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The Khubsugul Phosphate-Bearing Basin: New Data and Concepts

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Abstract—The Khubsugul phosphate-bearing basin divided into the western and eastern zones. Phosphorites composed of alternating structureless phosphate layers (1–3 cm) and thinner lenticular dolomite laminae prevail in the western zone corresponding to the distal part of the sedimentation profile. Contents of all trace elements are approximately equal and correspond to the clarke level in both phosphate and dolomite layers. The laminae are also identical in terms of the low (–7‰ PDB) $\delta^{13}C$ values. Phosphorites of the western zone were rapidly buried and the presence of dolomite intercalations is explained by postsedimentary segregation. The eastern proximal zone is dominated by the so-called dolomitic phosphorites with variable-size irregular fragments of phosphate matter enclosed in the later dolomitic matrix. Relative to structureless varieties, granular (pelletal) phosphorites of the basin are subordinate and enriched in trace elements (particularly, rare earth elements). Phosphate facies are replaced by black shales on the western side of the basin.

The comprehensive study of the Khubsugul phosphate-bearing basin (KHPB) began in the 1970s–1980s soon after its discovery. It was carried out in the framework of the Joint Soviet–Mongol Expedition pioneered and headed by Yanshin (1986). Main phosphorite deposits were prospected during this period (Osokin *et al.*, 1973). Works by Byamba (1996) played a significant role in the investigation of the basin and assessment of the phosphorite potential of Mongolia. The study of the basin was carried out simultaneously with works in the framework of the IGCP "Phosphorites" project. One of its field excursions was dedicated to the Mongolian phosphorites (*Putevoditel'*..., 1980). The participation of Russian geologists in works on this project made it possible to apply the wealth of experience accumulated in other regions of the world to the study of KHPB phosphorites.

Data on the Khubsugul Basin were significantly refined and supplemented with new materials in the last 10–15 years. This period was marked by the assessment of the role of microbial processes in the phosphorite formation (Zhegallo *et al.*, 2000), the elaboration of a new concept of the nature of phosphate grains (Kholodov and Paul, 1995), and investigations of the isotopic composition of strontium, carbon, and oxygen, as well as geochemistry of trace elements in phosphorites of the KHPB and other ancient basins (Ilyin and Volkov, 1994; Ilyin, 1998, 2002). New data on the Late Precambrian–Cambrian tectonic evolution of the southern Siberia–northern Mongolia region (Khain and Rudakov, 1995; Kuz'michev, 2001) were of key significance for the paleotectonic and paleogeographic interpretation of the KHPB evolution.

This period was also marked by a significant progress in the study of phosphogenesis, in general (Garrison and Kastner, 1990; Glenn *et al.*, 1994; and others), and ancient phosphorites, in particular (Shields *et al.*, 2000). These achievements have not yet been sufficiently comprehended relative to the Khubsugul Basin. This basin is less scrutinized in some aspects relative to other cognate ancient basins of Africa (Flicoteaux and Trompette, 1997) and Asia (Banerjee *et al.*, 1997). Studies of these basins showed that intense phosphogenesis was one of the links in the chain of interrelated geological (paleogeographic, tectonic, climatic, and biological) processes in the early Phanerozoic (Ilyin, 2000).

The aim of the present communication is to analyze and interpret new (published and unpublished) data on the Khubsugul Basin on the basis of experience of the study of other ancient phosphate-bearing basins.

BRIEF GEOLOGICAL CHARACTERISTIC

Phosphorites of the Khubsugul Basin are confined to the Khesen Formation composed of various siliciliths, black shales enriched in organic carbon, and other biogenic rocks. The Khesen Formation is a member of the thick (no less than 3 km) Khubsugul Group (Ilyin, 1973) of the upper Vendian– Middle Cambrian carbonate (mainly, dolomitic) rocks (Korobov, 1980; Terleev, 1998). In the KHPB area, the Khubsugul Group is spatially associated with the terrigenous rocks of the Darkhat Group. The boundary between these groups is marked by glacial sediments (*Putevoditel'*..., 1980; Kuz'michev, 2001) and an ancient weathering crust that preceded the formation of the Khubsugul Group (Kuz'michev, 2001).

Tectonic Position and Basement of the Basin

In terms of tectonic structure, the Khubsugul Basin belongs to the Tuva–Mongolian Massif (Ilyin, 1971), which, in turn, is a constituent of the Caledonian Sayan–Baikal foldbelt (Kuz'michev, 2000). In the Late Riphean, the Tuva–Mongolian Massif represented a microcontinent spatially isolated from other continental terranes and the Siberian Platform. The massif slightly consolidated as a result of the Late Baikalian orogeny. In the Vendian–Cambrian, the study area accumulated carbonate sediments and transformed into a carbonate platform that was still separated from the Siberian continent by a spacious ocean (Kuz'michev, 2001). The Tuva–Mongolian Massif joined the Siberian Platform as a result of collision related to the Salairian orogeny (Khain and Rudakov, 1995). Subsequently, together with the Dzabkhan, Central Mongolia, and other microcontinents, the Tuva–Mongolian Massif made up the Caledonian Sayan–Baikal fringing of the Siberian Platform. Thus, former concepts on the paleogeographic integrity of the Siberian continent and Tuva–Mongolian Massif in the Vendian–Cambrian (Zaitsev and Ilyin, 1970; Ilyin, 1991) are now disproved. Consequently, ideas of direct genetic relations between evaporites of the Siberian saliferous basin and phosphorites of Mongolia appear to be invalid.

As was shown (Kuz'michev, 2001), the pre-Vendian KHPB basement is heterogeneous (Fig. 1). This is reflected in both the distribution and dislocation pattern of phosphorites. Archean (?) granulites of the Gargan Block located immediately north of Lake Khubsugul represent the oldest (Rb–Sr age >800 Ma) component of the basement. Vendian–Cambrian sediments of the carbonate platform are underlain over a large area by graywackes and volcanics of the Oka Group (Sm–Nd and U–Pb ages >760 Ma). The ophioltic complex of the Shishkhid arc (Rb–Sr age 630 Ma) represents another component of the basement. In the present-day structure, ophiolites are thrust along the Khugein Thrust over the Khubsugul Basin.

The Late Baikalian consolidation was followed by rifting in the Tuva–Mongolian Massif, formation of intracontinental (Darkhat–Khubsugul, Sarkhoi, and others) rifts, and disintegration of the continental crust (Ilyin, 1982). The subsequent spreading produced the Central Asian (Zonenshain, 1977; Ilyin, 1991) or Dzhida (Kuz'michev, 2001) paleocean. Thus, the Tuva–Mongolian Massif became an element of the continental margin. The thermal contraction of the basement beneath this margin and tectonic subsidence were responsible for the formation of the shelf. The subsidence was compensated by deposition of carbonate sediments on the shelf.

Ancient rifts of the Tuva–Mongolian Massif are mainly filled with arkoses of the Darkhat Group that unconformably overlies the pre-Vendian basement. The Darkhat Group includes the following units (from bottom to top): conglomerates, gravelstones, and sandstones that enclose lenses and interbeds of oncolitic dolomites near the roof. The upper part of the Darkhat Group section is characterized by the presence of specific shales named as "perforated shales" (Ilyin, 1973) because of holes in the exposures formed as a result of the fallout of angular dolomite inclusions. Dolomite fragments and blocks, probably, represent dropstones transported by floating ice. They are compositionally alien for fine-grained terrigenous sediments on the basin floor. The sediments were sufficiently indurated and slightly lithified during the settling of dropstones. This was probably responsible for their poor cementation with host rocks and fallout of dolomitic inclusions from exposures. The perforated shales are supplemented with diamictites, varvites, and other glacial rocks (e.g., conglomerate-type dolomites composed of materials evidently redeposited by fluvioglacial flows) in basal layers of the Khubsugul Group near the base of the Khesen Formation (Osokin and Tyzhinov, 1998).

