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Uraniferous Phosphorites in Bottom Sediments of Lake Baikal

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Interest in the study of deep-water sediments of Lake Baikal is governed by the possibility of using the characteristic features of their composition for paleoclimatic reconstructions [1, 2]. The distribution of a number of microelements, especially U, in bottom sediments is one of the important signals of paleoclimatic variations [1, 3, 4]. In the study of sediments by the method of autoradiography, we established U-rich bands corresponding to phosphorites in composition. Phosphates in the form of crystalline aggregates, concretions, and kidney-shaped formations of diagenetic vivianite have long been known and are widespread in the sediments of Lake Baikal [5]. Recently, ferrophosphate crusts (P₂O₅ up to 21.8 wt%) were found within the boundaries of the Northern Depression and Akademicheskii Ridge. These crusts are compositionally similar to vivianite, but at the same time differ in a number of indicators, such as X-ray amorphism and relationships between Ca, P, and Fe, which prevented the authors from relating these formations to the apatite group minerals [6].

In the present work, the spatial distribution of U was studied using the method of (*n, f*)-autoradiography from fission tracks of ²³⁵U. The distribution of P was studied using the method of activation (*n, β*)-autoradiography by the radioactivity of ³²P. The column of bottom sediments was obtained using the method permitting the extract sediments samples with intact initial structures. The technique for producing preparations, regimes of irradiation, and methods of obtaining and analyzing (*n, f*)-autoradiograms have been described previously [7]. Relative concentrations of radionuclides in irradiated preparations were determined on the Inter-

technique apparatus complex. Weighted portions of 10–50 mg each, were taken from the core parts remaining after sawing, and the instrumental neutron-activation analysis (INAA) was carried out on them. The composition of phosphorite was determined on a MAR-4 microprobe. The morphology of phosphate grains and their qualitative elementary composition were studied on a Jeol scanning electron microscope with the Kevev device to determine the composition at local sites (the probe diameter was 2–3 μm).

The spatial distribution of U and P was studied in the column of bottom sediments of Lake Baikal obtained from the core St 11, GC (53°33'51" E; 108°00'05" N), Sec 2 (interval 88–125 cm from the sediment surface), taken from deposits of the elevated (277 m water depth) axial part of the underwater Akademicheskii Ridge. Column St 11 GC correlates well with other columns taken from the Akademicheskii Ridge [1] based on the primary description and diatome analysis data. Its upper layer (0–18 cm from the sediment surface) belongs to the Holocene, while the underlying clayey interval (18–96 cm) with an insignificant content of diatoms and sand lenticles belongs to oceanic stages 2–4. The clayey interval is composed predominantly of dispersed yellow to brown clay minerals (possibly with iron hydroxides) (dimensionality less than 50 μm). At a depth of 96 cm, the gradual transition boundary between glacial clays and diatomaceous oozes is established. The latter continue to 125 cm. The diatomaceous unit is mostly composed of diatomaceous algae (85–95%). Diatomaceous sediments in the studied interval of 106–125 cm belong to warm stage 5a (maximum 70–80 ka B.P. [8]).

The stratigraphic correlation is unambiguously confirmed by the composition of diatoms: the *Aulacoseira baicalensis* species dominates at a depth of 110–125 cm (28 mln valves/g), and the species *Cyclotella minuta* and *Cyclotella baicalensis* (about 2 mln valves/g), as well as *Stephanodiscus grandis* (0.6 mln valves/g) are accompanying. No other Upper Pleistocene diatomite layers has this species composition [1]. In the interval from 106 to 110 cm in diatomite, the buried ferromanganese crust, which is composed of iron and manganese hydroxides, make up bands (1–10 mm) and thin (2–5 mm) black and dark brown crusts. At 1.5–2 mm below the

