematic structure of the productive (Chulaktau) Formation of the Lesser Karatau across profile I–VI. (1) Dolomites and limestones of the Shabakty Formation (Cambrian–Ordovician); (2–12) productive (Chulaktau) Formation: (2) ferromanganese horizon; (3–8) phosphate horizon: (3) phosphate gravelstones, (4) phosphate conglomerate-breccia, (5) carbonate phosphorites, (6) monomineral and carbonate phosphorites, (7) carbonate-siliceous phosphorites, (8) carbonate-siliceous shales; (9–10) siliceous horizon: (9) cherts, (10) "basal" phosphorites; (11–12) "lower" dolomites: (11) stromatolitic block, (12) bacterial-algal; (13) carbonate conglomerate-breccia of the Kyrshabakty Formation; (14) volcanosedimentary rocks of the Kurgan formation (Vendian).

layers, and films of pelitomorphous phosphorite. The phosphate pellets are rounded and morphologically diverse phosphate aggregates with a complex internal structure. Their size varies from 0.01 to 0.1 mm.

The phosphate horizon of the Lesser Karatau changes along the strike from the carbonate variety in southwest to carbonate-siliceous phosphorites in northeast (Fig. 1b). The largest deposits occur in the northwestern part of the region, while the thickness of productive formation is sharply reduced and the role of coarse-clastic material increases significantly in the southwest and northeast (Fig. 1b).

The ferromanganese horizon crowns the phosphate-bearing sequence. It consists of pinkish-vinous and black dolomites impregnated with iron and manganese hydroxides. Rocks of this horizon are characterized by wavy-banded stromatolitic algal structure and the presence of carbonate oncolites up to 22 mm across. Its total thickness is no more than 3–3.5 m.

All horizons are characterized by small thickness, strong facies variability, frequent shrinkage cracks, zoned layering, and biomorphogenic structures and textures. All these features indicate the existence of hot arid climate during the formation of the Chulakta Formation.

The great transgression in the upper Lower Cambrian produced thick sequences of phosphate-free dolomites and limestones of the Shabakty Formation, which are associated with carbonate platforms (Kholodov, 1999).

MATERIAL AND TECHNIQUE

Data used in this work were obtained during long-term investigations at different objects of the Lesser Karatau. Pellets from profile I–VI (Figs. 1a, 1b) including all type sections of the productive formation were taken for electron microscopic study. Approximately 50 samples were taken from the Baba Ate, Gerese, Koks, Akdzhar, Dzhan, and Kyrshabakty sections (Fig. 1). The most complete section is observed at the Koks deposit (Fig. 1, section III). The section contains three phosphate units separated by carbonate-siliceous shales and mainly composed of carbonate and monomineral phosphorites (phosphate pellets in phosphate material). The Geres deposit (Fig. 1b, II) includes a thick monotonous sequence of carbonate phosphorites with negligible siliceous horizon and shales. The Akdzhar deposit (Fig. 1b, IV) comprises a thick unit of intercalating cherts, carbonate-siliceous phosphorites, and shales. The Dzhan phosphate occurrence (Fig. 1b, V) includes a reduced section of the Chulakta Formation with the major siliceous horizon and productive horizon composed of siliceous and carbonate-siliceous phosphorites. Horizons of the Baba-Ata (Fig. 1b, I) and Kyrshabakty (Fig. 1b, VI) areas are characterized by extremely reduced thickness and abundance of clastic material, suggesting their formation in a shallow-water

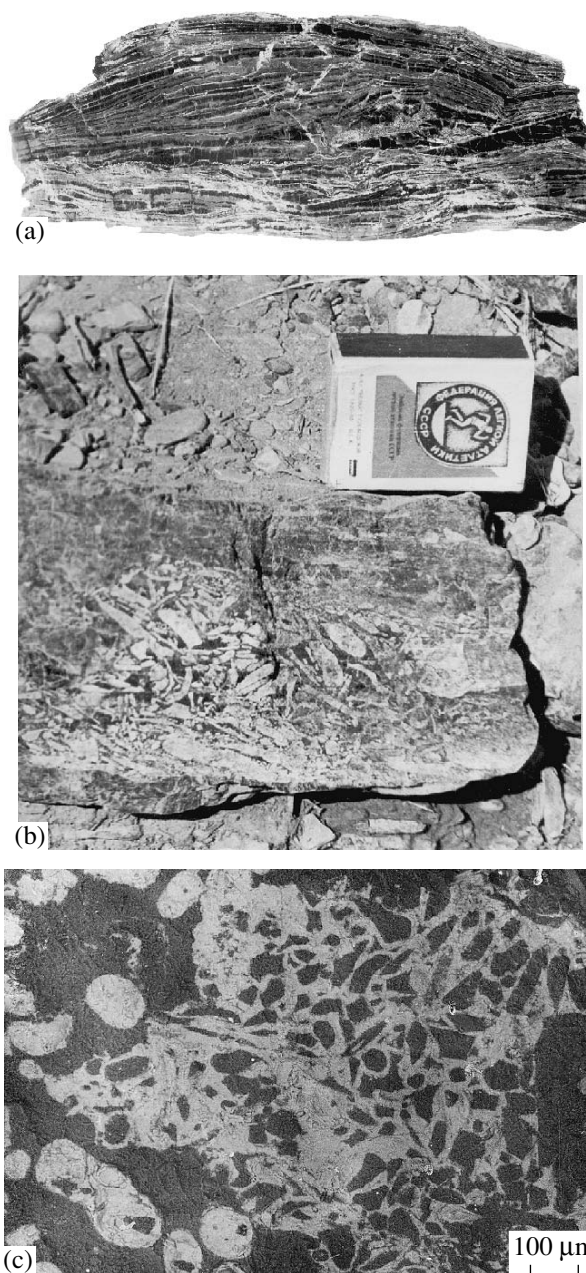


Fig. 2. Phosphate-siliceous bed at the base of siliceous horizon of the Chulakta Formation ("basal" horizon, Dzhan River). (a, b, c) Basal horizon: (a) thin laminated with characteristic curving of beds, (b) stromatolitic algal structure, (c) reticulate microstructure of the rock under electron microscope (phosphate-carbonate pellets are light, silica is dark).

tidal setting. The more detailed lithofacies analysis of horizons of the productive formation is given in (Tabyldiev and Cherbyanova, 1976; Eganov and Sovetov, 1979; Kholodov and Paul, 1996, 1999; Litvinova, 2000, and others).