The weathering crust formed prior to accumulation of the Khubsugul Group is another remarkable feature of the Khubsugul/Darkhat boundary interval. In the Bokson River basin of the eastern Sayan region, diabases are transformed into breccia-conglomerate down to a depth of 15 m from their contact with dolomites (Kuz'michev, 2001). They grade upsection into diabase sandstones and clayey ferruginous rocks of the weathering crust. Sandy–shaly rocks in the weathering crust are transformed into the chaotic mixture of variable-size rock fragments and shingle. The crust is only locally preserved as a result of erosion and exaration. Products of its redeposition make up the so-called subphosphate member composed of fine-grained quartz sandstones marked by bright brown and red colors in exposures (*Putevoditel'*..., 1980).

Present-Day Structure of the Khubsugul Basin and Its Primary Configuration

The KHPB structure is governed by both tectonic processes in the Neoproterozoic/Phanerozoic boundary period and tectonic reactivation during the Phanerozoic. The Phanerozoic tectonic events were eventually responsible for the significant destruction of the ancient basin. Therefore, the present-day configuration reflects only to a certain extent the primary dimensions and outlines of the basin. The most significant role in this process belonged to the formation of large plutons that accompanied the early Caledonian or Salairian collision (Kuz'michev, 2001). Granitoid intrusions are widespread in the entire KHPB territory, particularly, in its southern part where Vendian–Cambrian dolomites and phosphorites in them are preserved only at the top of granitoid massifs. Similar situation is also typical of

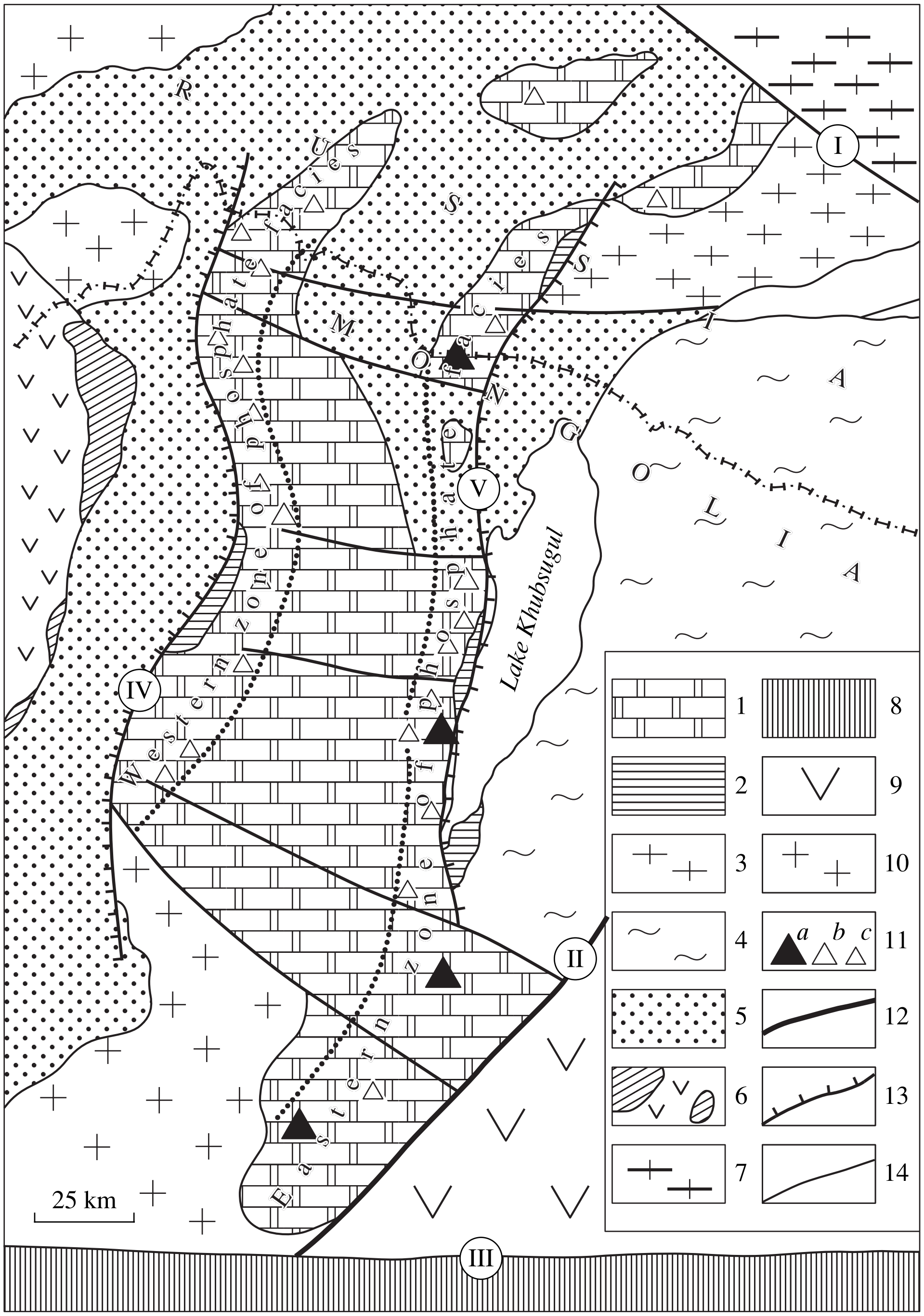


Fig. 1. Schematic geological structure of the Khubsugul Basin and adjacent areas. (1–2) Vendian–Lower Cambrian sediments: (1) Khubsugul Group (dolomites crowning the Khesen phosphate-bearing formation, (2) Darkhat Group (arkoses); (3–6) pre-Vendian complexes of the basement: (3) granulites of the Gargan Block (Proterozoic), (4) crystalline schists and marbles of the Khamar-Daban and Eastern Prikosogol'e areas (Upper Riphean), (5) graywackes and andesite-dacite volcanics of the Oka Group (Upper Riphean), (6) ophiolites of the Shishkhid arc (Upper Riphean); (7–9) fringing of the Tuva–Mongolian Massif: (7) Siberian Platform, (8) Dzabkhan (pre-Vendian) microcontinent, (9) Dzhida oceanic zone (Vendian–Cambrian); (10) Early Paleozoic granitoids; (11) large phosphorite deposits: (*a*) proven, (*b*) assumed; (*c*) phosphate occurrences; (12) suture (accretionary) zones: (I) Great Sayan Fault, (II) Agaringol Fault, (III) Khangai–Khengei Fault (1905 earthquake line); (13) thrusts bordering the Khubsugul Basin: (IV) Khugein-gol, (V) Pribrezhnyi; (14) ancient faults in the basement governing the block structure of the basin.

the northern Khubsugul Basin where the Vendian–Cambrian cover is only preserved in the form of xenoliths among granitoid massifs.

The present-day KHPB structure was to a significant extent developed during the formation of the Cenozoic Baikal rift system. It is composed of blocks separated by the orthogonal system of faults The blocks inherit ancient structural elements. Sublatitudinal faults, which separate these blocks, are of ancient origin. They reflect the heterogeneity of the basement and are responsible for its synsedimentary differentiation during the accumulation of sediments of the Khesen Formation. Cenozoic displacements along submeridional tectonic fractures bordering the basin on the west and east (i.e., along the Khugein and Pribrezhnyi thrusts) were also inherited movements (Fig. 1). The basement heterogeneity was also responsible for sharp differences in the dislocation pattern of phosphate-bearing sediments that retained subhorizontal attitude in areas where the sediments are underlain by Archean granulites (Ilyin, 1982), and overturned eastward along the Khugein Thrust and westward in the Pribrezhnyi Thrust zone. The formation of the Baikal rift system was accompanied by differentiated subvertical displacements of basement blocks. The uplift of some blocks (e.g., the Lambishtig and Tabain blocks in the northern KHPB) resulted in almost complete erosion of Vendian–Cambrian phosphorites and other sediments, which are sufficiently well preserved in the northern Ukhagol and southern Uleindabin blocks (Ilyin, 1990).