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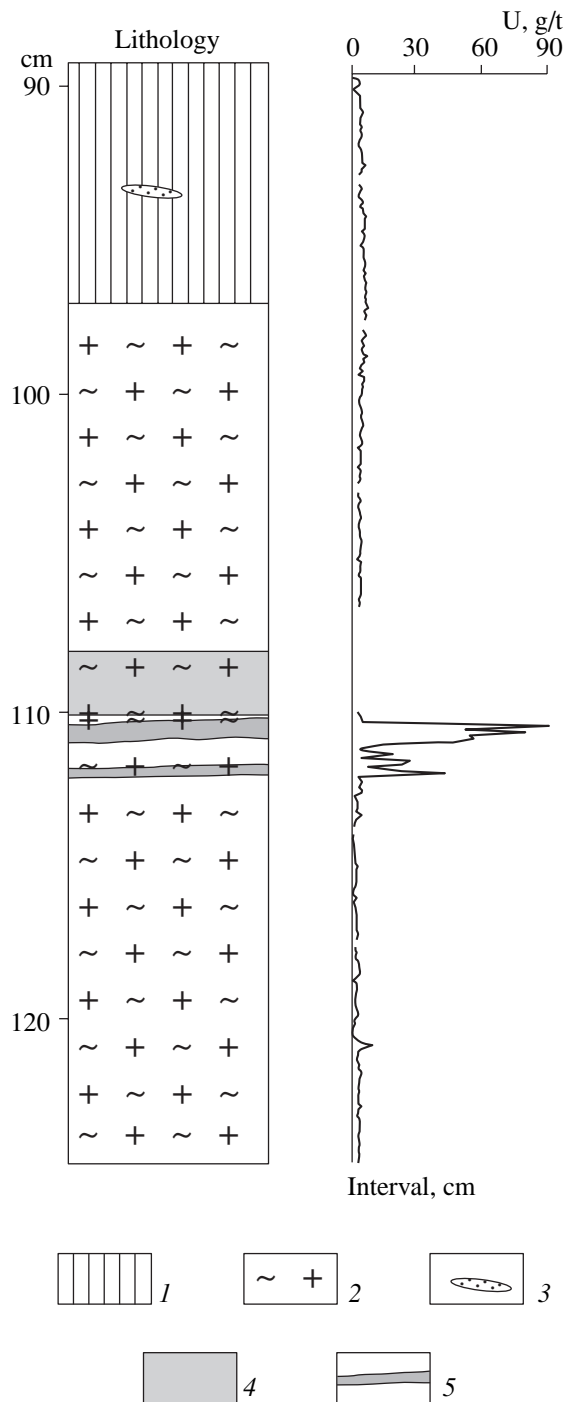


Fig. 1. A fragment of the bottom sediment column from Lake Baikal (the Akademicheskiiy Ridge, St 11, GC, Sec 2) and plots showing variations of the dispersed U concentration ((*n, f*)-autoradiography data). (1) Glacial clay; (2) layer of diatom valves; (3) sand lens; (4) ferromanganese crust; (5) band of uraniferous phosphorite.

crust, a phosphorite band 5–6 mm thick was detected. Another phosphorite band, 1–1.5 mm thick, was detected at 8 mm below the first band.

The profile of U concentrations in bottom sediments of the St 11 core (step 1 mm) is presented in Fig. 1. The

