Lithology and Mineral Resources, Vol. 39, No. 5, 2004, pp. 437–453. Translated from Litologiya i Poleznye Iskopaemye, No. 5, 2004, pp. 504–522.

Upper Oligocene Sediments of the Ciscaucasus, Volga–Don, and Mangyshlak Regions (Central Part of the Eastern Paratethys): Communication 3. Metal Potential and Formation Conditions of Fish Bone Detritus and Iron Sulfide Deposits

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Received December 19, 2002

Abstract—The structure of bone detritus and iron sulfide deposits is scrutinized based on the abundant analytical data on their component composition and metal potential. It is shown that maximal concentrations of bone detritus and iron sulfides are usually spatially separated. The metal potential of bone detritus does not depend on sulfides. Moreover, its massive accumulations are usually characterized by low uranium and REE contents in the phosphate matter of fish remains. Phosphate matter in the relatively deepwater deposits usually characterized by a lower content of bone detritus has the highest metal content. Deposits formed in the relatively shallow-water settings are characterized by a higher concentration of bone detritus and lower metal content. It is emphasized that sources of rare elements and iron remain unclear.

Issue of the metal potential of fish bone detritus (FBD) deposits came into open publications only during recently, because data on uranium were considered classified material for a long time. It should be noted that V. G. Melkov established the presence of uranium in fossil fish remains of the Cherkessk deposit in the northern Caucasus soon after the World War II. The discovery, however, did not stimulated practical interest due to low uranium contents in ores (0.002–0.008%), and such sedimentary uranium concentrations were classified as low-grade type with respect to its industrial potential.

The situation sharply changed in the 1950s when large deposits with higher uranium contents were discovered in Mangyshlak. We were pioneer researchers of this almost unexplored region. These works resulted in the stratigraphic subdivision of the entire Maikop Group (Stolyarov, 1958) and elucidation of the stratigraphic position of FBD deposits within the thick clayey sequence of the Karagie Depression. The materials obtained at that time made it possible to substantiate geological–prospecting works and discover commercial uranium deposits in Mangyshlak (Melovoe and other deposits).

By analogy with Mangyshlak, another large field of uranium deposits was subsequently discovered in the Ergeni district.

Ample drilling and mining works carried out in these areas promoted the comprehensive study of lithology and metal potential of deposits. The main results obtained are considered below.

As was mentioned, materials dedicated to the metal potential of FBD deposits were initially published without information on uranium. However, this did not distort general concepts of their composition and structure (Kochenov and Zinov'ev, 1960; Kochenov and Stolyarov, 1960; Mstislavskii and Kochenov, 1960; Kochenov *et al.*, 1970).

The composition of these deposits is best scrutinized in (Kochenov *et al.*, 1970). Using the data on REE distribution, the following features were identified: (1) the positive correlation between the REE and P_2O_5 contents; (2) the higher REE contents in smaller bone remains as compared with their larger fractions; (3) the lower REE concentrations in monolith (massive) bone remains, including the strongly mineralized remains with pores filled with authigenic minerals (calcite, celestine, and barite): and (4) the highest REE contents in peripheral parts of bone remains. It was emphasized that the availability of free internal surface in phosphate matter or its dispersion degree is the main factor responsible for the REE distribution. This parameter closely associates with the organic matter (OM) content in bones, because the OM concentration in phosphate mass prevents crystallization of calcium phosphate, increasing its surface and, consequently, sorption ability. The usually observed inverse correlation of the OM content with the bone remain size is responsible for the higher metal content in smaller bone

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fragments. Thus, the relationship of external properties of bones, their internal structure, and the OM content with the REE concentration was outlined. Subsequently, we showed that uranium distribution in the FBD is governed by the same factors, which were established for the REE (Stolyarov *et al.*, 1991). Uranium is also largely concentrated in small bone fragments of the sandy–silty fraction, dark porous bones containing OM admixture without authigenic mineralization, and so on. Some differences in the REE and U concentrations depending on facies conditions of deposit formation will be discussed below.

Fish remains in the FBD deposits are supplemented with abundant bones of aqueous mammalians, reptilians, and birds. The metal potential of these remains does not differ from that of similar (in size) fish bone remains. This statement is also valid for diagenetic phosphate nodules. At the same time, phosphorite pebbles are always characterized by lower metal contents. All these features indicate the diagenetic character of REE and U concentrations in phosphate matter of deposits. It was also established that coalified wood fragments almost always lack metals.

In metalliferous deposits, U is supplemented with Sc in bone remains and with Re in sulfides (Stolyarov *et al.*, 1991). Like REE and U, Sc is always present as a minor component in fish remains (0.002–0.006%; concentration clarke is 2–3) and host clayey sediments (0.002–0.0025%).

All deposits contain Re up to 0.3–0.4 ppm (concentration clarke is up to 3000), which is the highest concentration among all elements in the studied deposits.

The metalliferous FBD deposits are defined as the *sulfide–phosphorus–uranium–rare metal* ore association (Stolyarov *et al.*, 1991).

RESULTS

Earlier, we considered the facies–paleogeographic constraints of FBD deposits with the Ergeni ore district as example and discussed differences in terms of their composition and metal contents in bone phosphates depending on facies formation conditions (Stolyarov and Ivleva, 1991).

The ore content in the Mangyshlak district was first characterized in (Stolyarov and Kochenov, 1995). We presented data on the average composition of all four commercial beds in the Melovoe deposit. We demonstrated that the uranium content in bone detritus distinctly correlates with its size and ranges from 0.1% in large (1–3 mm) fractions to 0.4% in small (<0.1 mm) fractions.

The REE composition is dominated by Ce, La, Y, and Nd (0.004–0.082%). The content of other elements is proportional to their clarke values varying from 0.0125 to 0.0010%.

The Sc content in ores of the Melovoe deposit depends on the FBD concentration and varies from 0.0025% (at P_2O_5 6–7%) to 0.0050% (at P_2O_5 14–15%). Clayey layers in Bed 2 are characterized by the lower Sc content (0.0012–0.0018%). The Re concentration in the Melovoe deposit is relatively constant (average 0.0001–0.0002%).

The lithology and structure of ore beds in the Melovoe deposit are scrutinized in (Sharkov, 2000).

We carried out the first complex study of deposits in the entire Mangyshlak–Ergeni ore province. The chemical composition of ores and distribution of Sc, Re, Ni, Co, and Mo in all deposits of the Ergeni district, as well as the comparative characteristics of ore compositions in all major deposits of the Mangyshlak and Ergeni areas, are given in (Stolyarov and Ivleva, 1995).

The genesis of manganese and uranium–rare metal ores in the Maikop Group is discussed in (Stolyarov and Kochenov, 1995; Kochenov and Stolyarov, 1996). We noted that the coexistence of geochemically different uranium–rare metal and manganese deposits is a unique phenomenon related to the development of H_2S contamination in sea basins of the Eastern Paratethys.

We noted the following main aspects of the metal content in FBD deposits.

Uranium. Stratiform FBD accumulations with the albumen OM preserved in bone fragments, generally, formed a distinct reducing environment in sediments that was most favorable for uranium concentration in bone phosphates. The bone detritus in relatively deep-water deposits is characterized by the higher U content (up to 0.4–0.5%) relative to deposits formed in shallower settings and carbonate facies (up to 0.06–0.10%).

Rare earth elements. In contrast to uranium, the REE concentration in Maikop fish remains is a relatively frequent phenomenon. High REE contents are established in fossil fish bones from sediments of different ages and lithology (Blokh and Kochenov, 1964). For instance, their content amounts to 1.0–2.8% in fish remains from Devonian red beds of the Russian Platform.

The delivery of REE and Sc referred to the group of low-soluble hydrolyzate elements is, probably, related to the terrigenous clayey material and iron oxides rather than seawater, in which their contents are extremely low. Like in the case of uranium, dissolution of these elements and their transfer to interstitial water was evidently stimulated by the water-soluble OM that plays a significant role in the migration of hydrolyzate elements. Like uranium, the hydrolyzate elements precipitated on the surface of bone fragments together with OM, resulting in the positive correlation between them.

Iron sulfides. The origin of iron sulfides (IS), a major component in FDB deposits, and the source of large IS concentrations, which are confined to FBD deposits or outlined as autonomous beds with subordinate bone remains, remain debatable so far (Kochenov and Stolyarov, 1960; Stolyarov and Ivleva, 1991, and others). The great diversity of sulfide minerals is remarkable. They are mainly developed as the carbonaceous cryptocrystalline pyrite (less commonly, marcasite) in the clayey matrix and pores in bone fragments. Sulfide concretions (up to 10 cm across) and pisolitic structures are also found.

Generally, the high sulfide aggregation in FBD accumulations can be attributed to the collective pyrite crystallization during the bacterial decomposition of albumen in bone remains. However, as will be shown below, the IS and FBD contents frequently show negative correlation, which complicates the genetic features of metalliferous potential.