The tectonic subsidence of the basement beneath the Khubsugul and Darkhat rifts resulted in the formation of deep riftogenic lakes in the terminal Miocene. In the Quaternary, Lake Darkhat was drained owing to intense backward erosion of Malyi Enisei that left signs of fossil shorelines on slopes of the Darkhat Depression. Phosphate-bearing sediments in the depression are buried under the thick sedimentary sequence Lake Darkhat.

The Baikal rift system formation was also accompanied by multiple eruptions of basalt flows that buried phosphorites in many parts of the basin, particularly in the Oka basaltic plateau of eastern Sayan.

Despite fragmentary preservation of phosphate deposits, one can reconstruct some trends in their primary distribution.

Collision zones bordering the Tuva–Mongolian Massif—the Great Sayan Fault Zone in the north and the Khangai–Khentei Fault (or 1905 earthquake) Zone (Ilyin, 1978) in the south—represent the northern and southern boundaries of the Khubsugul Basin (Fig. 1). One can distinctly outline the main KHPB zone that accommodates the largest deposits and corresponds to the western Khubsugul region and western slope of the Darkhat Depression. Deposits of the phosphate facies distinctly pinch out toward the Tuva–Mongolian Massif on both northern and southern sides of this main zone. Phosphorites are sequentially replaced by the phosphate-bearing and phosphate-free dolomites.

The most important regularity in phosphorite distribution consists in the distinct confinement of all phosphorite deposits and occurrences to two submeridional (western and eastern) zones of phosphate facies (Ilyin, 1981). The first zone extends along the western slope of the Darkhat Depression, while the second zone extends parallel to the western shore of Lake Khubsugul (Fig. 1). The distance between these zones is approximately 80 km. The synclinal structure of the basin (Zaitsev and Ilyin, 1970) promoted the deep subsidence of the basal section of the Khubsugul Group (Khesen Formation) in the axial part, which is insufficiently studied because of the location in the not easily accessible alpine Khoridulin Sardig Ridge. However, the base and lower part of the Khubsugul Group are well exposed in some areas along the Arasana River. In all these areas, the Khubsugul Group is exclusively composed of dolomites. Phosphorites and associated biogenic rocks are absent. This situation is also observed in local erosion outliers among loose sediments of the Darkhat Depression. Thus, phosphate facies are presumably localized in two zones. The eastern (Khubsugul) zone corresponds to the inner shelf, whereas the western (Darkhat) zone corresponds to the deeper-water zone (Ilyin, 1998).

Phosphate facies in both eastern and western zones are characterized by sharp variations in thickness and number of phosphate beds and phosphate contents therein. Each block of the formerly single basin is marked by specific character of the pre-Vendian basement and tectonic subsidence (correspondingly, sedimentation) rates in the Vendian–Cambrian. This is reflected in the stratigraphic position of the Khesen Formation relative to the base of the Khubsugul Group. For instance, the thickness of the subphosphate dolomite unit is not more than 300 m in the Urundush Block, which accommodates the Khubsugul deposit (Ilyin, 1990), and increases to 600 m in the neighboring block (Ulin-daba deposit). Such variations combined with substantial differences in quantitative parameters of deposits provoked erroneous concepts of twofold (Osokin, 1998) or even threefold (Zhuravleva, 1975) occurrence of phosphate-bearing sequences within the Khubsugul Group. The negligible probability of such assumptions was proved during the detailed study of these deposits (Zaitsev, 1992).

THE KHESEN FORMATION: STRATIGRAPHY, AGE, AND LITHOLOGY

The typical stratigraphic section of the Khesen Formation (Fig. 2) begins with the lower or main bed of high-grade phosphorites (approximately 210 m thick, on the average) and is crowned by a layer of low-grade phosphate sandstones or sandy phosphorites (*Putevoditel'*…, 1980). The main bed is overlain by several (up to four) thinner beds separated by phosphate-bearing (eastern zone of phosphate facies) or phosphate-free (western zone) dolomites. The total thickness is 150 m, approximately 70 m of which is composed of phosphate-free dolomites underlying phosphate sandstones. Above these sandstones, the phosphate content in dolomites is close to the clarke value.

The lower boundary of the main (lower) bed is sharp and accompanied by the stratigraphic rather than angu-