Study with the scanning electron microscope was carried out after the examination of polished thin sec-

tions with the consideration of the following fact: we can distinguish the constituents of rocks under microprobe by their chemical composition but not by optical properties. Therefore, pellets in the phosphate cement or phosphorites composed of cement-free pellets were considered a single homogenous field. We deliberately avoid acid etching because of the following reasons: first, researchers from the Paleontological Institute (Russian Academy of Sciences) have performed (and are continuing) similar works; second, we believe that this method slightly distorts and complicates the morphology of particles, thus preventing their study; third, the etching of rocks completely obliterates the distribution of chemical elements in pellets.

The study of polished thin sections allowed us to select samples of carbonate and siliceous phosphorites with pellets of different morphologies. However, the microparticles could be cut off during sample preparation or are invisible under electron microscope owing to their identical composition with host rocks. High resolution of electron microscope changes the appearance of rocks. Therefore, some selected samples were discarded in the case of the analysis of rocks. We studied transparent and opaque thin sections and rock specimens. As opposed to thin sections, specimens provide an opportunity to study relief and a larger area. However, sample preparation in this case is a more laborious and long procedure.

The samples were studied on a Comscans scanning electron microscope equipped with EDS LINK-860 (analysis area 1 μm , light matrix sensibility 0.001%). This device allows one to determine virtually all trace elements, except organic matter, because thin sections and specimens are preliminarily sputtered with graphite. We used both uncovered thin sections and specimens cut across the required surface. Samples prepared within a day were placed in vacuum apparatus, and air was evacuated. The duration of evacuation depends on the porosity of material: on the average, up to 30 min for thin sections and 1 to 3 h for rock specimens. Using electron microscope, we studied pellets, their structure, distribution of chemical elements in them, and composition of host rock.

COMPOSITION AND MORPHOLOGY OF PHOSPHATE PELLETS

The study of pellets from different objects of the Lesser Karatau showed that phosphorites of the basin include several types of microparticles. Figure 3 demonstrates all morphological types found in the pellets and their composition.

The morphology of many microparticles presented below is close to the detailed description based on the optical study of thin sections. Results of electron microscopic study confirmed morphological features of microparticles based on the study of thin sections and conservatism of most forms noted in (Kholodov and

Paul, 1993, 1995, 1999). In addition, these researches provided new insights into the internal structure of pellets and the distribution of chemical elements in them.

Let us consider the structure of pellets in detail. They occur as rod-shaped, conical, oolitic (with numerous phosphate shells), oval, dumbbell-shaped, triangular, box-shaped, cubic, hexahedral, ellipsoid, and circular, varieties. One can also see intricate particles with several pellets rimmed by a common shell (Fig. 3).

All these pellets have rounded outlines and distinct patterns owing to the stability and rigorous differentiation of their chemical composition (Fig. 3). The pellets are always composed of phosphorous and calcium oxides (19 and 39%, respectively) incorporated in the crystal lattice of F-apatite $\text{Ca}(\text{PO}_4)_2\text{F,OH}$. The exception is rod-shaped microparticles (probably, sponge spicules), which can consist of both phosphate and siliceous material. The pellets strongly resemble microorganisms typical of sediments of the Vendian–Cambrian and older age. In Fig. 4, each pellet is shown together with morphologically similar microbial–algal organisms or others.

Phosphate pellets can arbitrarily be subdivided into three groups. The first group includes microparticles represented by phosphate sheath (or shell) of variable shape. The composition of internal part of these pellets and enclosing material (silica or dolomite) are always identical (Fig. 3). They have oval (Fig. 4p), rounded (Fig. 4b), rounded-square (Fig. 4c), dumbbell-shaped (Fig. 4d), triangular (Fig. 4q), or cubic (4r) shape. The phosphate sheath of this group also has different morphologies (Fig. 3). Usually, each pellet has a single monolithic shell with constant thickness from 5 to 10 μm thick (Figs. 4b, 4c, 4d). Some particles have two shells. The sheath of some rounded pellets is composed of tiny rounded granules (Fig. 5h). Triangular and cubic microparticles are rimmed by shells with fine fibrous structure: tiny filaments are rimmed by fragments of carbonate or silica crystals (Figs. 4a, 4q, 4r). The phosphate shell is 20–40 μm thick. Filamentary sheaths could be remains of one or several oscillatory cyanobacteria (Sergeev, 1992). Round (Fig. 4b) and oval (Fig. 4p) pellets with monolithic shell are morphologically similar to the so-called empty crusts (Fig. 4b') or hollow phosphate sheaths (Fig. 4p') obtained during experimental study of fossilization (Westall and Walsh, 2002; Gerasimenko and Ushatinskaya, 2002b). These experiments showed that trichomes can quit an unfavorable environment (for example, high phosphorus contents) and the retained phosphate shells can be very similar to pellets of the first group (Figs. 4b, 4p). This is consistent with conclusions of other researchers indicating that deepening of basin during the formation of the lower phosphate bed led to the replacement of the littoral facies by the deeper-water varieties (Kholodov and Paul, 1999). The authors suggested that the H_2S pollution of acid-bearing marine waters was accompa-