LITHOFACIES AND METALLOGENIC CHARACTERISTICS OF DEPOSITS

The studied exotic sedimentary deposits have a highly variable component composition. In different deposits or even in different parts of the same deposit, the FDB content varies from a few percents to 60–75%; i.e., bone remains can locally form "bone concentrate" with the sulfide–clayey interstitial cement. The P_2O_5 content ranges from 1 to 25%. Iron sulfides also show variations from 10 to 58% (S_{pyr} 5–29%). Their maximal concentrations (40–58%) are noted in sulfide beds usually with low FBD contents ranging from 3 to 6% (P_2O_5 1–2%). The sulfide content in host clays amounts to 3–7% (S_{pyr} 1.5–3.5%). The proportion of clayey material in deposits is usually 30–60% (Al_2O_3 5–10%) and locally decreases to 5–10%. The Al_2O_3 content is 18–20% in host clays.

On the whole, the deposits can be subdivided into three types: high-phosphorus deposits (P_2O_5 > 10%), high-sulfur deposits (S_{pyr} > 12.5%), and high-alumina deposits (Al_2O_3 > 8%) (Stolyarov and Ivleva, 1991).

Based on a large body of analytical data, we shall attempt to define some trends of U and REE accumulation in bone phosphates depending on quantitative proportions of FBD and IS. First, we discuss the Ergeni district where some deposits are characterized by very contrasting facies settings ranging from the deepest to shallowest ones recorded for this type of accumulations.

The **Stepnoe deposit.** The Stepnoe deposit is confined to the deepest part of a paleobasin in the Ergeni–Mangyshlak paleogeographic system of the outer shelf. The deposit located on the relatively steep northwestern slope of the Terek–Kuma Trough at a distance of up to 50 km from small archipelagoes is controlled by the prominent bottom scarp (Stolyarov and Ivleva, 1991, 1995). The deposit extends along this structure over more than 11 km and sharply bifurcates in the southeast to form a fish tail-type structure with two zones located a distance of 2–3 km and thickness increasing to 6–8 m (Fig. 1).

The Stepnoe deposit is noted for the high sulfide content averaging 35% (locally, 50–55%). The S_{pyr} varies from 16–17% and 25–28%, respectively. Areas with the highest sulfide content are usually characterized by the lowest FBD concentrations (up 2–5%). The average FBD content is 15% (P_2O_5 4.8%). All these features indicate that the structure of the deposit is mainly governed by the distribution of iron, which is replaced toward deeper parts of the basin by clayey interlayers in the sulfide mass.

Before proceeding to discussion of the metalliferous potential of bone phosphate deposits, we present for the first time some data on the composition and structure that reflect sedimentation environments in the area.

The Stepnoe deposit is characterized by both compact and layered structure. The compact northwestern part (0.5–0.6 km wide) shows clear contacts with host clayey sediments. The thickness varies from 0.1–0.5 m in the pinchout area to 3–4 m in the middle area and 6–8 m in the southeastern layered area.

Fish remains are composed of small ribs, scales, flat head and fin bones, rare small teeth, and relatively well-preserved vertebrae. The color of bone detritus ranges from brown to black. Light-colored remains mainly occur as well-preserved scales in thin (up to 0.2 m) carbonate (calcite, dolomite, and siderite) interbeds.

The size of bone fragments ranges from 0.*n* to 1–2 cm, the prevalent size being 0.2–0.5 mm. The sand- and silt-sized bone detritus universally bears signs of redeposition (subangular fragments). Some larger (3–5 cm) fragments (ribs and vertebrae) are ubiquitous, but they are more abundant in the basal part mainly composed of sulfides and with an insignificant FBD content (up to 1–2%). The FBD content universally increases upsection to 20% or more, while the sulfide content changes insignificantly (S_{pyr} from 13–16 to 18–21%). This feature emphasizes the autonomous nature of IS and FBD accumulation.

Bone remains are supplemented with diagenetic phosphate nodules of spherical, oval, and less common elongated shapes with yellowish color and loose earthy structure. The nodules vary from 3–8 to 20–25 mm in size and are most abundant in the areas of maximal FDB concentration.

The coalified wood remains make up elongated (1–6 cm) dark brown to black inclusions which are usually compact and fragile, with the occasional cellular texture (lignite). They occur in different parts of the deposit, but the largest remains are confined to its base. Some wood fragments contain pyrite and less common sphalerite dissemination.

Glauconite is universally developed in the form of small (0.02–0.03 mm) dark green rounded grains.

Terrigenous minerals are primarily found as rounded and subrounded, sand- to silt-sized quartz dispersion in the rock. Thin (1–2 mm) powdery quartz dissemination at bedding surfaces is common. The quartz content averages 1–2%. It is accompanied by feldspar, garnet, muscovite, biotite, hornblende, anatase, rutile, tourmaline, zircon, sphene, pyroxene, and epidote.

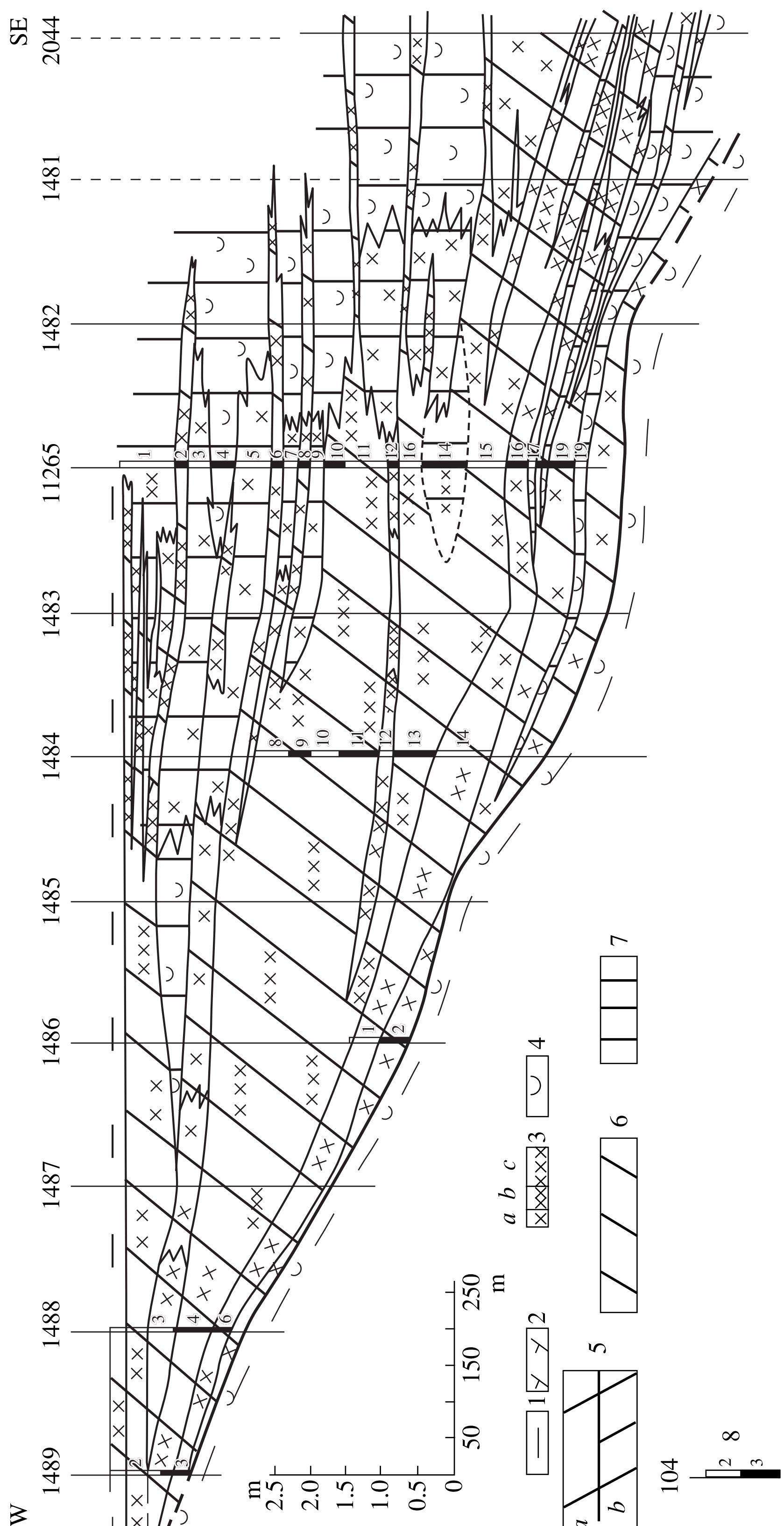

Fig. 1. Transverse section of the Stepnoe deposit. (1) Clay; (2) carbonate rocks; (3) FBD with the P_2O_5 contents: (*a*) up to 2%, (*b*) 2–5%, (*c*) 5–7%; (4) dispersed fish remains; (5–7) dominant component in ores: (5) bone detritus: (a) moderate prevalence, (b) sharp prevalence, (6) iron sulfides, (7) clayey material; (8) boreholes and their numbers (sample numbers on the right side).

Thus, the Stepnoe deposit is a giant sulfide deposit with the total sulfur reserves of approximately 7 Mt and a subordinate FDB content, particularly in its lower part (P_2O_5 0.2–1.6%).

The deposit is characterized by the IS accumulation and FBD influx (up to 20%) that was most intense during the middle and later formation stages. Keeping this in mind, let us consider the available data on U and REE concentrations in bone phosphates (Table 1).