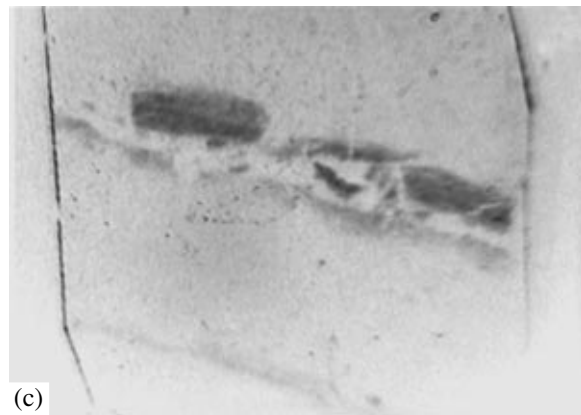
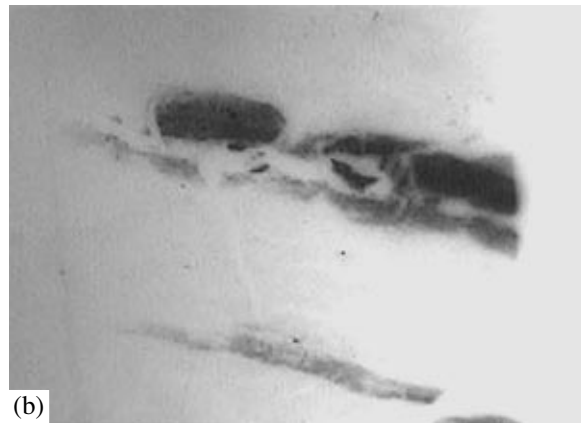
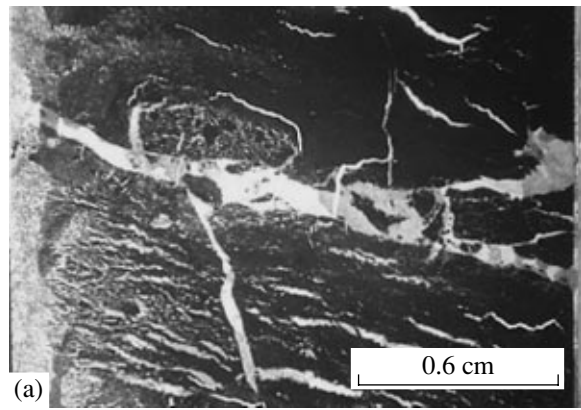


Fig. 2. Autoradiograms recording the spatial distribution of U and P in the fragment of the clayey–diatomaceous sediment column containing phosphorite bands. (a) Photomicrograph of the fragment of the bottom sediment column with phosphorite bands; (b) (*n, β*)-autoradiogram of P (the detector is nuclear emulsion AF); (c) (*n, f*)-autoradiogram of U (the detector is synthetic fluorphlogopite). The integral flow is 1×10^{16} neutron/cm², magn. 3.5.

local U distribution in sediments is characterized by a uniform pattern devoid of any signs of layering. This type of U distribution is observed both in diatomaceous oozes and in glacial clays. A basically different form of distribution associated with grains of U-concentrator

Chemical composition of rocks near the phosphorite band, wt %

Rock	P ₂ O ₅	CaO	FeO*	SiO ₂	Al ₂ O ₃	MnO	MgO	TiO ₂	Na ₂ O	K ₂ O
Phosphorite band (110.1–110.7 cm)	13.9	8.9	24.3	21.3	5.0	0.5	0.8	0.12	0.38	0.4
	14.0	9.2	21.1	24.1	4.0	0.12	1.2	0.11	0.33	0.41
	15.8	9.5	29.8	19.5	4.6	0.34	0.8	0.41	0.59	0.71
	19.2	12.1	25.6	21.4	4.1	0.27	0.8	0.11	0.76	0.87
Diatomite outside of the phosphorite band (113.1–114.0 cm)	0.21	0.93	12.5	46.6	9.7	0.6	1.0	0.19	1.4	1.3
	0.34	0.9	5.5	38.9	9.9	0.7	1.0	0.14	1.0	1.1
Concentrations of vivianite, after [5]	27.3	0.26	43.8	1.05	1.0	0.16	0.27	Traces	0.02	0.11

Note: Analyses were made on a MAR-4 X-ray spectral microanalyzer (N.S. Karmanov and S.V. Kanakin, analysts).

FeO* = FeO + Fe₂O₃.

mineral such as zircon, ilmenite, monacite (seldom), and others that are registered on the detector in the form of fields with a high track density or peculiar stars, has been universally established.