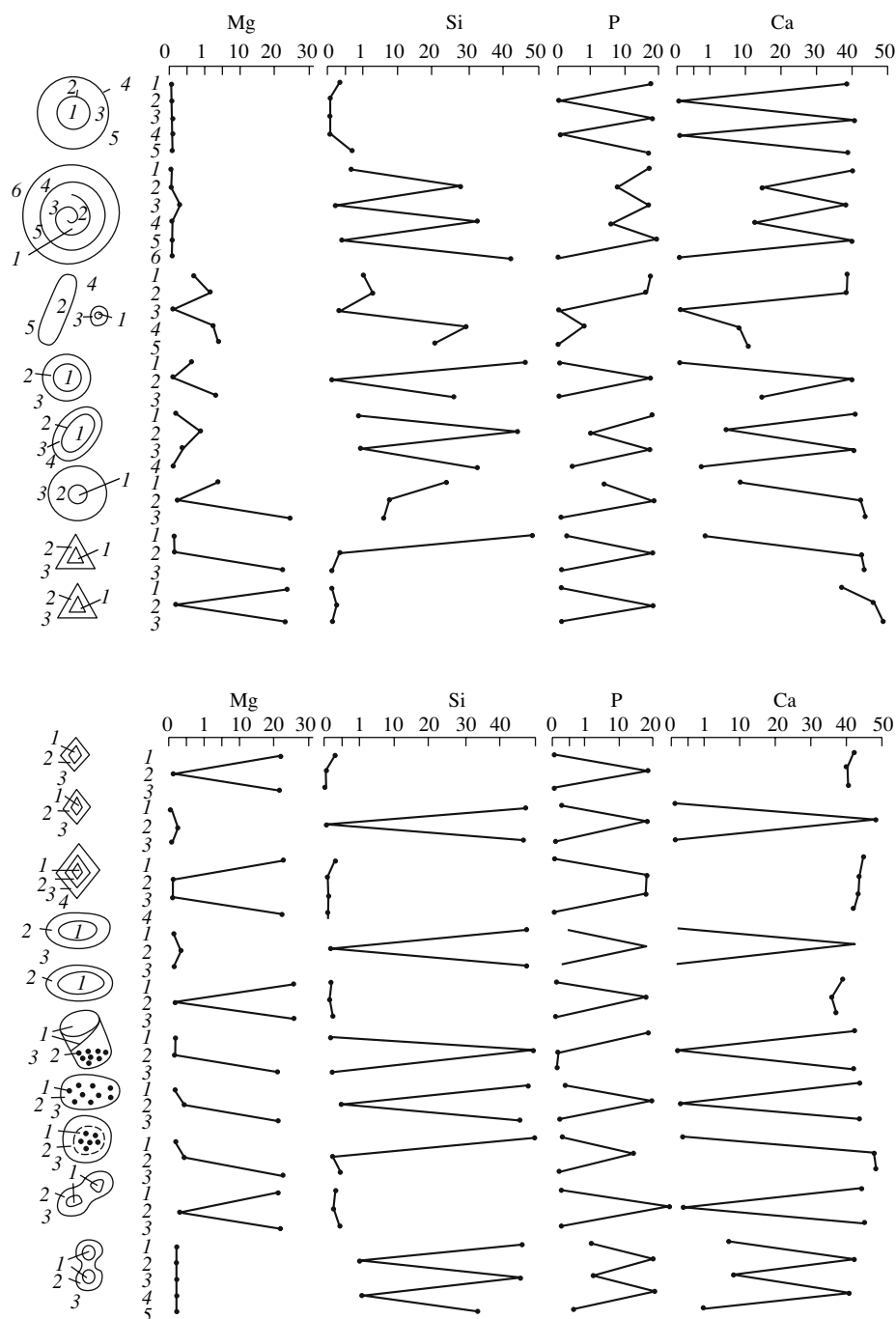


Fig. 3. Major element distribution (%) in the pellets and host rocks. (1) Inner core of the pellets, (2–9) shells of pellets and host rock.

nied by the rearrangement and suppression of microbial–algal biota.

The second group includes pellets that are completely composed of phosphate mineral. They are characterized by conical and ellipsoidal microparticles, pellets with numerous phosphate sheaths, helical, rod-shaped, rounded, and oval pellets similar to those in the first group. The conical microparticles are up to 200 μm long (Fig. 5a). Ellipsoidal pellets are typically 90 μm

across (Fig. 4f). Since the pellets are separated from host rocks by silica sheath, they are well recognized even within monomineral phosphorites. Pellets often contain loosely distributed conical and ellipsoidal silica spherules (Fig. 4e). In terms of size, composition, and morphology, they are identical to microfossil colonies (Fig. 4e") reported from Vendian rocks in the Chichkan Formation of the Lesser Karatau (Sergeev and Ogurtsova, 1989).

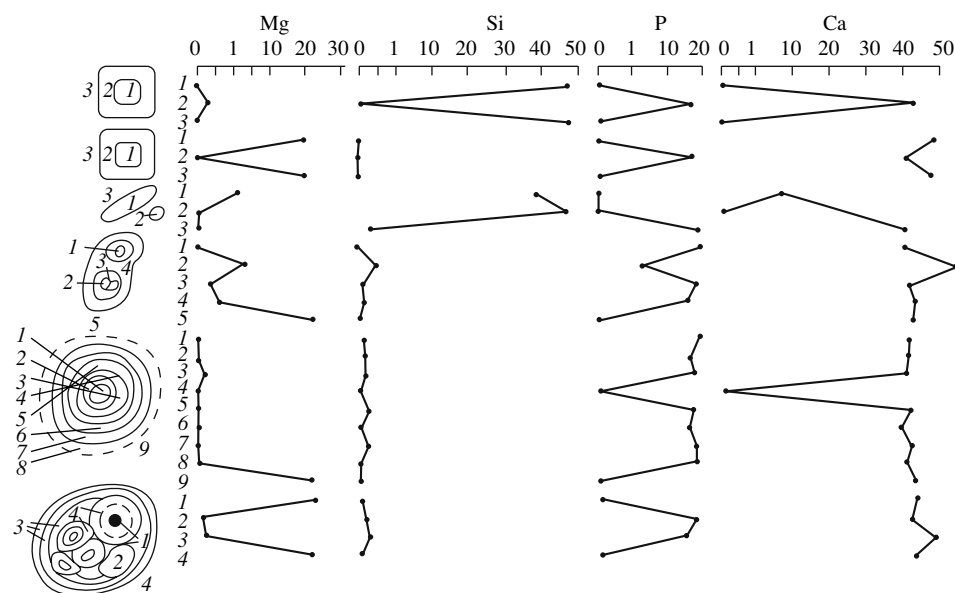


Fig. 3. (Contd.)

Microparticles previously termed as oolites (Zavartskii, 1929; Tushina, 1960; and others) have a very interesting internal structure. They are composed of numerous shells (up to 10 specimens) of similar or almost similar thickness (Fig. 4n). Space between the shells can be filled with silica oxide, and each spherule can contain a lesser spherule in line with the “matreshka” principle (Kholodov and Paul, 1999), i.e., stepwise change in particle growth. In our case, such spherule-in-spherule structure can be observed within a single form. Pellets of this type are subdivided into symmetric (70 μm across) and asymmetric subtypes. The symmetric pellets typically occur as agglomerate of three to six pellets of the matreshka type. The asymmetric larger (120 $\times$ 140 μm) pellets are scattered among particles of different morphologies. The electron microscopic study confirmed that pellets of the oolith type are subordinate (Litvinova, 1991).