The U and total REE contents in the Stepnoe bone phosphate average 0.34 and 1.44%, respectively. These values are close to prevalent estimates obtained by analytical methods and are highest for deposits of this type.

The bone–sulfide part of the deposit (excluding clayey interbeds) shows variations of the S_{pyr} and P_2O_5 contents equal to 10.9–28.6 and 1.0 9.8%, respectively (Table 1, boreholes 1306, 1308, and 1265). The U content in bone phosphates is as high as 0.22–0.45% and locally decreases to 0.11% or increases to 0.55%(maximum 0.9–1.2%). The REE content commonly varies from 1.3 to 1.5%, but its maximal variation range is 1.1–2.1%).Depending on proportions of FBD and IS in the deposit, the metal content in bone phosphates can demonstrate the following variation (Fig. 1). For instance, in Bed 13 (Borehole 1265 0.5 m) characterized by the highest FBD content (P_2O_5 9.8%, S_{pyr} 17.5%), the U content in bone phosphates represents one of the lowest values for the entire deposit (0.25%). In contrast, the sharp decrease in the FBD content (P_2O_5 1%) and the high sulfide content (S_{pyr} 21.5%) are accompanied by one of the highest U contents (0.9%) in bone phosphates (Bed 8, Borehole 1265).

Such relations between the FBD content and its metal potential are evident in a more smoothed form in Borehole 1244, %: S_{pyr} 19–20, P_2O_5 4.8–6.9, U 0.26–0.39, and REE 1.3–1.5 (Table 1). In beds with the lower FBD content (P_2O_5 1.2–2.3%, S_{pyr} 22%), the metal content in bone phosphates substantially increases (U up to 0.39–0.41%, REE up to 1.7–2.1%).

The presented data imply that the metal potential of FBD increases in beds with a low FBD content (up to a few percents) and a relatively constant high sulfide concentration, which presumably did not affect the U and REE concentrations in bone phosphates.

This is also evident from the extremely high U content (0.45–1.20%) in phosphate matter from clayey interbeds (P_2O_5 0.2–0.8% and S_{pyr} 2.0–7.0%) alternating with sulfide ore (Fig. 1, Borehole 1265, beds 5, 17, and 19).

The relatively high metal concentration is also noted in the FBD of some carbonate interbeds in the deposit. For instance, the U and REE concentrations are as high as 0.27 and 1.35%, respectively, in the carbonate interbed in Borehole 1330 enriched in P_2O_5 (3.13%), S_{pyr} (12.0%), Al_2O_3 (4.0%), and CO_2 (14.5%) (Table 1).

On the whole, the Stepnoe deposit is characterized by extremely high enrichment in iron sulfides. Morphology of this deposit is primarily governed by the

Table 1. Composition of ores in the Stepnoe deposit

Borehole and sample nos.	Content, %				
	P_2O_5	S_{pyr}	Al_2O_3	U recalculated for P_2O_5	REE recalculated for P_2O_5
A. In boreholes along the transverse section					
1489-2	2.0	18.0	–	0.45	–
1489-3	2.0	18.0	–	0.36	–
Average for borehole	2.0	18.0	–	0.40	–
1488-3	3.4	19.0	–	0.30	–
1488-4	4.6	18.0	–	0.29	–
1488-5	2.4	19.8	–	0.40	–
Average for borehole	3.46	18.9	–	0.33	–
1486-1	2.8	–	–	0.32	–
1486-2	1.4	–	–	0.22	–
Average for borehole	2.1	–	–	0.27	–
1484-8			–	0.24	–
1484-9		–	–	0.27	–
1484-10		–	–	0.29	–
1484-11	6.4	15.5	–	0.33	–
1484-12			–	0.11	–
1484-13			–	0.23	–
1484-14	2.6	15.8	–	0.39	–
Average for borehole	4.5	15.65	–	0.26	–
1265-1	2.4	6.5	–	0.27	–
1265-2	4.0	21.0	–	0.36	–
1265-3	1.0	5.0	–	0.33	–
1265-4	0.4	3.2	–	0.45	–
1265-5	0.8	6.5	–	0.45	–
1265-6	3.0	19.0	–	0.32	–
1265-7	0.6	4.8	–	0.55	–
1265-8	1.0	21.5	–	0.90	–
1265-9	1.0	9.0	–	0.36	–
1265-10	5.0	20.0	–	0.31	–
1265-11	7.0	20.0	–	0.24	–
1265-12	1.8	4.5	–	0.33	–
1265-13	9.8	17.5	–	0.25	–
1265-14	7.0	3.5	–	0.28	–
1265-15	4.0	20.5	–	0.33	–
1265-16	1.3	19.3	–	0.39	–
1265-17	0.4	7.0	–	1.06	–
1265-18	1.6	17.5	–	0.34	–
1265-19	0.2	2.0	–	1.20	–
Average for borehole	2.75	12.04	–	0.46	–
Average for section	2.96	16.14	–	0.34	–
B. In other boreholes within the deposit contour					
1244-1	6.13	18.92	5.70	0.29	1.53
1244-3	6.90	19.13	6.74	0.26	1.36
1244-4	4.81	19.95	8.11	0.31	1.32
1244-5	2.28	22.26	7.72	0.41	2.12
1244-6	1.23	22.02	9.77	0.39	1.67
1330-2	6.48	18.67	7.04	0.23	1.40
1330-3	3.13	12.04	4.01	0.27	1.35
1308-1	0.70	28.56	5.31	0.30	0.86
1306-1	5.10	19.0	6.52	0.28	1.30
1306-2	4.54	10.94	4.39	0.29	1.40
C. Beyond the deposit contour					
2521-1	2.38	21.15	–	0.16	–
2523-2	5.86	7.65	–	0.06	–
2523-3	9.50	20.84	–	0.12	–
2523-4	3.28	6.27	–	0.05	–

Note: Here and in other tables, dash designates the absence of data.

spatial distribution of ferrous material rather than the FBD concentration pattern, which is typical of most other deposits of the considered type. The ferrous material alternated with clayey matter during sedimentation and formed the fish tail-type structure inclined toward deeper parts of the basin. The FBD served in this process as an accompanying material, which did not influence the structure of the deposit.

It should also be noted that sulfide interbeds (up to 1 m or more in thickness) extend over several kilometers beyond the deposit and contain a substantial FBD admixture locally reaching 10–20% (Stolyarov and Ivleva (2004a, Fig. 4). The U content, however, is lower as compared with that in the Stepnoe deposit. For instance, in beds with P_2O_5 and S_{pyr} contents of 3–9% and 20–21%, respectively, the U concentration is only 0.12–0.16%. The U concentration decreases to 0.05–0.06% in clayey beds with the P_2O_5 and S_{pyr} contents of 3–6 and 6–7%, respectively (Table 1, boreholes 2521, 2523). The causes of this phenomenon remain unclear so far.

As is seen, the metal potential of FBD can also substantially vary in relatively deepwater facies settings. In the Stepnoe deposit, the metal content is most significant and inversely correlates with the FBD content, while the sulfide concentration is relatively constant. At the same time, the metal content in the FBD can substantially decrease beyond the deposit, although facies settings of sedimentation remain stable.

The **Shargadyk and Bogorodsk deposits.** In terms of facies–paleogeographic settings, the area of these deposits substantially differed from that of the Stepnoe deposit. It occupied a relatively shallow-water zone on the eastern slope of the Beloglinsk and Remontnoe archipelagoes (Stolyarov and Ivleva, 1991). The FBD material accumulated in a large area (up to 20 × 30 km) and beyond the deposits as well.

The **Shargadyk deposit** is closest to the Beloglinsk Uplift. The deposit is 0.2–4.8 km wide and extends to the northeast over 9.4 km. It is a compact relatively thin (up to 1.2 m) bed lying on clays (Fig. 2). The basal erosional wavy surface includes fragments of the clays. Large FBD inclusions (1–10 cm) also commonly occur in the basal section.

Mainly sand- to silt-sized fish remains are very irregularly distributed as lenses and interbeds with various shapes and FBD contents. One can also see lenticular intercalations (3–4 cm) cemented by carbonates (calcite and siderite), marl beds, and the remarkable lenses of coalified wood remains (up to 5 × 30 cm in size) with a dark brown color and well-preserved wood texture.

The average component composition of the Shargadyk deposit is atypical and characterized by high FBD (P_2O_5 13.6%) and IS (S_{pyr} 15.4%) contents and low alumina (Al_2O_3 5%) contents (Stolyarov and Ivleva, 1991). At the same time, ores with high contents of both sulfur ($S_{pyr} > 12.5\%$) and phosphorus ($P_2O_5 > 10\%$) are subordinate. The major components are usually differentiated in space. The FBD prevails in the lower and middle parts of the deposit, while iron sulfides dominate in its upper part (Fig. 2). In terms of the component composition, one can recognize two major ore types. The first type is characterized by high contents of phosphorus and low contents of sulfur and alumina (hereafter, high-phosphorus type), while the second type is marked by low contents of phosphorus and high contents of sulfur and alumina (hereafter, high-sulfur type).