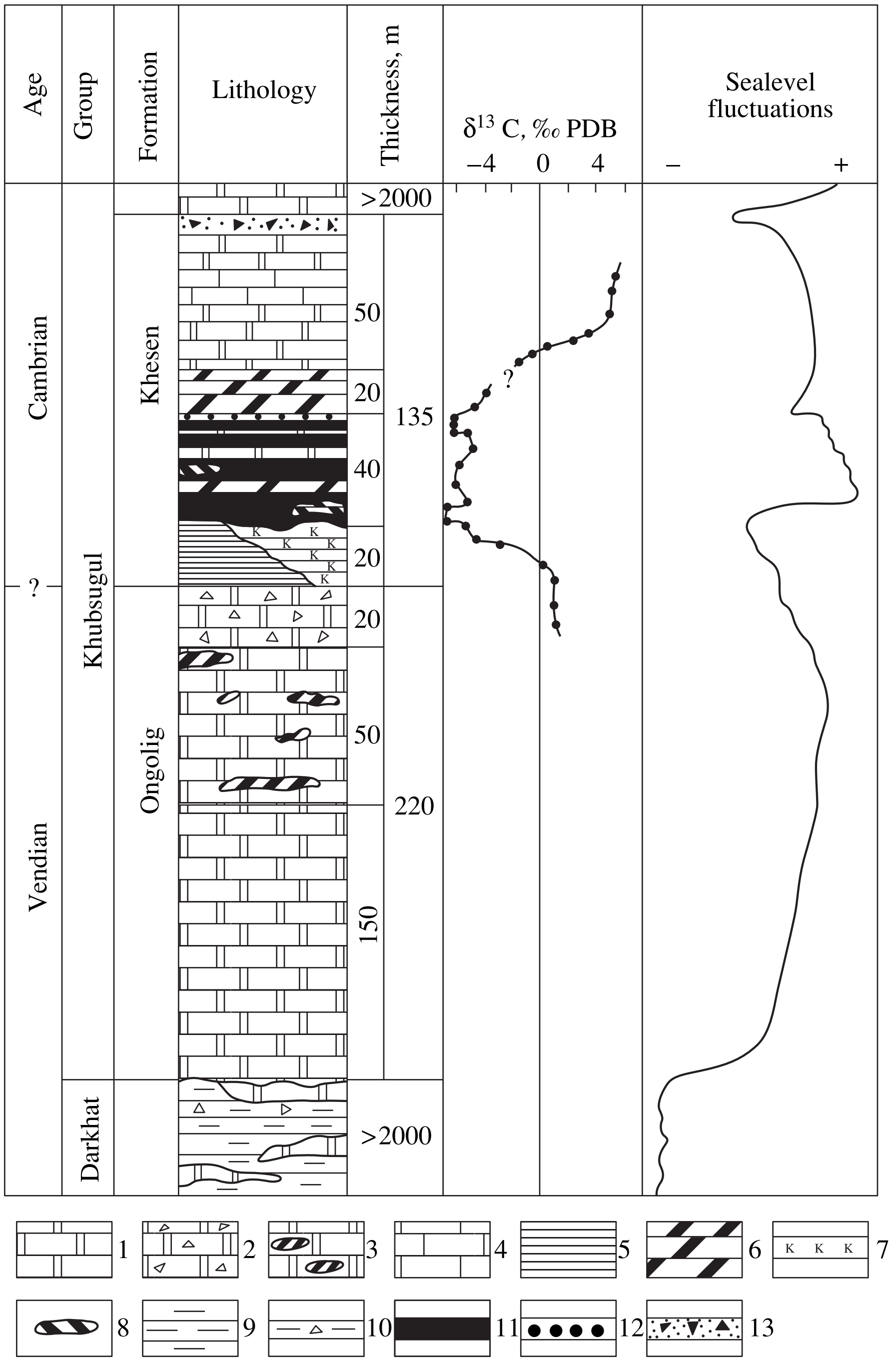


Fig. 2. Lithostratigraphic section of the Vendian–Cambrian rocks, distribution of $\delta^{13}C$ in the Khesen Formation, and plot of sea level variations. (1) Dolomites; (2) breccia-type dolomites; (3) dolomites with chert nodules; (4) limestones; (5) black shales and thin-platy limestones enriched in C_{org}.; (6) black cherts; (7) "red" (sub-phosphate) member; (8) light opoka-type bedded phosphorites; (9) arkosic phosphorites; (10) "perforated" shales; (11) structureless bedded phosphorites; (12) granular phosphorites; (13) sandy phosphorites.

lar unconformity. The bed is usually underlain by the red subphosphate member. This horizon is frequently occupied by black thin-platy limestones or carbonate-free varved black shales. Like limestones, the black shales are enriched in organic matter (C_{org} up to several percents). The upper phosphate-free dolomite section is often underlain by the bed of spongolite cherts. The Khesen Formation and enclosed phosphorites demonstrate significant facies variations (Ilyin, 1973).

The age of the Khesen Formation is estimated based on its localization 400–450 m (Zhegallo *et al.*, 2000) below the layers with oldest trilobite finds (Korobov, 1980). The Khesen Formation contains microphytolites (Zhuravleva, 1975), catagraphites, acritarchs, and filamentous cyanobacteria (Zhegallo *et al.*, 2000). Based on this evidence, the formation is attributed to the Tommotian Stage, although its Late Vendian age cannot be ruled out (Terleev, 1998).

The attempt to date phosphorites from the Khubsugul and related basins using the Sr isotope method (Shields *et al.*, 2000) failed to obtain more accurate age estimates, but the results showed that phosphorites from three large (Karatau, Khubsugul, and Lesser Himalaya) basins slightly differ in age. The Karatau Basin is the youngest structure among them. Moreover, the Khubsugul Basin is probably slightly younger than the Lesser Himalayan Basin (Fig. 3).

The carbonate carbon was also used for the chemostratigraphic correlation of the Khesen Formation. In the carbon isotope curve obtained for the lower part of the Khubsugul Group, phosphorites and dolomites of the Khesen Formation correspond to the distinct negative anomaly with $\delta^{13}C$ values of –3 to –7‰ PDB (Ilyin and Kiperman, 2002). At the base and top of the formation, these values become "normal," i.e. close to zero. It is worth noting that phosphate-bearing dolomites (P_2O_5 1–2%), which are stratigraphically equivalent to the Khesen Formation, do not show negative anomalies in neighboring areas of eastern Sayan (Pokrovskii *et al.*, 1998) and western Mongolia (Brasier *et al.*, 1996). Thus, the negative $\delta^{13}C$ anomaly is spatially limited by the Khubsugul Basin and cannot be used for interregional correlation (Ilyin and Kiperman, 2002).

The Khesen Formation largely composed of biogenic rocks is marked by diverse lithology. In addition to phosphorites, which are discussed in the next section, various siliciliths and organic-rich carbonate-bearing and carbonate-free rocks are also present (Fig. 4).

Siliciliths are represented by dark amorphous cherts and light finely porous opoka-type rocks (*Putevoditel'*..., 1980). Cherts are present in the form of more or less thick beds and irregular nodules occurring among both phosphorites and dolomites.

The main bed of black cherts (20–30 m thick) extends over tens of kilometers between the lower part of the Khesen Formation and the overlying phosphate-free dolomites. It is composed of amorphous massive chalcedony with the glassy fracture. Thin sections demonstrate the presence of rare hexantinellid sponge spicules several millimeters long. The spicules were probably intensely dissolved during diagenesis. The cherts lack phosphate and organic carbon.

Light porous opoka-type rocks are mainly localized in phosphorite beds in the form of lenticular inclusions 10 to 20 cm wide and 1 to 2 m long. In thin sections, one can see the less common globular texture with chalcedony spherules 1–2 μm across. Thus, the light porous rocks locally resemble the Mesozoic opokas from central Russia. One can also find remains of organisms similar to those described from cherts of the Chulaktau

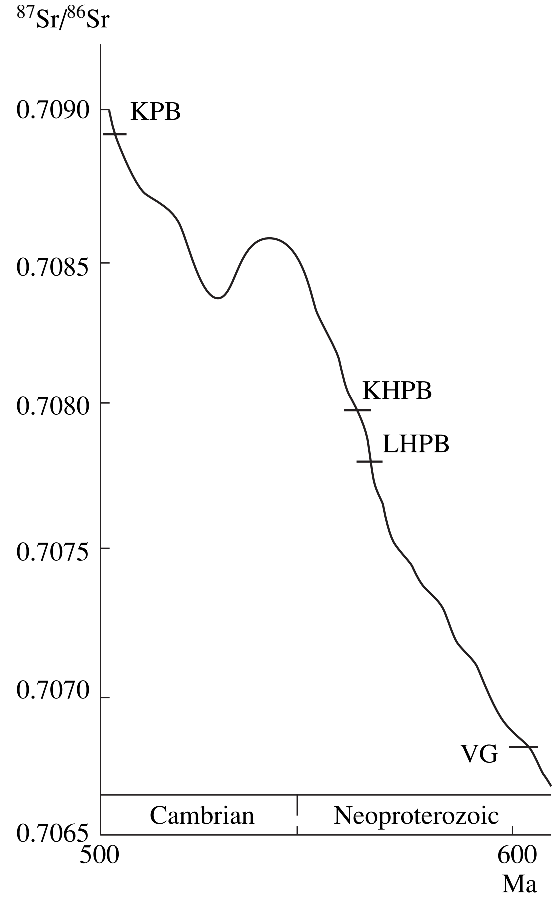


Fig. 3. Variations in the $^{87}Sr/^{86}Sr$ ratio at the Neoproterozoic/Cambrian boundary and age of phosphate-bearing basins based on the Sr isotope ratios (Shields *et al.*, 2000). Phosphate-bearing basins: (KPB) Karatau, (KHPB) Khubsugul, (LHPB) Lesser Himalaya. (VG) Varangerian glaciation.

Formation in Karatau, where they were identified as diatoms (*Putevoditel'*..., 1984; Ilyin, 1998).

Black organic-rich shales were previously unknown in the Khubsugul Basin, although Cook and Shergold (1986) had reported that phosphorites always closely associate with black shales in every phosphate-bearing basin.

The Khesen Formation in the Khubsugul deposit usually encloses two organic-rich beds. The lower bed (10 m) is composed of black thin-platy limestones, while the upper bed (approximately 5 m) is composed of shales. The C_{org} content in them varies from 3 to 5%. The distribution of other elements is presented in Fig. 5.