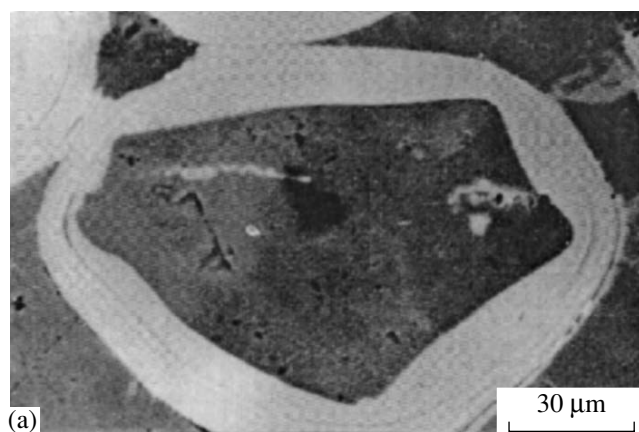
The morphology of helical particles strongly differ from that of pellets with numerous shells of similar thickness: the diameter of their outer sheath gradually increases (Fig. 4m).

Oval microparticles (70 $\times$ 120 μm) can be monolithic or characterized by complex internal structure (Figs. 4k, 4l). One can often see footprint-shaped pellets with peculiar structure (Fig. 4l). Rod-shaped microparticles (10 $\times$ 30 μm) are very similar in appearance (Fig. 4i) to sponge spicules, with the central part representing a hollow channel well seen both in transverse (Fig. 4j) and longitudinal sections.

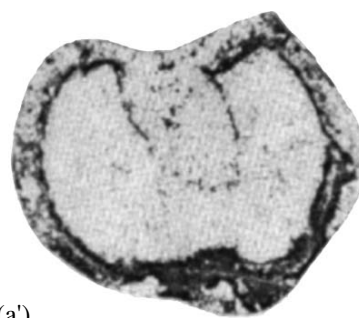
The third group includes complex particles subdivided into two types. The type represents particles consisting of several pellets (from 2–3 to 8–9 specimens) with a common shell (Fig. 4g). The size of these particles is 180 $\times$ 200 μm or more depending on the number and dimension of constituent microparticles. The second type is observed as large pellets (up to 200–220 μm across) with numerous identical spheroidal microparticles (Fig. 4o), the internal structure of which is distinguished by very thin carbonate rims. These pellets approximate palmelloid coccoidal colonies of microfossils (Fig. 4o') described in (Sergeev, 1992).

The shape, size, structure, and, occasionally, composition of the pellets are similar to the microbial–algal and other organisms (Fig. 4) reported from Vendian–

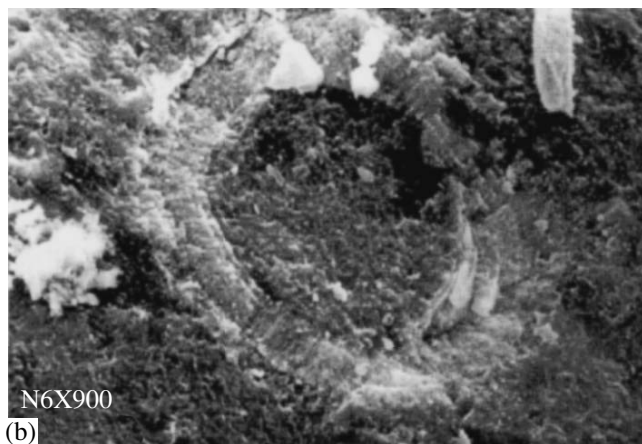
Fig. 4. Comparison of pellets and microorganisms. (a–r) Phosphate pellets of diverse morphology; (a'–p') microorganisms similar in structure to phosphate pellets: (a') *Fransuasuocyathu subtumulus secundus*, Zhur. (Rozanov and Missarzhevskii, 1966), $\times 19$; (b') empty crust obtained during experimental fossilization of bacteria, scale 0.2 (Westall and Walsh, 2002); (c') *Trachyhystrichosphaera* cf. magna Allison, 1989, scale 50 μm (Sergeev, 1992); (d') *Tetraphycus ampilus* Golovenok et Belova (figure) (Sergeev and Ogurtsova, 1989); (e') *Lapworthella* cf. nigra Cobbold, $\times 100$ (Rozanov and Missarzhevskii, 1966), $\times 6$; (e'') *Tetraphycus ampilus* Golovenok et Belova, scale 10 μm (Sergeev and Ogurtsova, 1989); (f') *Trachyhystrichosphaera* cf. magna Allison, scale 50 μm (Sergeev, 1992); (g') sketch of a pair of spheroids of coccoidal microfossils (Sergeev and Ogurtsova, 1989); (h') *Eogloeocapsa avzyanica* Sergeev, scale 10 μm (Sergeev, 1992); (i') *Archaeoellipsoides grandis* (Sergeev, 1992), scale 50 μm ; (j') *Tomocyathus Kundatus* Roz., $\times 2.5$ (Rozanov and Missarzhevskii, 1966); (k') *Obruchevella parva* Reitlinger, scale 10 μm (Sergeev and Ogurtsova, 1989); (l') *Membranacyathus reptitae* Roz., $\times 5$ (Rozanov and Missarzhevskii, 1966); (m') nitrifying bacteria *Nitrobacter* sp., complete cell, STM $\times 10000$ (Vorob'eva et al., 2002); (n') sketch of multishell single spheroid (Sergeev, 1992); (o') palmelloid colonies of coccoidal microfossils (Sergeev, 1992); (p') hollow phosphate sheath of *Microcoleus* left by trichome (Gerasimenko and Ushatinskaya, 2002a).