On the whole, the dispersed U distribution, similar to the previously described one [1, 4, 6], is registered on autoradiograms obtained from bottom sediment preparations in the entire interval from 88 to 125 cm except for 110–111.5 cm. Bands with extremely high U contents (up to 80–89 ppm) and P (up to 19 wt% of P₂O₅) and with uniform U concentrations were fixed within the interval 110–111.5 cm (Fig. 2, table). Analyzing the ratios and correlations between the elements, one may suggest that the aggregate of phosphorite bands belongs to hydrous calcium ferrophosphates and most nearly corresponds to calcioferrite Ca₃Fe₃(PO₄)₄(OH)₃ · 8H₂O. However, having investigated this phosphate in detail by infrared spectroscopy and X-ray diffractometry, we have failed to detect any crystalline phosphorus-bearing phases except X-ray amorphous compounds. At the same time, based on the TEM, microprobe, and SAED data (a JEM-100CX microscope with the line resolution of 2 Å), it has been established that the phosphate substance represents microcrystalline Ca-poor hydroxylapatite (hereafter, CaPHA). In photographs, the CaPHA is observed as aggregates of poorly crystallized microcrystals varying in size from 0.01 to 0.5 μm. Its SAED pattern is characterized by diffuse rings with *d/n* close to 3.4, 2.3, and 2.3 Å, which correspond to hydroxylapatite. Evidently, Fe is present in the CaPHA in the form of finely dispersed hydroxide impregnating aggregates of microcrystals. It represents the initial phase in the crystallization of apatite with a well-developed surface and uncompensated structural elements (the calcium deficiency). Therefore, it is as a powerful sorbent. Its formation and prolonged storage are accomplished at a pH equal to 6.94–7.5 (such pH values have been registered in Lake Baikal at a depth of about 250 m [4]). If the alkalinity of the medium increases, the mineral transforms to stoichiometric apatite. If the pH is reduced, it dissolves or forms octacal-

cium phosphate, given that ratios of Ca and P in solution are stable.

It has been established by SEM that phosphate grains in phosphorite bands have different morphologies. Xenomorphic phosphate grains and colloform formations with indistinct diffuse outlines are most abundant. Phosphatized diatoms are also sufficiently widespread. In all cases, internal parts of diatoms restricted to the surface by the P-free siliceous shell (diatom valve) were first and foremost phosphatized (Fig. 3). Chains of diatoms in the form of ribbons are often observed. The highest P concentrations comparable with those of Ca and Fe have been detected at the end of such ribbons. On the whole, the P contents and its relationships with other elements vary over a wide range, which is clearly seen on the energy dispersion spectra.

The neutron-activation analysis of phosphorite contained in the diatomaceous sediment next to the band 30 mm below the hydroxide crust points to a weak enrichment in REE and significant enrichment in As, Fe, and Mo with respect to the sediment. High U contents revealed by the radiographic method are also confirmed. In the phosphorite, contents of the majority of REE are two to three times higher than in diatomaceous and clayey sediments; the As content is six to seven times higher; the U and probably Mo contents are twenty to thirty times higher, and the Th/U ratio is less than 0.1. At the same time, the sediments surrounding phosphorite are relatively enriched in Cr, K, Cs, and Ba.

The chemical composition of phosphorites found in sediments of Lake Baikal differs from that of the known oceanic phosphorites in the CaO contents (9–12 and 17–54 wt%, respectively). In all analyses of Lake Baikal phosphate, Ca is depleted with respect to phosphorus and the CaO/P₂O₅ ratio varies from 0.60 to 0.66. This ratio varies from 1.1 to 1.7 in apatites and from 1.1 to 3.1 in oceanic phosphorites [9]. The contents of FeO (total), SiO₂, and Al₂O₃ are high. The concentrations of N₂O and K₂O are similar to those in oceanic phosphorites, while the concentrations of MgO are lower.

It is known that 80% of P (4.4 kt/yr) is supplied into Lake Baikal in the form of mechanical suspension and 20% of P (1.9 kt/yr) is supplied in dissolved form [10]. The overwhelming amount of the suspension precipitates near the shores and at the bottom of depressions. The terrigenous suspension during warm periods does not practically precipitate on the Akademicheskii Ridge. The correlation of the Baikal sedimentation record with the global oceanic and glacial records indicates that the climate was warm during the deposition of sediments containing phosphorite bands (stage 5a). In full compliance with this, the analysis of phosphorite bands showed that their REE composition sharply differs from the REE composition of apatites from phosphorus deposits located in the Lake Baikal basin, i.e., the bands were formed not as a result of the terrigenous suspension transport.

The analysis of phosphorite distribution in present-day marine landscape and climatic zones indicates that phosphorites are observed as chemogenic, postsedimentary, and biogenic accumulations in subtropical and tropical conditions [9, 11], especially in upwelling zones where cold waters mix with warm waters.