The C_{org}-rich black shales in the Khubsuhul Basin usually associate with phosphorites. However, this feature does not reflect their real distribution pattern. Debris of black bituminous shales with a peculiar kerosene odor and dusty pyrite dissemination was recorded at the bottom of one of the canyons 40 km west of the Khubsugul phosphorite deposit in the axial part of the

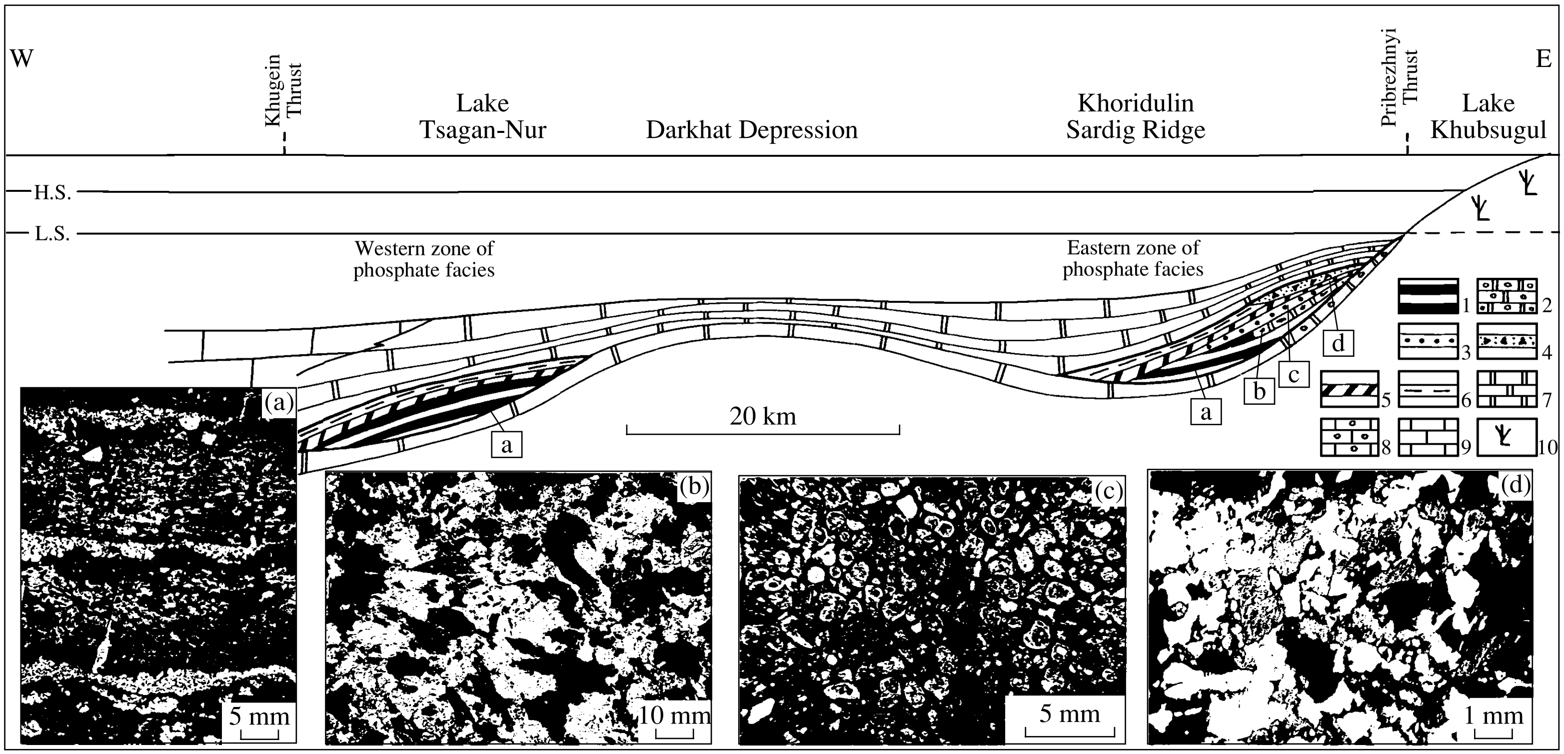


Fig. 4. Transverse cross section of the Khubsugul Basin. (H.S.) Highstand of sealevel; (L.S.) lowstand of sealevel. (1) Structureless phosphorites; (2) dolomitic phosphorites; (3) granular phosphorites; (4) phosphate sandstones; (5) black cherts; (6) black shales; (7) dolomites; (8) breccia-type dolomites; (9) limestones; (10) provenance. (a–d) Photomicrographs of phosphorite thin sections: (a) structureless, (b) dolomitic, (c) granular, (d) sandy.

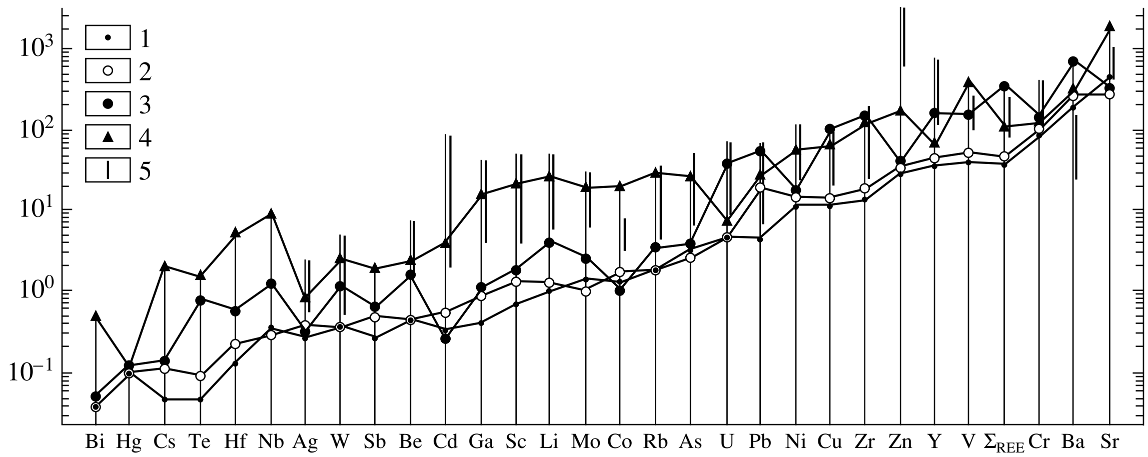


Fig. 5. Plots demonstrating variation in trace element contents, ppm. (1–4) Khubsugul phosphate-bearing basin: (1) dolomite and (2) phosphate laminae in bedded structureless phosphorites (Fig. 4a), (3) granular phosphorites from Bed 5 of the Khubsugul deposit, (4) black shales enriched in C_{org} (~5%) from the lower part of the Khesen Formation; (5) Upper Cretaceous–Paleogene phosphorite deposits of the Tethyan (Morocco, Jordan, and Tunisia) province (based on the author's data; data on Israel are adopted from (Soudry *et al.*, 2002)). Vertical lines designate intervals of average values for 12 deposits.

alpine Khoridulin Sardig Ridge. These shales have been studied only along a system of rare profiles.

In the Sangilen Highland west of the basin, where the carbonate sequences continue, carbonate and clayey rocks containing up to 20–30% of C_{org} are widespread in the Changus Syncline and other areas (*Geologiya…*, 1966). The Vendian age of these rocks has been proved (Terleev, 19998). Thus, carbonate sediments in the Sangilen Synclinorium are close in age to or even coeval with the Khubsugul Formation, as it was assumed earlier (Ilyin, 1982). They represent the western deeper part of the shelf, while the Khubsugul phosphorite basin corresponds to the inner part of this shelf. This regularity is also typical of other regions and particularly well manifested in the Yangtze Platform (Ilyin, 1990).

PHOSPHORITES

The Khubsugul phosphorites formed during the so-called ancient epoch of phosphogenesis demonstrate a certain relationship with other phosphate-bearing basins of the same epoch. In all these basins, phosphorites are confined to the lower part of the dolomite sequence that postdated glacial sediments. Phosphorites of all basins are close in age and located in the stratigraphic succession that underlies layers with the oldest trilobites. They always associate with sequences enriched in organic carbon and, particularly, spongolite cherts. In contrast to Phanerozoic phosphorites, ancient phosphorites are not characterized by the association with glauconite.