The high-phosphorus deposits are characterized by the sharp prevalence of FBD (P_2O_5 up to 20–22%) over IS (S_{pyr} up to 10%) and, particularly clayey material (Al_2O_3 1–4%). They represent a redeposited loose lenticular-bedded material (natural "bone concentrate") with local debris appearance or calcareous admixture (CO_2 2–5%) (Table 2). Bone fragments (up to 0.5–1.0 cm or more) are chaotically distributed and frequently clustered. They are colorless or brown (owing to OM). High-sulfur ores (S_{pyr} 20–25%) are distinguished by black color, massive structure, subordinate content of FBD (P_2O_5 3–7%), and high content of clayey material (Al_2O_3 up to 8%) (Table 2).

Evidently, the Shargadyk deposit also contains ores with the intermediate composition, such as varieties with prevalent clayey material or high carbonate contents (CO_2 18–22%) and high FBD concentrations (P_2O_5 6–10%) and low contents of S_{pyr} (3–7%) and Al_2O_3 (2–3% (Table 2).

Let us dwell on some peculiarities of the metal distribution in bone phosphates depending on changes in the component composition of the Shargadyk deposit. This deposit differs from other deposits of the Ergeni district by the lowest average contents of U (0.1%) and REE (0.84%) in the FBD (Stolyarov and Ivleva, 1991). The variation limits for the U and REE contents are 0.04–012 and 0.67–0.96%, respectively.

The sufficiently distinct spatial differentiation of high-phosphorus- and high-sulfur ores within the deposit obviously suggests substantial changes in its sedimentation and diagenetic settings. This should apparently affect the degree of U and REE concentration in bone phosphates. However, this is not observed in reality.

The highest FBD concentrations (P_2O_5 15–21%) with subordinate IS content (S_{pyr} 8–12%) are usually characterized by the U content in bone phosphates ranging from 0.06 to 0.1%. The high-sulfur ores (S_{pyr} 15–25%) with the typical low FBD concentration (P_2O_5 3–10%) usually show similar high or low U contents in the phosphate matter (0.10–0.12 or 0.04%) (Fig. 2, Borehole 104). Beds with similar contents of FBD (P_2O_5 10–15%) and IS (S_{pyr} 12–15%) are commonly marked by the high U content (0.08–0.12%) (Table 2).

It is worth noting that thin carbonate interbeds (CO_2 18–22%) with the high P_2O_5 and near-clarke S_{pyr} contents (up to 10 and 2.5–7.6%, respectively) are charac-

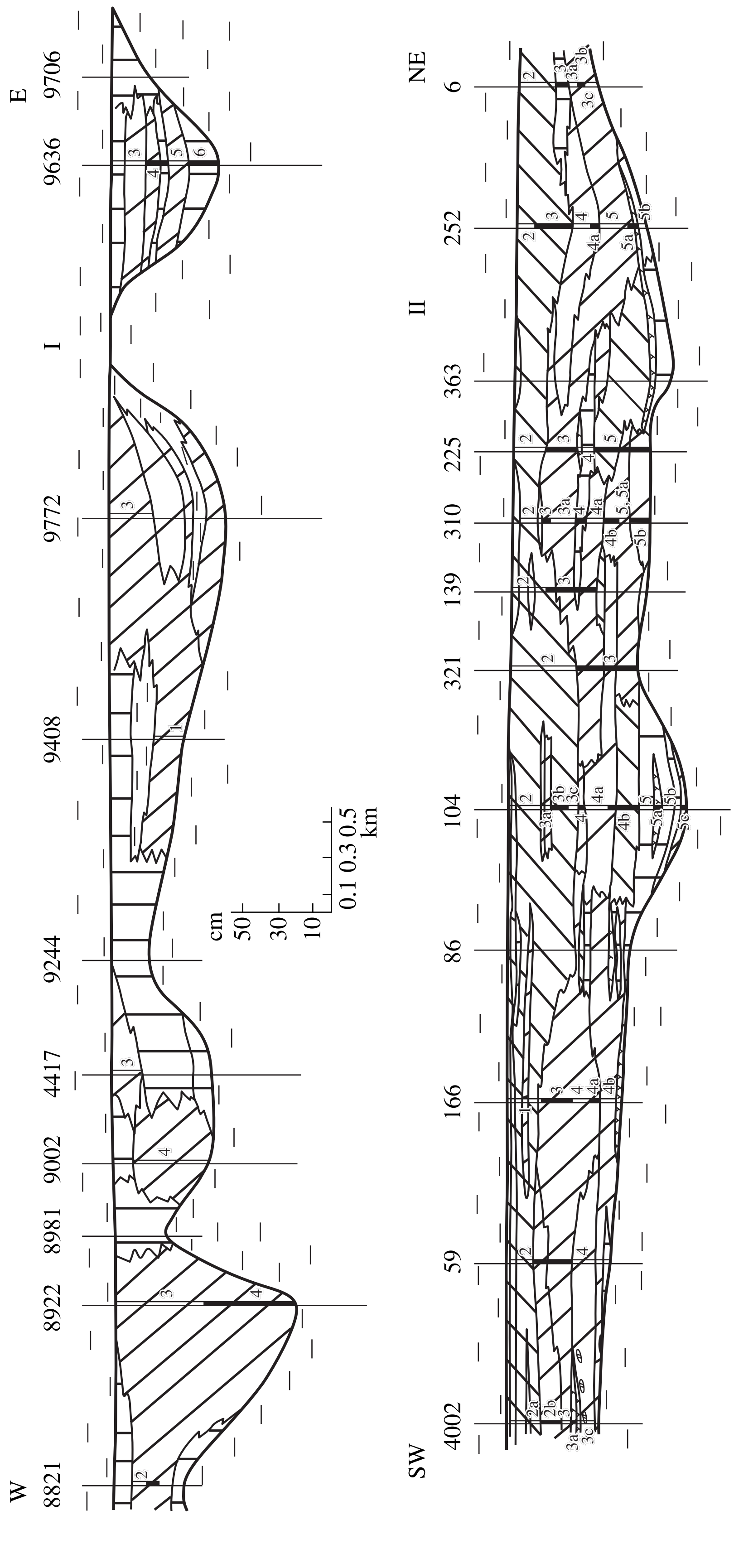

Fig. 2. Longitudinal sections of deposits. (I) Northeastern part of the Bagaburul ore field; (II) Shargadyk deposit. Other symbols as in Fig. 1.

Table 2. Distribution of examined components in ores of the Shargadyk deposit

Borehole and sample nos.	Content, %					
	P_2O_5	S_{pyr}	Al_2O_3	U recalculated for P_2O_5	REE recalculated for P_2O_5	CO_2
4002-2a	6.86	21.48	6.72	0.08	1.19	–
4002-2b	18.90	8.91	3.96	0.06	0.93	2.86
4002-3	20.73	9.94	2.61	0.07	–	2.20
4002-3a	10.83	2.52	2.19	0.05	–	21.56
4002-3c	14.42	8.69	6.94	0.07	–	1.45
Average for borehole	14.35	10.31	4.48	0.06	–	
166-2	8.86	19.01	5.26	0.07	–	–
166-3	21.26	9.96	2.15	0.07	–	2.64
166-4	21.47	8.00	2.70	0.06	–	2.86
166-4a	17.80	12.38	3.39	0.06	–	1.94
166-4b	18.83	9.54	3.37	0.08	–	2.95
Average for borehole	17.64	11.77	3.37	0.07	–	
104-2	6.64	19.30	5.12	0.09	–	–
104-3a	11.14	15.35	6.55	0.08	–	–
104-3b	5.50	21.42	6.55	0.10	–	–
104-3c	2.87	25.35	5.97	0.09	–	–
104-4a	11.19	15.68	4.91	0.06	–	–
104-4b	9.95	21.85	6.92	0.04	–	–
104-5	14.92	7.65	4.87	0.08	–	3.65
104-5a	1.92	3.79	16.34	0.12	–	–
104-5b	16.08	9.27	4.77	0.07	–	5.72
104-5c	2.88	6.08	14.32	0.10	–	–
Average for borehole	8.31	14.57	7.63	0.08	–	
310-2	6.37	25.05	6.20	0.09	–	–
310-3	17.47	9.23	4.58	0.05	–	1.94
310-3a	18.84	10.73	3.48	0.09	–	1.80
310-4a	18.49	11.07	3.09	0.08	–	3.21
310-4b	17.98	9.95	4.04	0.09	–	2.38
310-5	20.49	7.75	2.47	0.08	–	4.93
310-5a	3.34	2.94	7.82	0.09	–	–
310-5b	15.37	8.02	5.78	0.10	–	3.16
Average for borehole	14.79	10.59	4.68	0.08		
252-2	4.64	22.66	6.55	0.06	–	–
252-3	6.18	22.26	6.65	0.12	–	–
252-4	10.29	16.05	6.11	0.08	–	–
252-4a	14.48	13.34	4.86	0.12	–	1.63
252-5	14.41	14.25	4.69	0.09	–	2.13
252-5a	6.12	7.62	2.63	0.09	–	22.44
252-5b	11.27	15.35	5.66	0.10	–	2.20
Average for borehole	9.63	15.93	5.31	0.09	–	
06-2	5.71	24.03	5.95	0.08	–	–
06-3	8.83	16.29	6.85	0.09	–	–
06-3a	14.42	14.69	3.96	0.11	0.5	1.67
06-3b	10.12	4.03	3.24	0.10	–	18.37
06-3c	13.80	15.99	3.69	0.08	–	2.42

Table 2. (Contd.)