The orthophosphate ion concentrations in present-day Lake Baikal vary from 0.2 μM at the surface to 0.5 μM in the deep zone (deeper than 500 m, [12]). The Ca^{2+} concentration is equal to 400 μM [13]. In accordance with the calculations for Lake Michigan [14], orthophosphate in this water reservoir is in equilibrium with oxyapatite, whose product of solubility in natural systems is

$$K_{\text{IAP}} = [\text{Ca}^{2+}]^{10} [\text{PO}_4^{3-}]^6 [\text{OH}^-]^2 = 10^{-100} - 10^{-122}.$$

For Lake Michigan, at the Ca^{2+} and orthophosphate concentrations equal to 800 and 0.02 μM and, respectively, at $\text{pH} = 8.2$, the specified product (corrected for the content of triple-charged anions of the sum of orthophosphate anions) is equal to 10^{-115} . For Lake Baikal, it is equal to 10^{-107} at $\text{pH} = 8$. Hence, formally, oxyapatite can be a stable phase and on one hand remove orthophosphate from the water body of Baikal, and, on the other hand, compensate for its deficit in near-bottom waters if its concentration drop below 0.5 μM .

The REE distribution in phosphate corresponds on the whole to the trend typical for clayey sediments of Lake Baikal and similar NASC sediments with a certain depletion in HREE. Comparison of the REE distribution in phosphorite, clayey and diatomaceous sediments, as well as in Lake Baikal, reveals opposite trends in water and sediments. The REE distribution is also different in water and phosphorite. These data suggest that the REE composition and concentration in Lake Baikal are governed by the water-suspension interaction and explain a relative enrichment of water in HREE. They also indicate that phosphate is formed from Baikal waters.

The bands with exceptionally high U and P concentrations have only been found in Baikal sediments at St 11.

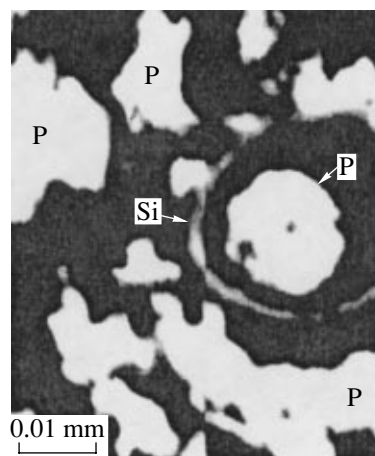


Fig. 3. Morphology of phosphatized diatomaceous algae and phosphate grains in the phosphorite band from the bottom sediment of Lake Baikal. Diatom shells are siliceous (Si); the internal part consists of iron and calcium phosphate (P). The cavity (black) is located between the internal part and the external shell of the diatom (SEM Jeol, back-scattered electron image).

Therefore, it seems very important that ferruginous phosphate-bearing crusts were detected within the boundaries of the Akademicheskii Ridge with minimal sedimentation rates at depths of 4–5 and 15 cm from the bottom surface. Especially important is the finding of thin layers of a reddish brown granular mass enriched in Fe, Ca, and P (depth 85 and 107.7 cm) (GCSt 307) [6]. These findings suggest the areal distribution of phosphorites within the boundaries of the Akademicheskii Ridge, despite the statements in [6] that phosphate in ferruginous crusts does not correspond to apatite and data on uranium are absent.

The detection of phosphorites (not vivianite) at the most elevated sites of the Baikal bottom with minimal sedimentation rates (0.026 mm/yr) is an established fact. High concentrations of phosphorus in local areas could have been explained by analogy with the ocean as a consequence of mixing of heated and cold waters. This scenario is possible but unlikely for the study station located on the axis of the Akademicheskii Ridge situated far from nearshore shoals. Moreover, the climate during stage 5a was quite similar to the present-day one, and the temperature of most heated surface waters in the center of Lake Baikal then did not exceed 15°C.