Some phosphorite varieties, e.g., characteristic oolitic-granular phosphorites with numerous phosphate films, occur in all of the basins. Therefore, they were termed "international" phosphorites in (Ilyin, 1981). In thin sections, such rocks from the Khubsugul, Karatau, and Yangtze basins are indistinguishable. This is evident from the comparison of Fig. 6a in (Ilyin, 1981); Fig. 2c in (Tushina, 1979); and Plate XVI in (Bushinskii, 1966). Oolitic varieties are also typical of all these basins (Ilyin, 1981).

Many, but not all, basins are composed of the fine-grained (0.1–0.2 mm) or pelletal phosphorites. Origin of these grains is far from being adequately understood (Glenn *et al.*, 1994). Tushina (1979) considered them as microconcretions that formed during the diagenetic transformation of primary siliceous–phosphate muds. Kholodov and Paul (1975) assigned their formation to microbial organism. Zhegallo *et al.* (2000) interpreted them as micronodules formed with the participation of cyanobacterial and red algae.

Along with features that are common for phosphorites from different ancient basins, each of these basins bears certain individual peculiarities. In the Khubsugul Basin, this is reflected in the abundance of phosphorites mainly consisting of alternating structureless phosphate and dolomite laminae and a subordinate amount of granular varieties, which are extremely widespread, for instance, in the Karatau Basin.

Comparison between the Eastern and Western Phosphate-Facies Zones in the Khubsugul Basin

Phosphorites in the eastern phosphate-facies zone, which comprises the large and sufficiently well prospected Khubsugul, Burenkhan, and Ukhagol deposits, is substantially better studied than phosphorites in the western zone where prospecting works were insignificant. Correspondingly, data on the eastern deposits are significantly more comprehensive than those on their western counterparts. At the same time, both sections of

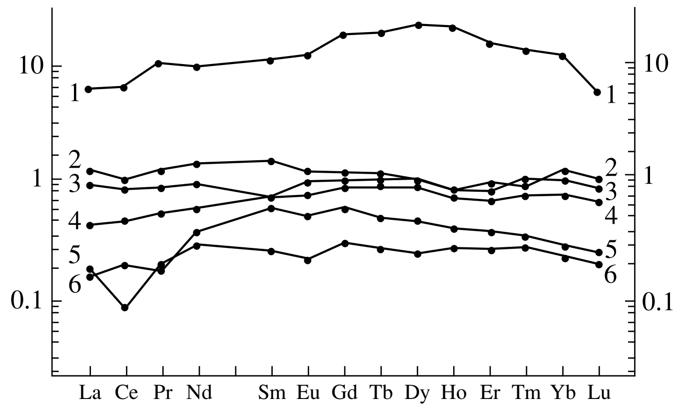


Fig. 6. Spidergrams for rare earth elements in phosphorites of the Khubsugul phosphate-bearing basin and waters of the Atlantic Ocean (10^5) at a depth of 900 m (Jarvis *et al.*, 1994). (1) Pelletal (granular) phosphorites from Bed 5 of the Khubsugul deposit; (2) dolomitic phosphorites; (3) Atlantic water; (4, 5) bedded structureless phosphorites composed of alternating dolomite lenses (4) and phosphate laminae (5); (6) chert from the Khesen Formation.

the Khesen Formation and phosphorites from these two zones are considerably different.

The Khesen Formation section presented in Fig. 2a characterizes the eastern zone and phosphorites typical of this zone are demonstrated in Figs. 4b–4d. The varieties termed as "dolomitic phosphorites" (Bushinskii, 1966) based on deposits of the Yangtze Platform are most widespread. In the Khubsugul Basin, they are composed of phosphate inclusions (Figs. 4b, 5) submerged into the dolomitic matrix. The inclusions have angular outlines, irregular shapes, and different (millimeter- to centimeter-scale) dimensions. The structureless phosphate matter is recognizable owing to black color against the background of lighter and distinctly younger dolomite cement that corrodes and replaces the phosphate (Ilyin, 1981). The second (sharply subordinate) variety is represented by granular or pelletal phosphorites that make up Bed 5 (*Putevoditel'…,* 1980) of the Khubsugul deposit (Fig. 4c). These phosphorites resemble Karatau ores, but their distribution in the Khubsugul Basin is restricted to a single bed. Phosphate sandstones with the terrigenous angular quartz grains prevailing over the phosphate grains (Fig. 4d) represent the third variety.

The western zone is barren of both granular phosphorites and phosphate sandstones. The Tsagannur deposit located in this zone is dominated by the structureless variety, which R. Sheldon proposed in 1980 to term as "primary bedded structureless phosphorite" in contrast to both granular phosphorites of Bed 5 in the Khubsugul Basin and well-known pelletal phosphorites of the Phosphoria Formation. The bedded structureless phosphorites include rhythmically alternating phosphate and dolomite laminae. The phosphate laminae are thicker (1–3 cm) and more sustained than the dolomite laminae (1–2 mm) that gradually pinchout (Fig. 4a). Phosphate is pigmented by organic matter that is concentrated at the base and top of interbeds. Such laminated varieties constitute the largest parts of beds, but they are frequently subordinate to dolomitic phosphorites that are typical of the eastern zone. In the west, phosphate components of dolomitic phosphorites are characterized by larger dimensions. They commonly represent variably disintegrated interlayers of the structureless phosphate. Primary bedding is retained in elongate fragments of layers. These fragments are separated by relatively large rhomboidal dolomite crystals.

The structureless and granular phosphorites are generally similar in the composition of main chemical components, except for the following distinctions. Relative to the granular phosphorite, the structureless variety is slightly enriched in P_2O_5 and depleted in SiO_2. The C_{org} content decreases from 1.0–1.1% in the first variety to 0.*n*% in the second variety.

Even larger differences are recorded for trace elements, the contents of which were determined in several samples using the ICP-MS method at the Certification Analytical Center (V.K. Karandashev, analyst). The granular varieties usually show notably higher concentrations of trace elements (Fig. 5). A substantial difference is also recorded for the total content of rare earth elements (Fig. 6) and, to a lesser extent, for the uranium content (Fig. 7). The Cd and V contents in the granular phosphorites are lower than those in the structureless varieties.

The distribution of trace elements was also separately estimated for the phosphate and dolomite laminae of the structureless phosphorites. We analyzed four samples from the lower (main) bed of the Tsagannur deposit including two samples each from the phosphate and dolomite laminae. The contents of trace elements in both phosphate and dolomite samples appeared to be very similar (Figs. 5, 6).

The comparison of two lower plots in Fig. 5 shows that phosphate and dolomite samples are almost identical in terms of the contents of all measured trace elements, including the total content and distribution of rare earth elements, as well as $\delta^{13}C$ values, which range from –5 to –7‰ PDB (Ilyin and Kiperman, 2002). The sole exception is provided by strontium, the content of which in the phosphate intercalations is slightly higher than in the dolomite laminae.