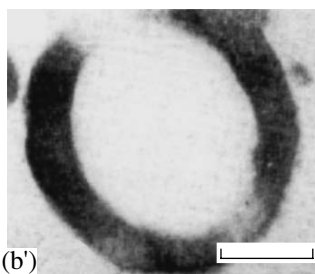
(a)



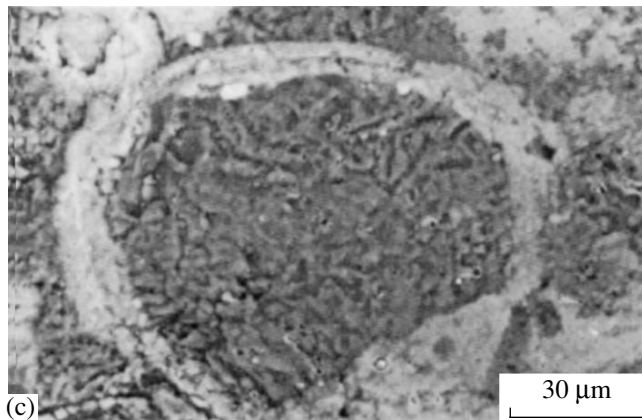
(a')



(b)



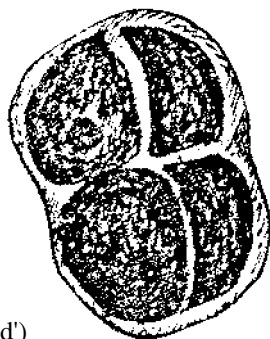
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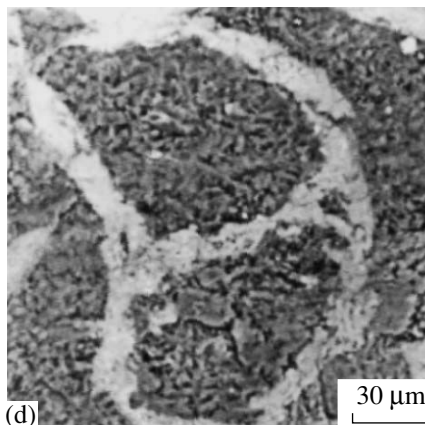
(c)



(c')



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(d)

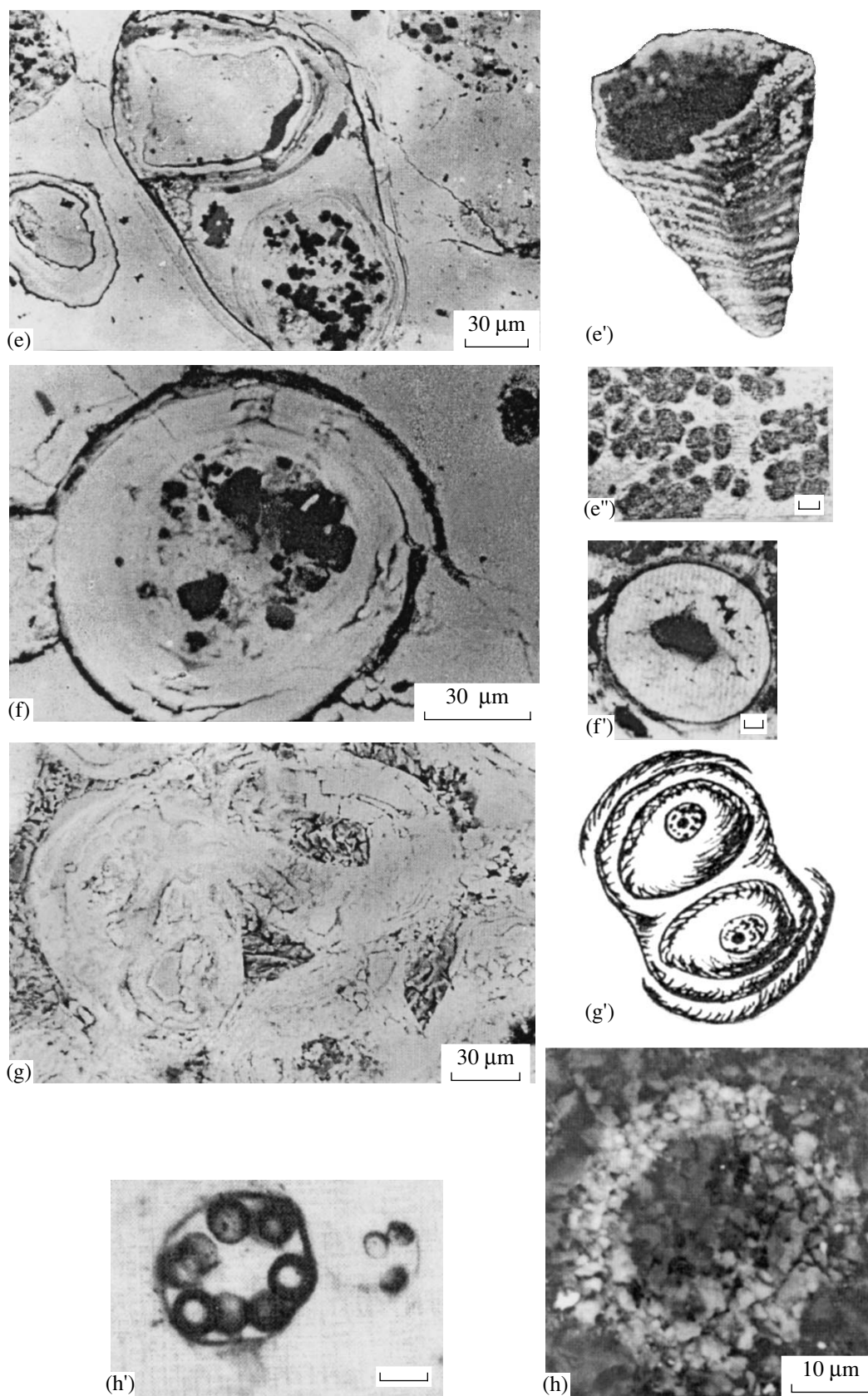
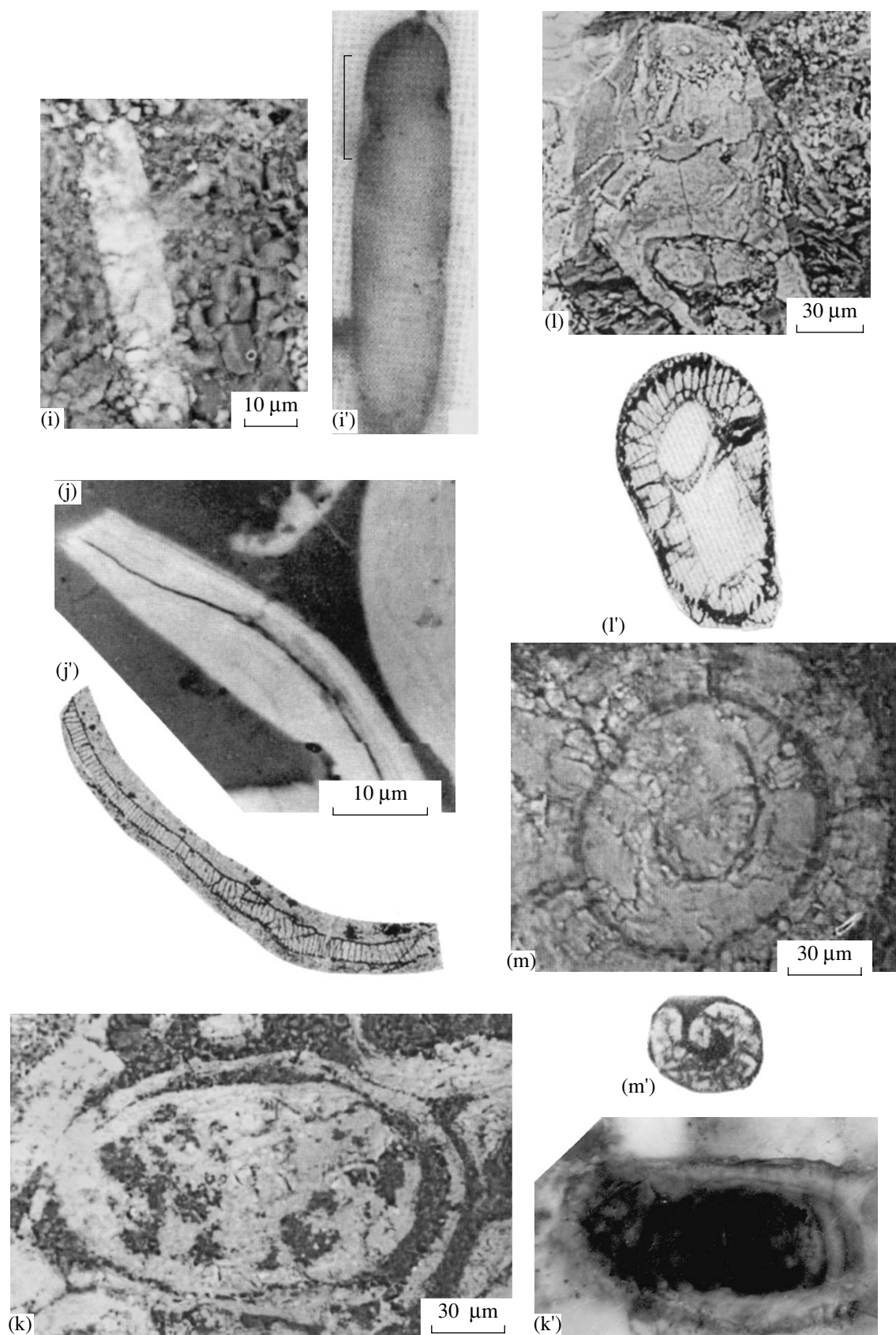