Borehole and sample nos.	Content, %					
	P_2O_5	S_{pyr}	Al_2O_3	U recalculated for P_2O_5	REE recalculated for P_2O_5	CO_2
Average for borehole	10.57	15.00	4.74	0.09	–	
139-2	6.20	22.56	–	0.10	–	–
139-3	12.62	9.18	–	0.10	–	–
Average for borehole	9.41	15.87	–	0.10		
59-2	7.22	21.19	–	0.07	0.88	–
59-3	15.25	9.40	–	0.10	0.93	–
59-4	12.12	12.41	–	0.06	0.75	–
Average for borehole	11.53	14.33	–	0.08	0.85	
321-2	5.40	20.46	–	0.06	–	–
321-3	15.50	14.67	–	0.09	–	–
Average for borehole	10.45	17.56	–	0.08	–	–
225-2	6.90	22.75	6.60	0.10	0.96	–
225-3	18.70	7.98	3.70	0.10	0.77	–
225-4	9.40	3.91	3.40	0.08	0.67	–
225-5	14.42	10.73	5.70	0.10	0.86	
Average for borehole	12.35	11.34	4.85	0.09	0.82	–
Average for section	11.90	13.73	5.00	0.08	0.81	

terized by the U content in phosphate matter close to the above-mentioned one (0.05–0.1%) (Table 2).

In some clayey interbeds with Al_2O_3, P_2O_5, and S_{pyr} contents of 14–16, 2–3, and 4–6%, respectively (Borehole 104, Bed 5), the phosphate matter is usually most enriched in U (0.10–0.12%).

Thus, sharp changes in the component composition of ore matter in the Shargadyk deposit virtually do not affect the U content in bone phosphates. In some sections (Fig. 2; boreholes 166, 139, and others), the high-sulfur and high-phosphorus ores are characterized by similar U contents.

The more limited data on the REE distribution show that it is similar to that of uranium. For instance, in boreholes 225 and 59, the REE content ranges from 0.77 to 0.93% in bone phosphates from the high-phosphorus ores (P_2O_5 14–19%, S_{pyr} 8–11%) and from 0.88 to 0.96% in the high-sulfur ores (S_{pyr} 21–23; P_2O_5 approximately 7%) (Table 2).

Thus, the presented analytical data indicate a sufficiently persistent metal content in bone phosphates against the background of sharp variations in the component composition of carbonate interbeds and ores. All these features hamper the interpretation of sedimentation conditions controlling the U and REE concentration in fish remains.

The **Bogorodsk deposit** is located 2–3 km southeast of the Shargadyk deposit in the open part of the basin. Both these deposits formed synchronously in line with a similar sedimentation scenario, which is reflected in the prevalence of FBD in the lower part of the Bogorodsk deposit. However, the FBD in this deposit is spatially more compact.

The morphology of the Bogorodsk deposit is noted for the presence of echelon series of narrow (50–125 m) and short (a few hundreds of meters) submeridional, relatively deep (1.5–3 m) scours where the FBD concentrated at the first stage of deposit formation.

The base of scours is usually uneven with erosion signs and the local development of cross bedding and small gagate lenses in bone accumulations. The high-phosphorus (P_2O_5 up to 22%) lenticular ores are characterized by the subordinate content of IS (S_{pyr} 6–10%) and, particularly, clayey material (Al_2O_3 3–4%).

Thin (up to 0.6 m) high-sulfur ores (S_{pyr} up to 20–23%) with the subordinate FBD (P_2O_5 5–10%) are spread over a large area (20 × 5 km) beyond the local scours.

The Bogorodsk deposit is characterized by slightly higher metal contents (U 0.16%, REE 1.06%) in bone phosphates as compared with the Shargadyk deposit (Stolyarov and Ivleva, 1991). At the same time, the contents of these metals insignificantly change in compositionally different ores of both deposits. The U content varies from 0.1 to 0.15% in the high-phosphorus ore and from 0.12 to 0.16% in the high-sulfur variety. Variations in the REE content are also insignificant (0.92–1.06%).

The factors responsible for the high sulfide content in the considered ores (typical of the deepwater phos-

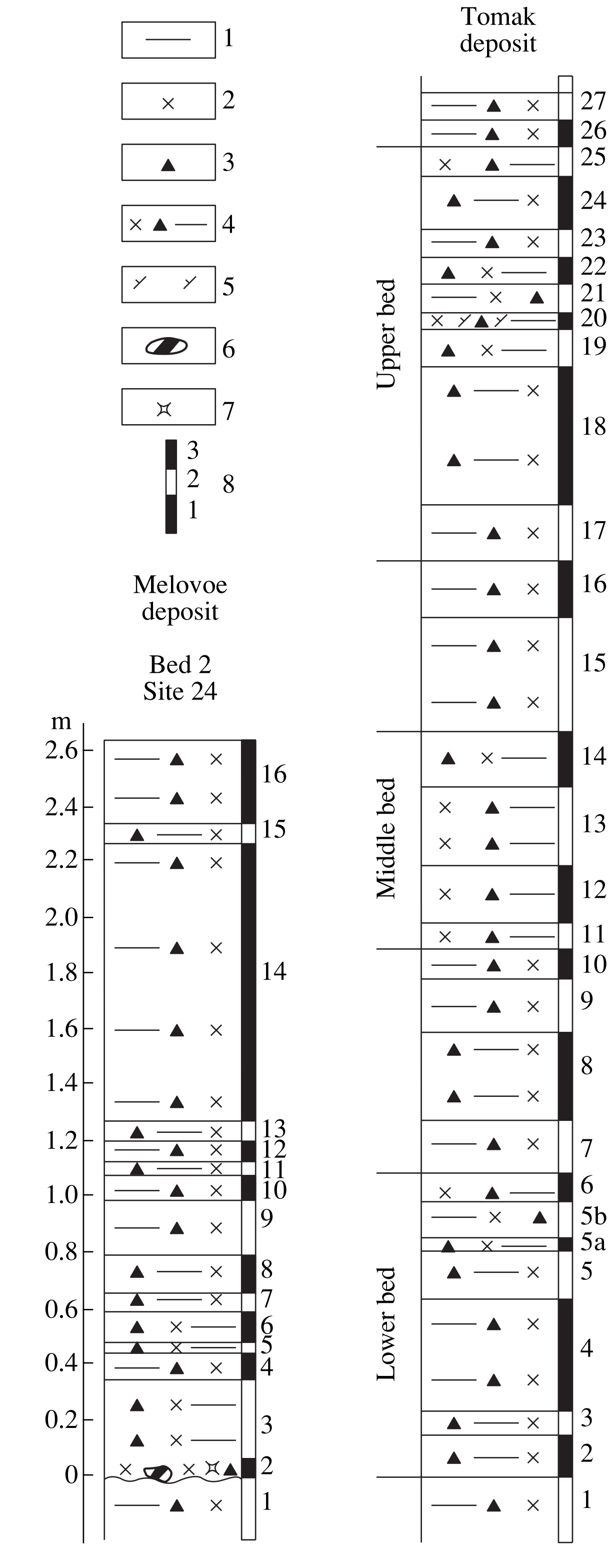

Fig. 3. Sections of ore beds in the Melovoe and Tomak commercial deposits. (1) Clay; (2) bone detritus; (3) iron sulfide; (4) ratio of components in ore (the dominant component is shown in the left); (5) carbonate interbed; (6) coalified wood remains; (7) large bone remains; (8) sample numbers.

phorus-poor Stepnoe deposit) in combination with the high FBD concentration (typical of relatively shallow-water formation settings) are unclear. At present, one can only affirm that the metal potential of bone phosphates is notably higher in the deeper sedimentation settings. This statement is particularly valid for uranium. For instance, the average U content in bone phosphates of the Bogorodsk deposit is two to three times lower relative to the Stepnoe deposit (0.1–0.16 and 0.3%, respectively), whereas the REE content decreases to a lesser extent (0.84–1.06 and 1.44%, respectively).

The **Bagaburul ore field** represents the shallowest-water type of high-phosphorus ores with relatively low sulfide content. The ore field is located in the eastern part of the Ergeni district as a narrow (1–2 km) band extending over more than 20 km (Stolyarov and Ivleva, 1991).

The ore field comprises approximately twenty lenticular-intricate bodies (up to 3.5 km long and 0.5–1.1 km wide) extending in the sublatitudinal direction. They are characterized by variable thickness (0.2–1.1 m) due to the uneven (Z-shaped) surface of the eroded underlying clays. Their angular fragments (up to 10–15 cm) locally occur at the periphery of lenses.

Let us consider the main features of the composition, structure, and metal potential of bone accumulations in individual lenses in the northeastern approximately 10-km-long sector of the Bagaburul ore field (Fig. 2).

Their composition is characterized by the following average values (%): P_2O_5 17.5, S_{pyr} 11.2, Al_2O_3 3.7, U 0.2, and REE 0.99 (Table 3). It should be noted that the carbonate material, a common constituent of the shallow-water ores, is always absent in the bone–sulfide ores.