Geochemical Specialization of Ancient Phosphorites

Phosphorites formed during the two giant (Vendian–Cambrian and Late Cretaceous–Recent) epochs of phosphogenesis display certain similarities and distinctions (Shields *et al.*, 2000). The discussion of this topic is beyond the scope of the present work and is considered only with respect to the behavior of trace elements, the data on which were obtained by the ICP-MS method. We examined the representative samples taken from different deposits that characterize both epochs. In Fig. 5, the contents of trace elements in phosphorites from the Khubsugul deposit are compared with respective concentrations in phosphorites from Upper Cretaceous–Lower Paleogene deposits of the Tethyan province (Morocco, Jordan, Tunisia, and Venezuela). All the samples are almost identical in terms of the P_2O_5 content (22–30%). Samples were taken from drill cores or quarries below the groundwater level; i.e., the samples were not subjected to secondary transformations. The contents of trace elements in the Tethyan phosphorites are shown as intervals of average values, which were calculated taking into account the recent published data on the concentration of trace elements in Campanian phosphorites of the Negev Desert in Israel (Soudry *et al.*, 2002) based on comprehensive studies. As compared with other deposits of the Tethyan province, these data can be estimated as most reliable.

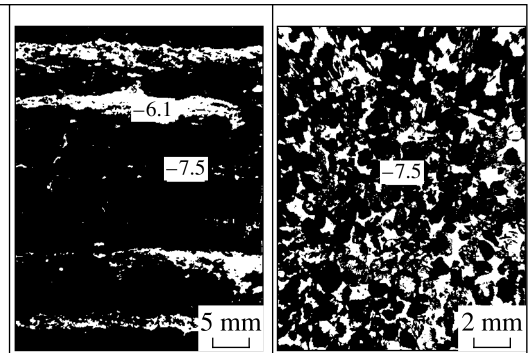
It should be noted that attempts to compare distribution patterns of trace elements in the Precambrian and Phanerozoic phosphorites were undertaken earlier as well (Ilyin, 1998, 2002). The inferences are generally consistent with the data shown in Fig. 5. The most significant differences are typical of two coherent elements (Zn and Cd). Substantial differences are also noted for U, REE, Y, and some other elements.

DISCUSSION

The intense phosphogenesis during the Neoproterozoic/Phanerozoic boundary period was caused by several interrelated geological processes. One of them was the Varangerian glaciation (Chumakov, 1978) that occurred in the initial Vendian 620 Ma ago (Hoffman *et al.*, 1998).

Bushinskii (1966) was first to note the co-occurrence of ancient phosphorites with tillites and other glacial sediments. He considered this phenomenon as paradoxical and assumed that the rocks viewed as tillites are alluvial sediments. The discovery of new phosphate-bearing basins in Asia (Khubsugul and Lesser Himalaya), Africa (Volta Syneclise), and Australia (Georgina Basin) revealed a certain trend in their distribution. Phosphorites at the base of dolomite sequences are universally underlain by glacial sediments. Cook (1992) scrutinized this issue and assumed that, despite their closeness in the stratigraphic section, phosphorites and tillites are significantly separated from each other in terms of geological time; i.e., dolomitic sediments commenced to accumulate tens of million years after the tillite formation. However, this assumption was not supported by dating (Flicoteaux and Trompette, 1997).

δ13C‰ PDB (numbers on photomicrographs of thin sections)



Content, ppm	(a)	(b)
U	4.3	9.1
Σ_{REE}	15	655
Y	30	270
Cd	4.71	1.68
Zn	5.1	21.2
V	50	20
C_{org}	0.96	0.31

Fig. 7. The content of some associated elements in (a) structureless and (b) granular phosphorites from the Khubsugul phosphate-bearing basin.

This issue can be explained in the context of the currently popular theory developed by geologists from Harvard (Hoffman *et al.*, 1998; Hoffman, 2001). According to this theory, glaciation was global and ice covered both continents and oceans. Duration of this glaciation based on the strong negative $\delta^{13}C$ anomaly caused by the collapse of biological activity and the corresponding shift in the carbon isotopic composition in seawater is estimated at 10 Ma (Hoffman and Schrag, 1999). The carbon dioxide, which issued during the continuous endogenic activity and was not consumed by exogenic processes because of global glaciation, gradually accumulated in the atmosphere and its concentration could reach values several hundreds of times exceeding the present-day one (Kasting, 1998). The increase of average temperature near the Earth's surface up to 50°C (Hoffman and Schrag, 1999) was a logical consequence of the greenhouse effect. Naturally, deglaciation occurred instantly (in terms of geological time) under such conditions, resulting in the intense chemical weathering of rocks, the more so as the rocks on ice-free continents were destructed by exaration processes.

The intensified river runoff provided the influx of nutrients and other weathering products into the ocean, which stimulated high bioproductivity in surface waters. This probably explains the successive bloom and disappearance of specific skeleton-free organisms known as Vendobiota (Seilacher, 1997). The logical consequence of rapid deglaciation was a sharp sea level rise and transgression termed postglacial (Hoffman, 2001). The transgression is marked by the thick dolomite sequence (cap dolomites).

The transgression peak corresponded to the initial phase of deglaciation when ice melting was most intense. Further development of the transgression was irregular and complicated by variations of higher orders. In the Tuva–Mongolian Massif one can see the second-order regression represented by the terrigenous subphosphate member. This regression was followed by rapid transgression, the beginning of which was marked by the formation of the lower (or main) phosphorite bed in the Khesen Formation. This type of transgression was named the "phosphate" transgression due to an extremely sharp contact of phosphorites at the base of the Phosphoria Formation (Hendrix and Byeers, 2000). Judging from the absence of terrigenous material in the main bed, the sealevel was highest during this transgression. The subsequent period was marked by several sealevel fluctuations of the higher order, e.g., regression noted at the level of Bed 5 where pelletal phosphorites are universally contaminated to a variable extent by the admixture of angular quartz clasts (Fig. 4). The spongolitic cherty bed crowning the pelletal phosphorites was also deposited during the regressive phase. The bottom of the slightly shoaled basin was populated by sponges. Their rapid dissolution and secondary mineralization of silica (Mazumdar and Banerjee, 1998) initiated the formation of the cherty bed. The complete decay of organic matter and absence of organic carbon in cherts were related to oxidizing conditions at that time. Dolomites and limestones crowning the cherty bed mark the next sea level rise, whereas phosphate sandstones at the top of the Khesen Formation reflect sharp regression and termination of the phosphorite accumulation period (phosphate transgression).

In the terminal Vendian–initial Cambrian corresponding to the Khesen Formation, the Tuva–Mongolian Massif (or carbonate platform) was the site of upwelling that stimulated high bioproductivity in surface waters. Phosphorus and other nutrients were delivered from the World Ocean, although, as it was mentioned above, the erosion of local weathering crusts could make additional contribution to this process. If local sources play the decisive role, the phosphorus influx from the neighboring land is accomplished in the form of its sorption on iron oxyhydroxides and subsequent desorption at the basin bottom (Glenn *et al.*, 1994). Such process is typical of epicontinental basins (e.g., the Mesozoic sea in Russia) and always reflected in the co-occurrence of phosphate and glauconite. As was shown, the glauconite is alien to phosphorites of both the Khubsugul (Ilyin, 1981, 1998) and other ancient phosphate-bearing basins (Cook and Shergold, 1986).

Examples of the Phosphoria Formation (Sheldon, 1987) or phosphorites of the Yangtze Platform (Ilyin, 1990) indicate that upwelling zones were spacious. In the Tuva–Mongolian Massif, the upwelling zone included the western Khubsugul region and the Shishkhid-gol and Sangilen highlands. Its eastern part corresponded to the inner shelf where the Khubsugul phosphate-bearing basin eventually formed. The western larger area, which is also composed of the Vendian–Cambrian carbonate sequences, was locally dominated by organic-rich siliceous and calcareous sediments (C_{org} up to 10–20%).The siliceous and carbonate rocks previously called carbonaceous quartzites and black "kerosene" limestones, respectively (*Geologiya…*, 1966), are widespread in the Sangilen Highland and marked by fine dissemination of pyrite and pyrrhotite. According to A.P. Bozhinskii (private communication), these rocks contain native gold and served as the source for gold placers of eastern Tuva.