Fig. 4. (Contd.)

**Fig. 4.** (Contd.)

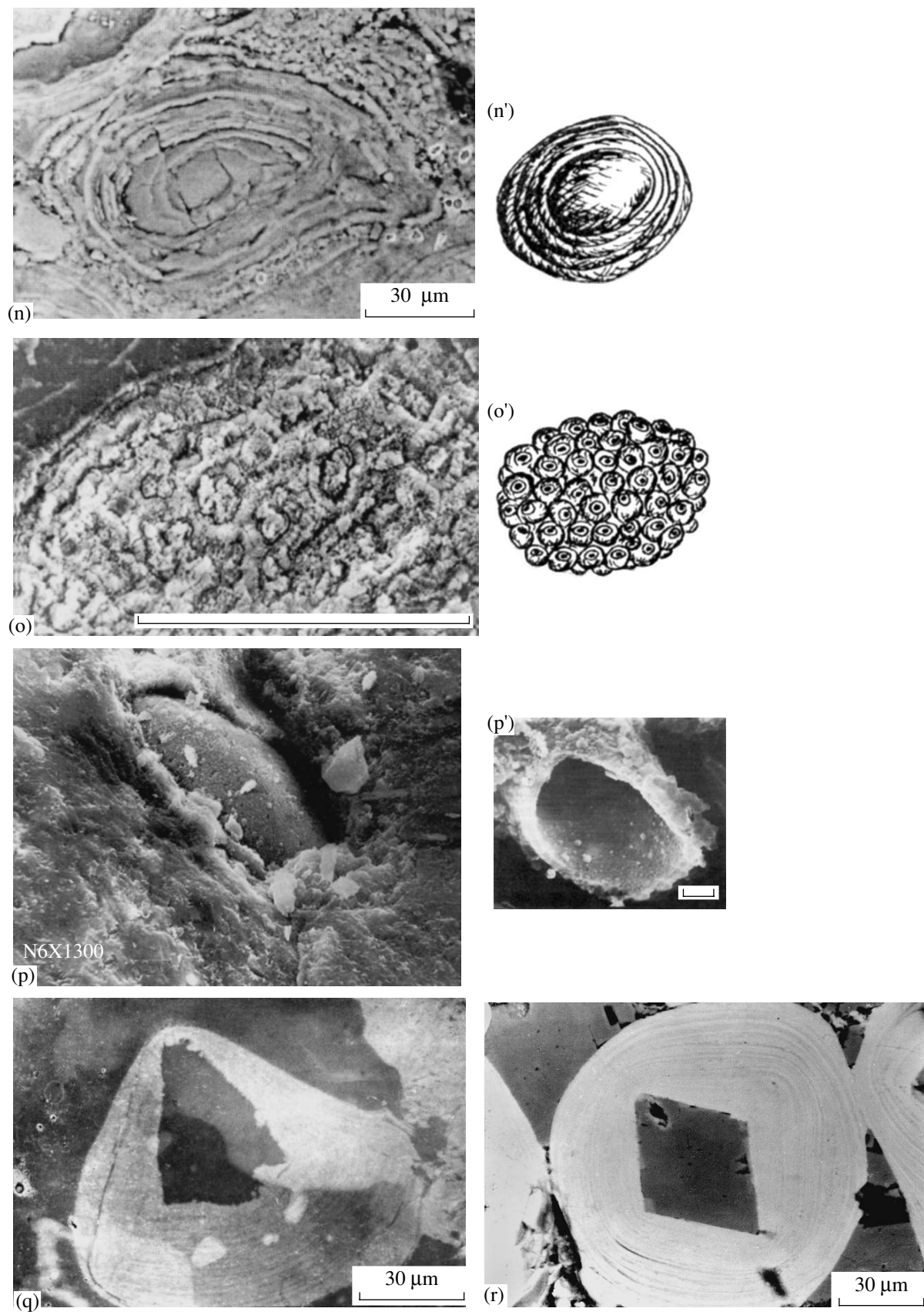


Fig. 4. (Contd.)