The contrast between phosphate contents in the phosphorite bands and in their host rock seems most surprising. These contents are equal to 20 and 0.35 wt% of P_2O_5 , respectively; i.e., they differ by a factor of approximately 60. The phosphate content on the order of tenths of a percent is not very surprising. In fact, according to [10], 900 t of dissolved phosphorus (2000 t of P_2O_5) is annually retained in Lake Baikal. With a lake bottom area of 15 000 km^2 and a sedimentation rate of 0.05 mm/yr [8], assuming the dry sedi-

ment density to be equal to 1, we obtain a calculated content equal to 0.26 wt% P_2O_5 . Based on the evaluation of Edgington [3], approximately 1 g/m² of organic carbon is buried annually at the bottom of Lake Baikal. Using the Redfield relationship for plankton (the molar ratio C/P = 106), we obtain the annual flow of P_2O_5 to the bottom amounting to 0.057 g/m². At the same assumption regarding the rate of sedimentation and the sediment density, the P_2O_5 content is 0.11 wt%.

Hence, there must be a mechanism of P concentration that ensures its growth in phosphorite bands compared to the background one by a factor of 60. The post-sedimentary diagenetic redistribution is one such mechanism. For example, the thickness of the diatomaceous ooze layer under the phosphorite band is 15 cm. The time of accumulation of this layer is about 3000 yr. Conditions facilitating the consumption of the phosphate ion by microorganisms and, thereby, the release of Ca from oxyapatite and its migration to the surface could exist in the sediment during this time period. Reacting with the excess of phosphate supplied from bottom or pore water, Ca cations could form near the surface a layer of concentrated insoluble oxyapatite. The concentration factor could be equal to the ratio of thicknesses of the Ca-free diatomaceous ooze layer and the phosphorite band, i.e., equal to 10 *n*. The behavior of the P–Fe pair of ions may be excluded from consideration in this context, since the iron phosphate solubility is much higher than that of oxyapatite [14]. This hypothesis, of course, needs verification. However, it can shed some light on the reason for anomalous uranium accumulation as well.

The U/ P_2O_5 ratio in oceanic phosphorites remains more or less constant and equal to $(1-3) \times 10^{-4}$ [9]. In Baikal phosphorite, this ratio is somewhat higher and equal to $(4.5-4.6) \times 10^{-4}$. Elevated U concentrations are typical for present-day oceanic phosphorites that are formed from water with higher (virtually by one order of magnitude) U concentrations compared to those in Lake Baikal water (3 and 0.4 µg/l of U, respectively). The ratios of U and P in Baikal phosphorite correspond to a certain extent to the U/ P_2O_5 ratio in phosphorites of the Phosphoria Formation in the Middle East. However, on the whole, these values are intermediate between those of oceanic phosphorites and Miocene phosphate-bearing rocks of Japan. The accumulation of such high U concentrations by phosphate can be explained by the sorption of U from water and pore solutions, since the Ca-deficient hydroxyapatite is an efficient sorbent. A similar process apparently takes place during the washout of fossil animal bones by groundwater. Previously, the suggestion regarding the possibility of oxyapatite formation and U concentration in sediments of Lake Baikal was expressed by Gol'dberg *et al.* [15]. The relatively high U concentration in diatomaceous oozes of Baikal beyond phosphorite bands do not evidently stem from the bonding of U with oxyapatite. In fact, if the U content is 100 g/t in phosphate with 20 wt% of P_2O_5 and this element is absorbed on phos-

phate, it could be expected that 0.9–2.3 g/t of U will be bonded in diatomaceous ooze, where the P_2O_5 concentration is equal to 0.2–0.5 wt%. In reality the U concentration in such layers attains 10–30 g/t. Widespread vivianite has very low U concentrations equal to 0.63 g/t (the average of two parallel determinations by the luminescent-laser method). Isolated clastogene monazite grains, rare in Lake Baikal sediments, are characterized by high Th and U concentrations and by a high Th/U ratio. Naturally, they cannot explain high U concentrations in diatomaceous ooze, which is almost free of the clastogene component.

The uniqueness of uraniferous phosphorites and phosphatized diatoms in Lake Baikal consists in the fact that they were formed in a freshwater basin. There is a sufficient number of questions that must be answered in order to relate the formation of these unusual rocks to the sedimentation and climatic conditions. Autoradiographic methods applied in the present work possess a unique potential for revealing fairly short-term variations in paleoclimates.

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