The FBD accumulations in the ore field are usually confined to erosional deeps separated by the prevalence or absence of the coeval clayey material. The FBD material prevails in some scours. In this connection, Borehole 8922 presents the most representative section (Fig. 2). The lower part of this section (0.5 m) is mainly composed of the friable FBD accumulation consisting of the prevalent platy and the less common rib bones (up to 1–2 cm) of mammalians and other animals (up to 3.5 cm). The sand- to silt-sized FBD is cemented by the bone detritus with an insignificant admixture of sulfides, which form only powdery films on the bone surface. The absence of the coarser basal layer is the characteristic feature of the studied section. The upper part of the section (0.5 m) encloses thin (0.5–2.0 cm) clayey laminae imparting the lenticular-bedded appearance to the rock.

Sediments in this scour have a remarkable uniform composition (%): P_2O_5 18–19, S_{pyr} 12, Al_2O_3 2–3, U 0.22–0.23, and REE 1.05 (Table 3).

The FBD also predominates in the neighboring shallower (0.5 m) scour (Borehole 9002, P_2O_5 17.86%), although the IS content is substantially higher

(S_{pyr} 15.8%). The sludge-type detritus is almost black owing to the presence of pyrite dissemination. However, the latter does not cement the bone mass. This section is characterized by the highest metal content in the FBD (U 0.27%, REE 1.22%), which is probably explained by the higher sulfide content in ores.

Sediments in the easternmost scour (Borehole 9636) are compositionally more differentiated. Beds with abundant FBD (P_2O_5 15.5–20.7%) and lower IS content (S_{pyr} 7–10%) contain a lighter (brown) bone detritus. It commonly occurs as platy, compact, and relatively large fragments (up to 0.5 cm) cemented only by the bone detritus (Al_2O_3 2–5%). Although the FBD in this scour is similar to that considered above, its metal potential is significantly lower (U 0.16–0.17%, REE 0.85%). The more clayey layers (Al_2O_3 8–10%) are also depleted in U and REE (Table 3).

Thus, the detailed consideration of deposits from the Ergeni ore district with substantially different paleogeographic settings does not provide an unambiguous answer concerning the correlation of metal content in bone remains with changes in their component composition.

New data on commercial deposits of the Mangyshlak district obtained during the study of ore beds in quarries of the Melovoe and Tomak deposits are presented below.

The Melovoe deposit. The composition, structure, and metal potential of the main industrial Melovoe deposit are discussed in several publications (Stolyarov and Ivleva, 1995; Stolyarov and Kochenov, 1995; Sharkov, 2000). In particular, it was noted that the U content in the FBD is substantially higher in the finer fraction (<0.1 mm) as compared with the coarser one (0.4% and 0.1%, respectively).

The average composition of four beds constituting the Melovoe deposit is presented in (Stolyarov and Ivleva, 1995; Stolyarov and Kochenov, 1995). In contrast to previously published data, the metal content in Table 4 is recalculated for P_2O_5.

As is evident, the deposit is composed of low-phosphorus (P_2O_5 4.20%), medium-sulfur (S_{pyr} 11.63%), and high-alumina (Al_2O_3 12.37) ores with average contents of U and REE being equal to 0.32 and 1.25%, respectively. The sulfide content is relatively low (S_{pyr} 8.4–9.1%) in two lower beds and higher (S_{pyr} 14.5%) in upper beds.

However, the noted differences in the component composition do not affect the metal content in bone phosphates. One can only note that Bed 3 with the highest sulfide content (S_{pyr} 14.6%) demonstrates the lowest concentrations of U (0.27%) and REE (0.98%).

Bed 2 (1.3 m thick) is characterized by the following average contents (%): P_2O_5 5.15, S_{pyr} 9.1, Al_2O_3 13, U 0.35, and REE 1.29. The bed contains the largest reserves of U and REE in the Melovoe deposit.

Table 3. Distribution of examined components in ores of the northeastern Bagaburul ore field

Borehole and sample nos.	Content, %				
	P_2O_5	S_{pyr}	Al_2O_3	U recalculated for P_2O_5	REE recalculated for P_2O_5
8618-1	9.53	4.67	11.80	0.16	0.79
8821-2	20.06	13.50	1.26	0.21	0.92
8922-3	18.40	12.08	2.94	0.23	1.05
8922-4	19.26	12.12	2.19	0.22	1.04
Average for Borehole 8922	18.83	12.10	2.56	0.22	1.04
9002-4	17.86	15.80	1.86	0.27	1.22
4417-3	18.64	12.91	1.92	0.22	1.18
9408-1	18.81	9.62	2.94	0.19	0.96
9772-3	20.64	12.85	0.96	0.20	0.95
9636-3	13.19	6.65	8.30	0.16	0.89
9636-4	16.52	10.25	4.74	0.16	0.86
9636-5	20.72	7.32	2.36	0.17	0.84
9636-6	10.84	6.94	9.57	0.16	0.95
Average for Borehole 9636	15.32	7.79	6.24	0.16	0.88
Average for deposit	17.46	11.15	3.69	0.20	0.99

Table 4. Distribution of examined components in ore beds of the Melovoe deposit

Bed no.	Average content, %				
	P_2O_5	S_{pyr}	Al_2O_3	U recalculated for P_2O_5	REE recalculated for P_2O_5
Bed 4	4.47	14.40	11.50	0.32	1.42
Bed 3	4.00	14.60	11.00	0.27	0.98
Bed 2	5.15	9.10	13.00	0.35	1.29
Bed 1	3.20	8.40	14.00	0.34	1.33
Average for all beds	4.20	11.63	12.37	0.32	1.25

The data presented below are related to the western part of Bed 2 formed in relatively deepwater settings.

The fish-facies clays underlying Bed 2 show the following composition (%): P_2O_5 0.4–1.0, S_{pyr} 2.8–4.0, Al_2O_3 17.6–20.2, U 0.3–0.46, and REE 1.2–2.6.

The basal part of the bed encloses a lens (up to 6 cm thick) with bone detritus up to 2.0–4.0 cm across. The latter includes rare cetacean bones, which are sometimes arranged vertically relative to bedding, and coalified wood remains (gagate). Despite the relatively coarse-detrital composition, the lens is enriched in the

Table 5. Distribution of examined components in Bed 2 of the Melovoe deposit

Section and sample nos.	Content, %					
	P_2O_5	S_{pyr}	Al_2O_3	U recalculated for P_2O_5	REE recalculated for P_2O_5	CO_2
24-16	1.50	7.12	15.73	0.26	1.49	–
24-15	5.99	11.14	10.79	0.16	0.86	0.57
24-14	0.78	5.02	15.90	0.22	1.47	3.34
24-13	3.25	15.64	11.93	0.25	1.58	0.22
24-12	1.29	6.56	13.39	0.28	1.10	5.12
24-11	4.52	12.60	10.67	0.26	1.07	1.10
24-10	3.00	11.90	12.04	0.27	1.41	1.01
24-9	2.19	12.54	13.10	0.30	1.17	0.79
24-8	7.20	10.03	8.91	0.26	1.43	4.53
24-7	3.89	12.68	10.87	0.34	1.40	1.04
24-6	10.83	16.49	6.34	0.30	1.23	0.75
24-5	11.97	13.23	6.81	0.30	1.36	0.88
24-4	8.27	9.86	10.46	0.32	1.21	0.53
24-3	11.62	12.02	7.37	0.32	1.30	0.79
24-2	16.89	9.99	5.14	0.37	1.24	1.36
Average for section	6.21	11.12	10.63	0.28	1.28	
Underlying clays						
24-1	0.41	2.80	20.02	0.46	1.18	0.22

FBD (%): P_2O_5 9–17; S_{pyr} 10–16, Al_2O_3 5–7, U 0.31–0.37, and REE 1.2.

Bed 2 demonstrates a layered distribution of FBD through the section (Fig. 3, Table 5). Its lower part (layers 3–6) with a total thickness of 0.6 m encloses high-phosphorus layers (P_2O_5 11–12%) characterized by stable concentrations of U (0.30–0.32%) and REE (1.2–1.4). Upward the section (layers 7–13), the bed is composed of relatively low-phosphorus (P_2O_5 1.3–7.2) ores with a lower U content (0.25–0.34%), but the REE concentration remains stable (1.0–1.6%).

In overlying clays (layers 14, 16) with FBD accumulations at bedding surfaces (P_2O_5 0.8–1.5%), the U content is even lower (0.22–0.26%), whereas the REE concentration remains high (approximately 1.5%). However, the thin (5 cm) layer 15 with decomposed red FBD (P_2O_5 5.99%, S_{pyr} 11.14%) shows the lowest contents of U (0.16%) and REE (0.86%) in the entire section. This anomaly is unexplainable so far.

The presented data indicate that the lower (relatively high-phosphorus) part of Bed 2 is also characterized by a substantially higher U content in bone phosphates (0.30–0.32%) as compared with its upper low-phosphorus part (0.25–0.34%). At the same time, the REE contents are relatively constant. The variations in sulfide concentration (S_{pyr} 6–16%) do not affect the metal potential of FBD.