Cambrian rocks of the Lesser Karatau (Rozanov and Missarzhevskii, 1966; Sergeev and Ogurtsov, 1989; Sergeev, 1992; Vorob'eva et al., 2002; Westall and Walsh, 2002).

DISTRIBUTION OF PHOSPHATE PELLETS IN THE CHULAKTAU FORMATION

Phosphate pellets are unevenly distributed over the productive formation. They are scanty in the "lower" dolomite, siliceous, and ferromanganese horizons. Moreover, they are characterized by simple structure and small size ($<30\text{ }\mu\text{m}$). In contrast, they are abundant and morphologically diverse in the "basal phosphorite" (or biostrome), which separates the Berkuta and siliceous horizons, and the phosphate gravelstone bed in the upper part of the productive horizon. The pellets are embedded in the siliceous matrix of the basal phosphorite and in the carbonate matrix of the phosphate gravelstone bed. Noteworthy is the evident similarity of pellet colonies in two thin layers virtually extending over the entire basin. The pellet layers mark the onset and termination of the Tommotian phosphate accumulation. Both these layers formed in a shallow setting at the regressive stage of basin evolution. The basal horizon is distinguished by the abundance of rod-shaped microparticles of both phosphate-carbonate and siliceous compositions. The siliceous horizon contains only silica rod-shaped particles, while the phosphate horizon contains phosphate-carbonate pellets.

The distribution of pellets is also irregular in phosphorites of different compositions. For example, increase of silica content in the host rock is accompanied by decrease in the number of microparticles and their size (up to $80\text{ }\mu\text{m}$). However, both the number and size of microparticles remain stable. These rocks often contain multishell pellets characterized by identical sizes ($70\text{ }\mu\text{m}$ across) and traces of erosion and washout in the host rocks. They typically form a single community with 6–10 specimens within the thin section area. The siliceous phosphorites virtually lack complex microparticles, which are abundant in the carbonate and especially monomineral phosphorites. The lesser abundance and smaller dimension of the pellets in these rocks are presumably related to the lower P_2O_5 content as compared to carbonate phosphorites.

Relatively large asymmetric multishell pellets ($\sim 200\text{ }\mu\text{m}$ across) are typically embedded in the carbonate cement. Complex aggregates (i.e., pellets with several microparticles of different structures fringed by a common shell) are most typical of the high-grade phosphorites in thick sequences of the Koksui and Akdzhar types.

Other types of pellets occur elsewhere within the entire phosphate horizon. The most abundant among them are rounded, oval, and rounded-square microparticles, which could be completely or partly (only sheath) composed of phosphate-carbonate material

compositionally identical to that of the host rock. It is worth noting that the rounded and oval microparticles occur in the entire section, whereas the rounded-square variety is confined to the lower phosphate horizon. Pellets in the productive horizon vary in size from 30 to 120 micrometers. Study of microparticle distribution in the phosphate horizon showed that the largest pellets are confined to its upper part (Kholodov and Paul, 1999). The authors also noted that simple forms are most widespread (46.9%), whereas complex pellets are subordinate.

Monomineral phosphorites typically occur as microscopic lenses and layers in the carbonate-phosphate sequences, and their content can reach 70 vol % at some deposits. Two types of phosphorites are rhythmically alternated in the sequence. Type 1 sequence is observed as thin intercalations of closely spaced pellets and carbonate phosphorites, which are composed of pellets and carbonate material (up to 35%). Type 2 sequence represents intercalations of pellets and pelitic phosphorites of variable thickness (0.1–6 mm). Such microzoning of rocks and structural features of pellets allow us to consider these phosphorites as fragments of bacterial-algal mats. Monomineral phosphorite beds are abundant in the Koksui and Akdzhar sections and subordinate in other sequences of the considered profile (Fig. 1b).

The ferromanganese horizon contains large (up to 25 mm) carbonate pellets (oncolites) of controversial genesis. They are interpreted as chemogenic (Rodionova, 1974) or as phytoliths (Eganov et al., 1997) formations. Kholodov and Paul (1999) believe that the oncolites are related to increase in size and amount of algae shells. Multishell pellets (ooliths) and carbonate pellets (oncolites) are characterized by identical morphology under electron microscope (Litvinova, 1998).

RESULTS AND DISCUSSION

The morphological similarity between phosphate pellets and microbiota in the Precambrian-Cambrian boundary sequences (Fig. 4) attests to the genetic affinity of their formations. The distribution of microparticles of certain morphology over the entire section, the confinement of individual types of pellets to a definite section, and the wide development of microzoned structure serve as evidence of their organogenic-sedimentation origin (Gerasimenko et al., 1999). The pellets presumably represent accumulations of organisms, which concentrated phosphorus and calcium oxides after death. The compositional stability of siliceous, carbonate, and monomineral phosphorites and the preservation of internal structure attest to a high rate of fossilization of phytoplankton (just a few hours). Otherwise, the phosphorites would acquire a different appearance, while the composition of pellets would be complicated and variable like that of the host rocks. Virtually instantaneous posthumous fossilization of cyanobacteria is confirmed by experimental data

(Lucas and Prevo, 1984; Gerasimenko and Ushatinskaya, 2002b).

The first significant influx of phosphorus to the sedimentation basin in the early Tommotian generated a microbial–algal colony, which produced the basal phosphorite–biostrome unit at the base of the siliceous horizon.

A short-term cessation of phosphorus influx in the northwestern Lesser Karatau did not terminate the bios evolution, as indicated by the presence of numerous stromatolitic buildups in the siliceous horizon (Eganov, 1988; Litvinova, 1990). Plankton is only represented by rod-shaped pellets (presumably, sponge spicules) composed of silicon oxides and by single small rounded phosphate microparticles with primitive structure. Other types of pellets are absent.

The next (more prolonged) stage of phosphorus influx to the Lesser Karatau basin occurred during the formation of the productive horizon. A significant increase in phosphorus concentration in the shallow, well heated basin simulated the development of bios. Investigations devoted to the purification of basin from phosphorus with the help of bacteria demonstrated that phosphorus serves as nutrient for the bios (Mino, 2000).

The periodical extinction of bios was related to the following reasons: (1) time factor, i.e., natural biological death; (2) influx of excess phosphorus, which is unfavorable for the vital activity of organisms; and (3) H_2S pollution of the basin in the case of decomposition of too large amounts of bios.