In both cases, primary sediments were presumably enriched in biogenic components, which could further evolve according to the following two scenarios. In a nearly oxidizing environment, they underwent decomposition and initiated the formation of phosphorites (e.g., the Khubsugul Basin). In a reducing environment, they retained the organic carbon and promoted the formation of black shales (e.g., metalliferous shales in Sangilen).

The Khubsugul phosphate-bearing basin appreciably differs from other ancient phosphate-bearing basins in the dominant role of phosphorites with autochthonous structureless phosphate-forming laminae. Such laminae alternate with thinner laminae and lenses of dolomite (Figs. 4a, 7). In terms of the morphology of phosphate components, the Khubsugul Basin differs, for instance, from the Karatau Basin where the leading role belongs to granular (pelletal) phosphorites (*Putevoditel'…*, 1980, 1984; and others).

It was believed not long ago that the multiple rewashing of primary sediments and the consequent removal of nonphosphate sediments and concentration of phosphate components is the main, if not unique, factor responsible for the accumulation of phosphate components and formation of commercial deposits (Baturin, 1978).

This concept was substantiated to a certain extent by the prevalence of regular spherical phosphate grains among phosphate components and their uniform dimensions implying perfect roundness. Phosphorites from the Khubsugul Basin suggest the possibility of another scenario, i.e., in situ occurrence of high-grade phosphorus accumulations. This was noted by R. Sheldon who was familiar with the autochthonous thin phosphate coatings and lenses in the Phosphoria Formation (Ilyin, 1981). Based on phosphorites of the Tsagannur deposit as example, Sheldon anticipated the much later and now widely accepted concept, according to which phosphate-rich phosphorites include two varieties. Garrison and Kastner (1990) were the first to scrutinize these two varieties and recognize them as "pristine and recycled phosphorites" on the basis of the study of Cenozoic (Miocene, Pliocene, and Recent) phosphorites of the Chile–Peru shelf. This concept was further developed in the subsequent works (Glenn *et al.*, 1994).

This classification of phosphorites into two categories was later successfully applied to phosphorites of the Phosphoria Formation (Hendrix and Byeers, 2000). Primary dolomitic phosphorites appeared to be confined to the western seaward part of the sedimentation profile, while the higher-grade pelletal varieties are concentrated in the eastern part. The most complete substantiation and paleogeographic and geochemical characteristics of the two phosphorite categories are available for the Campanian deposits of Israel belonging to the Tethyan province (Soudry, 1992; Soudry *et al.*, 2002). Primary (or pristine) phosphorites of the Negev Desert in Israel are localized in synsedimentary depressions, whereas recycled pelletal varieties form condensed sections of uplifts. Relative to the recycled variety, the primary ores are one order of magnitude depleted in REE and Y and significantly depleted in U. At the same time, they are almost one order of magnitude enriched in Cd and zinc and several times enriched in V (Soudry *et al.*, 2002).

In terms of trace elements, except Cd and V (Ilyin, 2002), structureless phosphorites from the Khubsugul Basin are notably depleted relative to granular varieties (Fig. 5). The U content in Khubsugul phosphorites is one to and one-half order of magnitude lower than in Upper Cretaceous–Paleogene phosphorites of the Tethyan province and Miocene ores from the Florida–Carolina province.

Remarkably different are structureless and granular phosphorites from the Khubsugul Basin with respect to REE contents, the total content of which is 15 ppm in the structureless variety and as much as 700 ppm in the granular variety (Ilyin, 1998). Moreover, some distribution patterns, such as the Ce anomaly and depletion in HREE, appear to be typical of both ores. As was shown, phosphate and dolomite laminae of structureless bedded phosphorites are identical in contents of trace elements, except Sr, Cd, and V, the content of which is higher in the phosphates relative to the dolomites. This implies that both minerals primarily contained equally insignificant quantities of trace elements. Their concentration took place in the course of transportation and redeposition and depended on the duration of interaction with seawater (Kholodov, 1994).

In the Khubsugul Basin, the structureless and granular phosphorite varieties are spatially separated and belong to different parts of the sedimentation profile (western and eastern phosphate-facies zones, respectively). Like in the Tethyan province, structureless phosphorites of the Khubsugul Basin are usually confined to negative synsedimentary structures of the seafloor (in general, the offshore part of sedimentation profile). The possible origin of grains as a result of the disintegration of structureless layers, their rewashing, and rounding remains a debatable issue. As for dolomitic phosphorites (i.e., variety with size-variable and irregular shaped fragments of structureless phosphate enclosed in the later dolomitic matrix), they probably originated from the bedded structureless varieties. Multiple sea level fluctuations could transform one variety to another. Amplitudes of these variations were commonly insignificant. They affected sedimentation only in the eastern (relatively shallower) part of the basin and not necessarily resulted in the disintegration of structureless phosphate beds in the western offshore (phosphate-facies) zone.

The typical feature of the Khubsugul phosphate-bearing basin (alternation of almost monomineral phosphate layers with dolomitic laminae and lenses) is most likely related to the postsedimentary phosphate and carbonate segregation. This is evident from their identical light carbon isotopic composition. Relative to this older dolomite, the younger variety, which corrodes phosphate layers, is characterized by the higher (normal marine) values of $\delta^{13}C$ approximating zero (Fig. 2).

The Khubsugul phosphorites differ from Cenozoic counterparts in the content of trace elements. The depletion of phosphate and dolomite laminae of structureless phosphorites in the majority of elements is evidently related to the rapid burial of primary organic-rich sediments. Concentration of trace elements in granular varieties is probably explained by the prolonged interaction of phosphate components with seawater and the sorption of these elements by phosphate. The biologic evolution is probably responsible for the sharp depletion of old phosphorites in biophile elements, such as Zn and Cd. It is known that phosphates inherit some elements accumulated by organisms during their life activity. Zinc and cadmium, as well as some other elements, represent enzyme metals (Jarvis *et al.*, 1994). It is also known that the Vendobiota was primitive with respect to physiological functions and biochemical reactions (Seilacher, 1997). Moreover, Cd and Zn participated in biochemical processes of organisms only in the Phanerozoic.

Geochemical and other features of phosphorites from the Khubsugul and other ancient phosphate-bearing basins have certain applied significance. Ancient phosphorites play a modest role in the resource balance of the modern phosphate industry. With the gradual exhaustion of intensely exploited Phanerozoic deposits, ancient phosphorite can acquire a greater significance.

In this case, the assessment of ancient phosphorite deposits will largely depend on their features exemplified by Mongolian phosphorites.

CONCLUSIONS

Unlike other ancient phosphate-bearing basins, the present-day structure of the Khubsugul Basin preserved the sedimentation profile with proximal and distal phosphate facies, which can reliably be reconstructed. The proximal facies is represented by granular (pelletal) phosphorites formed during the multiple rewashing and redeposition. They correspond to the regressive phase of basin development, which affected only the shallow proximal zone. The distal facies is represented by structureless phosphorites formed as a result of rapid burial of primary sediments. Quantitatively, phosphorites of the distal facies sharply prevail over those of the proximal facies. In the Sangilen Highland west of the Khubsugul Basin, phosphate facies are replaced by offshore black shales.

Relative to structureless varieties, granular phosphorites are enriched in trace elements (particularly, REE and Y) and depleted in Cd and V. As compared with the Late Cretaceous–Cenozoic phosphogenesis epoch, ancient phosphorites are one to and one-half order of magnitude depleted in U and Cd and two orders of magnitude depleted in Zn. Geochemical specifics of ancient phosphorites can influence the ecological assessment of their deposits.

Two giant (Vendian–Cambrian and Late Cretaceous–Cenozoic) phosphogenesis epochs seem to be equal in scale, but the knowledge of ancient phosphorites is far from that of their younger counterparts.

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