The **Tomak deposit** is located 12–15 km north of the Melovoe deposit (Stolyarov and Ivleva, 1995). The NW-trending deposit, 18–20 km long and 1.0–1.5 km wide, is controlled by the bottom scarp. It accumulated in shallower settings accompanied by the formation of sedimentation breccia. The Tomak deposit differs from the Melovoe deposit by a two times higher FDB concentration (P_2O_5 8.5%) and lower contents of U (0.22%) and REE (0.93%).

Ores of the deposit are mainly confined to three beds. Their composition and structure were studied in wall sections of the industrial quarry. The results are presented in Fig. 3 and Table 6.

The *lower bed* (1.1 m) demonstrates significant variations in the component composition and metal potential of FBD through the section. For instance, the basal part of the bed (layers 2, 3; 0.25 m) with large bone fragments is characterized by the highest content of S_{pyr} (17–21%), low content of P_2O_5 (4.3–4.8%), and extremely low contents of U (0.07–0.08%) and REE (0.24–0.32%).

In layers 5a and 6 with the highest P_2O_5 concentrations (13.0–13.5%), brown FBD detritus, and signs of underwater slumping(, the metal content is significantly higher (U 0.18–0.20%, REE 0.30–0.65%). Similar metal concentrations (U 0.17–0.08%; REE 0.69%) are also typical of bone phosphates from the clayey layer 4 with the P_2O_5 content of only 0.61%.

The *middle bed* (0.8–1.5 m) is notable for its general enrichment in the brown FBD (P_2O_5 10.8–15.4%, average 12.5%) that forms lenslike accumulations with large bone fragments and coprolites. The bed is characterized by relatively constant contents of U (0.14–0.17%) and REE (0.67–0.75%). The basal section includes a lenticular layer (up to 0.1 m) enriched in the brown FBD and gagate inclusions (layer 11). It is sharply enriched in phosphorus (P_2O_5 23.78%, S_{pyr} 5.1%, Al_2O_3 2.26%), but its metal potential is similar to that of the lower bed (U 0.19%, REE = 0.70%). In enclosing clays (layers 10, 15; P_2O_5 0.22–0.34%), the phosphate matter is most enriched in U (0.25–0.34%) and REE (1.25–1.80%).

The *upper bed* (up to 1.5–2.5 m) is characterized by similar U (0.14–0.18%) and higher REE (up to 1.13%, average 0.85%) contents as compared with the middle bed. However, this bed is marked by significant variations in the composition of FBD (P_2O_5 2.3–14.7%, average 8%) and other components through the section. Layer 20 (0.1 m) in this bed demonstrates an unusual composition. It is enriched in FBD (P_2O_5 14.77%) with carbonate cement (CO_2 12.81%) and depleted in IS (S_{pyr} 9.2%) and, particularly, clayey material (Al_2O_3 2.2%). The phosphate matter shows an anomalously high U concentration (0.55%), while the REE content is ordinary (0.70%).

Table 6. Distribution of examined components in ore beds of the Tomak deposit

Sample nos.	Content, %					
	P_2O_5	S_{pyr}	Al_2O_3	U recalculated for P_2O_5	REE recalculated for P_2O_5	CO_2
Overlying clays						
27	0.21	3.00	19.00	0.15	3.03	–
26	0.46	3.10	19.20	0.15	1.51	–
Average for clays	0.33	3.05	19.10	0.15	2.27	–
Upper bed						
25	14.70	7.80	6.60	0.15	0.62	–
24	3.75	22.05	6.65	0.17	1.13	–
23	2.27	11.00	13.80	0.14	1.10	–
22	8.53	14.60	8.45	0.16	0.78	–
21	8.09	6.00	11.00	0.14	0.83	–
20	14.77	9.20	2.20	0.55	0.70	12.84
19	10.11	10.60	7.65	0.16	0.69	–
18	6.56	13.47	9.99	0.14	0.78	0.35
17	2.95	4.60	15.0	0.18	1.01	–
Average for section	7.97	11.03	9.03	0.19	0.85	
Intermediate clays						
16	0.20	1.20	21.40	0.15	1.51	–
15	0.22	4.14	17.70	0.34	1.80	–
Average for clays	0.21	2.67	19.55	0.24	1.65	
Middle bed						
14	11.25	13.49	6.73	0.14	0.67	0.84
13	15.38	8.64	5.96	0.15	0.71	1.14
12	10.81	9.29	8.59	0.17	0.75	0.92
11	23.78	5.10	2.26	0.19	0.70	2.16
Average for section	15.30	9.13	5.88	0.16	0.71	
Intermediate clays						
10	0.34	2.71	19.19	0.25	1.25	–
9	0.48	2.30	18.53	0.25	0.82	–
Average for clays	0.41	2.50	18.86	0.25	1.03	
Lower bed						
8	2.95	16.65	11.02	0.48	1.54	–
7	0.22	1.73	19.16	0.29	–	–
6	12.97	11.63	6.53	0.20	0.65	0.88
5b	9.29	7.22	10.37	0.15	0.49	0.62
5a	13.51	15.53	4.78	0.18	0.30	0.88
5	6.56	18.03	7.90	0.22	0.97	0.31
4	0.61	1.79	19.87	0.17	0.69	0.26
3	4.30	21.41	7.65	0.08	0.24	–
2	4.79	16.95	9.42	0.07	0.32	–
Average for section	6.13	12.33	10.74	0.20	0.65	
Underlying clays						
1	0.60	2.04	19.10	0.14	0.70	–

For comparison, it should be noted that layer 25 (0.1 m) located at the top of the bed is also enriched in the brown FBD (P_2O_5 14.7%), but it is carbonate-free. The U content in phosphate (0.15%) is similar to the values typical of the upper bed and the deposit as a whole.

Thus, the FBD material accumulated in relatively deepwater settings in both Mangyshlak and Ergeni ore districts. It is generally characterized by the high metal contents (U 0.35% or more, REE 1.3%), the ores are depleted in sulfides (S_{pyr} 9% versus 16% in the Stepnoe deposit). Deposits accumulated in relatively shallow-water settings demonstrate relatively higher FBD concentration and lower metal contents (U 0.2%, REE 0.9%).

DISCUSSION

The materials presented in this communication show that, despite the sufficient knowledge of FBD deposits, many aspects of metal distribution in them remain unclear so far.

In this connection, it should be noted that phosphate matter in sedimentary rocks usually contains rare metals, including uranium that attracted the highest interest some time ago. Issue of phosphorites as a complex mineral resource was first put forward by Kholodov (1963) who reported that the phosphorites are characterized by wide variations in the concentration of U (0.0007–0.06%) and REE (0.02–0.14%, average 0.08%). In the latest work dedicated to uranium in phosphorites, Baturin and Kochenov (2001) demonstrated that the U concentration in phosphorites of the Precambrian and younger periods range from 20 to 130 ppm (75 ppm, on the average).

As compared with the values mentioned above, the U and REE contents in bone phosphates are always substantially higher (more than an order of magnitude). For example, average U and REE contents in the Ergeni district estimated for 13 deposits range from 0.10 to 0.31% (average 0.21%) and from 0.84 to 1.44% (average 1.14%), respectively. In Mangyshlak (6 deposits), these value range from 0.10 to 0.32% (average 0.2%) and from 0.70 to 1.25% (average 0.92%), respectively (Table 7).

As is evident, the average U content in the FBD from deposits of the Ergeni and Mangyshlak districts are similar (0.20–0.21%), while REE concentrations slightly vary from 0.92 to 1.14%. The average U and REE contents in these ore districts are 0.2 and 1.03%, respectively.

The higher metal contents in bone phosphates, relative to the traditional chemogenic phosphorites, can logically be explained by the presence of reactive albumen OM in bone remains, which resulted in the formation of a highly reducing (H_2S-rich) environment that was most favorable for the fixation of rare elements. Their concentration increased in the porous (nonmineralized) phosphate matter owing to the increase in the free surface of the phosphate material of bone remains that controlled their sorption capacity (Kochenov and Stolyarov, 1996; and others).

It was assumed that highly reducing environments could stimulate the generation of iron sulfides and associated chalcophile elements (Ni, Co, Mo, and others).

Summarization of the available ample material pertaining to the considered problem and the description of the structural and geochemical features presented in this communication for some types of deposits make it possible to scrutinize some previously hushed up aspects of metal distribution in FBD deposits.

It should primarily be noted that the FBD and IS display coexistence (paragenesis), but they substantially differ in quantitative terms. This is evident from the regular general differentiation of deposits by their component composition: high-sulfur deposits are usually depleted in phosphorus and vice versa (Table 7). The Shargadyk deposit represents the only exception. However, high-phosphorus and high-sulfur ores are spatially separated in this deposit as well.

It is obvious that iron sulfides were not a simple product of bacterial decomposition of albumen OM in bone accumulations, because iron was independent to a certain extent in the sedimentary process. It was delivered to sea basin, but its source and some sedimentation features, such as the extension of sulfide beds over tens of kilometers, remain unclear (Kochenov and Stolyarov, 1960, 1966; Stolyarov and Sharkov, 1976; and others).

The Stepnoe (Ergeni district) and Cherkessk (northern Caucasus) deposits extending over more than 50 km are the most remarkable examples of giant sulfide accumulations (Stolyarov and Ivleva, 2004a, 2004b).