Let us consider the effect of each of these factors in detail.

(1) Increase in the phosphorus content provoked the death of plankton. The H_2S pollution in bottom waters related to the natural extinction of even a large amount of plankton does not affect significantly the vital activity of organisms dwelling in the surface water. At present, this process can be observed in the Black Sea, where organisms can flourish in the upper zone, although the H_2S -polluted deep zone is lifeless.

(2) In the case of intense influx of phosphorus to the basin, the phosphorus is accumulated in cells in 3 h, and this process is completed in one day (Gerasimenko et al., 1999). Bacteria can accumulate a great (but limited) amount of phosphorus (Mino, 2000). According to experimental data (Gerasimenko and Ushatinskaya, 2002a), cell can accumulate the maximal amount of phosphorus if the P content in water is 18–36 mg/l. If the P content decreases, the growth of bacteria also decreases up to the point of complete cessation. This phenomenon is presumably responsible for the tiny dimension of phosphate pellets in siliceous and ferromanganese horizons. However, extreme concentration of this element leads to the accumulation of intracellular phosphorus instead of the growth of biomass. In this case, the phosphate material does not enter the tri-

chomes. They either die or abandon the deadly shelter and rapidly migrate toward the light, where they can attempt to regain the phosphate–carbonate sheath. Such sheaths can develop repeatedly around the same species (Gerasimenko and Ushatinskaya, 2002a). Phosphate sheaths are left if the trichomes quit the shelter. Both the internal part of such phosphate sheaths and the host rock have similar compositions (Figs. 4a–4d). If the trichomes die away, the internal part of the sheath is further filled with the phosphate–carbonate material, resulting in the formation of oval or rounded structureless pellets that are widespread in phosphorites.

(3) Cyanobacterial community consisting of diverse bacteria is an integral complex system. Its vital activity generates an aerobic–anaerobic setting in the basin. The photosynthesis of cyanobacteria promotes high oxygen content in the upper layers of mat and the simultaneous generation of H_2S in the internal part (Gerasimenko et al., 1999). Such a layering could occur within a few millimeters, resulting in the formation of geochemical barrier, changes in pH and Eh values, and the ultimate precipitation of sediments.

During the accumulation of the phosphate horizon, closed or semiclosed basins of the Lesser Karatau type served as sedimentation traps (Gerasimenko et al., 1999). Moreover, the initial influx of phosphorus led to bloom of biomass, whereas the subsequent excess of this element caused death of colonies. History of the vital activity of cyanobacterial community is traced very well in the microzoning of phosphorites. The aerobic–anaerobic setting is distinctly recorded in the rock as alternations of thin layers of hollow pellets, microparticles filled with phosphate–carbonate material, and layers of pelitomorphous phosphorite formed after the decomposition of necromass.

The amount of pellets, as well as their evolution and growth, are directly related to the phosphorus content in water. Judging from the considered profile, the maximal flux of phosphorus is traced in the Koksuy section area (Fig. 1, section III) containing monomineral phosphorites (Fig. 1b, section II). Carbonate pellets (Geres River) occupy an intermediate position in terms of the quality of phosphorites and the amount of pellets. Increase in the siliceous material (Dzhilan River) is accompanied by decrease in the P_2O_5 content. The thick intercalation of cherts, carbonate–siliceous phosphorites, and shales of the Akdzhar deposit (Fig. 1b, IV) appeared in the deepest part of the paleobasin. The formation of such deposits was promoted by constant water flows that delivered the silty–muddy material. The distribution of pellets is extremely irregular in sections of this type, because the carbonate–biogenic sedimentation periodically gave way to precipitation of the terrigenous–chemogenic material, resulting in dilution of phosphates by the terrigenous component.

Intense shallowing of the basin led to the formation of a thin ferromanganese horizon and virtual termination of the influx of phosphate material. However, stro-

matolitic algal structure of the horizon attests to a significant role of bios during its formation.

CONCLUSIONS

1. Phosphate material was intensely delivered to warm shallow well-aerated basin within a relatively short period of geological time (Barenbaum and Litvinova, 2002). The presence of phosphorus provided a favorable setting for the bloom of bios. This environment was also essential for vital activity of the microbial–algal colony.

2. The abundance and diversity of biogenic micro-particles (pellets) in the entire Chulaktau Formation indicate that the cyanobacterial community was a complex system of interaction between various bacteria (Zavarzin, 2002; Gerasimenko et al., 1999) and other associated microorganisms. Phosphates supplied the essential resources and provided the bioenergetic processes in bacterial mats.

3. Photosynthesis of cyanobacteria and other organisms provided an aerobic–anaerobic setting in the basin. During the aerobic stage, bacteria accumulated phosphate, which was removed during the anaerobic stage by the hydrolysis of intracellular polyphosphates with the consumption of glucose. This process provided energy for the reworking of previously released phosphate (Mino, 2000). With the growth of culture, the pH value increased to 9–9.6 in the photosynthesis zone reduced to 7 below the 1-mm zone (Gerasimenko and Ushatinskaya, 2002a), and remained unchanged in the internal part of cyanobacteria (Merz et al., 1993). The appearance of geochemical barrier fostered the precipitation of sediments, and extremely low permeability of mats prevented the dilution of material.

4. Periodic anaerobic postmortal decomposition of necromass fostered a significant increase of phosphorus content at the water–sediment interface and the precipitation of phosphate sediments, which were later transformed into thin interlayers and films of pelitomorphous phosphorite often observed in thin sections. Anoxic setting could arise fairly often at the bottom in different parts of the shallow-water basin.

5. Very fine differentiation of silicon, calcium, and phosphorus oxides in the pellets and their steady composition attest to virtually instantaneous posthumous fossilization of cyanobacteria due to the further concentration of phosphorus in water. The mineral sheath of pellets is continuous and phosphorus is often present in the internal of many cells. Hence, the P content in water was very high.

6. This scenario is also valid for other Lower Cambrian (Tommotian) phosphate-bearing basins, which served as sedimentation traps. Thus, the stratified fine-grained phosphorites are composed of phosphate pellets, which initially represented a colony of intricate bacterial–algal and other organisms. They inhabited shallow-water seas of the lagoonal (or semilagoonal)

type and played a decisive role in the formation of microzoned structure of rocks. This conclusion is consistent with lithological, paleogeographic, and paleontological data on the Lesser Karatau and other Lower Cambrian (Tommotian) phosphate-bearing basins.

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