Apparently, the high-sulfur ores, which formed in the most reducing environments, should always be characterized by the high metal concentration in the FBD. Indeed, the phosphate matter of the Stepnoe deposit (average S_{pyr} 16%) is generally marked by the highest concentrations of U (0.25–0.45%, average 0.31%) and REE (1.2–2.1%, average 1.44%). In contrast, other high-sulfur (S_{pyr} 15–16%) deposits (Shargadyk, Bogorodsk, and Cherkessk) are characterized by low concentrations of U (0.10–0.16%) and REE (0.48–1.0%) (Table 7).

Thus, the metal content in the FBD generally does not depend on the sulfide content in ores. However, one can observe some regular relationships between the FDB content and its metal potential. For instance, high-phosphorus deposits (P_2O_5 > 10%) are usually characterized by lower U contents in the FBD (0.10–0.24%) as compared with medium-phosphorus deposits (up to 0.29–0.31%) (Table 7). Separate parts (beds) of deposits display even greater differences in U contents ranging from 0.07–0.20% in the high-phosphorus ores to 0.2–0.5% in the low-phosphorus varieties.

The REE behavior is similar. Their content is higher (1.0–1.5%) in deposits with the lower FBD content

Table 7. Average composition of ores from Upper Oligocene deposits of the central Eastern Paratethys

Deposit	Average content, %				
	P_2O_5	S_{pyr}	Al_2O_3	U recalculated for P_2O_5	REE recalculated for P_2O_5
Mangyshlak ore district					
Melovoe	4.20	11.63	12.37	0.32	1.25
Tomak	8.50	11.20	11.50	0.22	0.93
Taibagar	8.00	9.30	10.0	0.16	0.79
Tasmurun	5.16	15.30	7.00	0.23	0.88
Sadyrnyn	3.14	9.50	12.00	0.21	0.96
Unerin	9.44	7.56	9.00	0.10	0.70
Average for all deposits	6.41	10.75	10.31	0.20	0.92
Ergeni ore district					
Stepnoe	4.80	16.00	7.50	0.31	1.44
Shargadyk	13.60	15.40	5.30	0.10	0.84
Bogorodsk	5.68	16.00	6.90	0.16	1.06
Bagaburul	17.40	8.10	6.00	0.13	0.98
Northeastern Bagaburul ore field	15.00	7.70	3.50	0.21	1.04
Yuzhnaya Burata	16.50	9.00	4.80	0.21	1.04
Prudovaya	17.80	8.60	8.00	0.27	1.18
Tsentral'naya	3.90	12.80	8.80	0.23	1.16
Nugra	6.00	5.00	8.10	0.27	1.50
Severnyi Kharabuluk	10.60	6.30	8.60	0.24	1.27
Yashkul	6.70	12.50	9.98	0.14	1.45
Troitsk	7.00	12.50	8.20	0.12	0.77
Chernye Zemli	2.11	11.80	–	0.23	0.85
Average for all deposits	9.80	10.90	7.14	0.21	1.14
Cherkessk (northern Caucasus)	1.40	15.80	–	0.13	0.48
Average for province	5.87	12.45	8.72	0.18	0.85

(P_2O_5 10%) and lower (0.8–1.2%) in the high-phosphorus varieties. The notable exception is the Cherkessk deposit (REE 0.48%, U 0.13%, and P_2O_5 1.4%).

In general, the phosphate matter of large FBD accumulations is usually characterized by low concentrations of metals (primarily, uranium) and very high REE/U values (up to 7 or 8 in the Shargadyk and Unerin deposits), whereas this value ranges from 4 to 6 in some high-phosphorus deposits.

The increase of metal content in phosphate matter with the decrease in the FBD content is also noted for low-phosphorus ores. For instance, the Stepnoe deposit (P_2O_5 4.8%, on the average) includes beds (P_2O_5 1.2–2.3%) high concentrations of U (0.39–0.41%, average 0.31%) and REE (up to 1.7–2.1%, average 1.44%) in the FBD (Tables 1, 7). Finally, clayey beds with the P_2O_5 and S_{pyr} contents of 0.2–0.8 and 3.2–6.5%, respectively, are characterized by the highest U contents recalculated for phosphate matter (0.45–1.2%). This phenomenon should probably be related to the high dispersion degree of phosphate material.

There are also opposite examples. The low-phosphorus (P_2O_5 6.7%) Yashkul deposit (Ergeni district) demonstrates very low U contents in the FBD (0.14%) and persistent high REE contents (1.45%). As a result, the deposit is characterized by the tenfold prevalence of REE over U.

Considering the dependence of metal content in bone remains on the component composition of ores, we should also emphasize the presence of carbonate material in them. As was noted in our previous works (Stolyarov and Ivleva, 1995; Stolyarov and Kochenov, 1996), the high carbonate content in some Mangyshlak deposits (Taibagar and Tasmurun) negatively correlates mainly with the U concentration in bone phosphates, which decreases to 0.16–0.23% (Table 7). However, carbonate material in the Stepnoe and Shargydak deposits does not significantly affect the metal potential of phosphate matter. Moreover, the Tomak deposit

(Mangyshlak) encloses 0.1-m-thick layer with an anomalous composition (CO_2 12.84%, P_2O_5 14.7%, Si_{pyr} 9.2%, and Al_2O_3 2.2%). The U concentration in the FBD is substantially higher (0.5%) against the background of its prevalent values (0.14–0.19%), while the REE content is relatively constant (0.7%). Reasons responsible for such behavior of uranium in the FBD of the high-phosphorus carbonate layer are unclear so far.

Variations in the component composition and metal potential of FBD deposits reveal the following facies peculiarities. The FBD concentration is higher in relatively shallow-water sediments relative to the deepwater sediments where the FBD is subjected to roiling and concentration. However, deposits accumulated in such settings (Tasmurun, Sadyrnyn, Yashkul, and others) are also frequently marked by low phosphorous contents (Stolyarov and Ivleva, 1991, 1995; Stolyarov and Kochenov, 1995; Sharkov, 2000).

The IS behavior is also ambiguous with respect to their facies settings. On the one hand, their intense development in the relatively deepwater sharply reducing settings with the formation of large sulfide deposits (Stepnoe) and extended beds seems natural. On the other hand, the large-scale sulfide formation is also typical of the relatively shallow-water zones of the basin (Cherkessk, Shargadyk, Tasmurun, and other deposits).

In this respect, the Melovoe deposit is very remarkable (Table 4). Beds 1 and 2 of this deposit formed in deeper settings show lower sulfide contents (S_{pyr} 8.4–9.1%), whereas beds 3 and 4 with signs of sedimentation in shallow-water environments are characterized by the high Fe sulfide concentration (S_{pyr} 14.5%).

The influence of facies environments on the metal content in the FBD is also frequently ambiguous. On the one hand, relatively deepwater zones with low FBD content is accompanied by the highest metal content, regardless of the IS concentration (Stepnoe deposit, beds 1 and 2 of the Melovoe deposit). On the other hand, the FBD can also contain some U (0.05–0.16%) in similar facies settings.

Regardless of FBD and sulfide concentrations, the metal content is decreased in the FBD material of the relatively shallow-water deposits. However, local variations can be very high (up to 0.27 and 1.5% for U and REE, respectively) (Table 7; Prudovaya, Nugra, and other deposits). These values are comparable with the values typical of the deepwater low-phosphorus deposits.

It is also worth noting that the impact of large carbonate accumulations on the FBD metal potential is not necessarily negative in some deposits. To the contrary, some carbonate layers demonstrate increase of the uranium content.

All the contradictions discussed above hamper the recognition of facies–geochemical environments promoting the concentration of U and REE in the phosphate matter of fish bone remains.

It should be emphasized that fish bone remains located in or beyond the deposits always represent metalliferous formations. The REE and U mineralization is recorded in dispersion haloes and sediments of the fish facies through the entire vast territory of the Late Oligocene sea basin (Ciscaucasus, Volga–Don, and Mangyshlak regions).

We attempted to estimate the average geochemical parameters that characterize the composition of FBD deposits in the Eastern Paratethys. The results obtained are as follows (%): P_2O_5 5.87, S_{pyr} 12.45, Al_2O_3 8.72, U 0.18 and REE 0.85 (Table 7).

As is evident, the FBD deposits within the reference Eastern Paratethys province are generally characterized by high average contents of U (0.0075%) and REE (0.08%), which are more than one order of magnitude higher relative to the traditional (chemogenic) phosphorites (Kholodov, 1963; Baturin and Kochenov, 2001).

Attention should also be given to the following important fact. The considered FBD deposits contain 25% of iron sulfides and 44% of clayey material. This is atypical of sedimentary phosphate ores. The cause-and-effect relations between the FBD and IS in the general evolution resulting in the formation of deposits remain unclear so far.

CONCLUSIONS

Many aspects concerning the formation conditions of metalliferous FBD deposits are still debatable.

In terms of metallogeny, the source of ore elements is the most urgent issue. For example, the available data do not indicate the presence of land provenances for huge masses of iron. One should also search other sources for all elements associated with the FBD.

At the same time, reliable evidence for the endogenic influx of the considered elements into the basin along deep faults is also absent so far.

Thus, the issue of the source of material for the formation of unique metalliferous FBD deposits requires further purposeful studies.

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