Micromapping of Uranium and Phosphorus in the Lake Baikal sediments (Academicheskiy Ridge, St8; St11)

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Introduction

The chemical elements local distribution data, particularly uranium and phosphorous, in the lake Baikal benthal sediments reflects the conditions of those sediments formation. These forming conditions directly associated with climate change in the past and could be used for the palaeoclimatic reconstructions. A microorganism, such as diatomic weeds, has a considerable influence to not only the silicon concentration increase, but also concentrations increase for phosphorous, uranium, precious metals and trace elements. Furthermore, diagenetic alterations lead to the considerable matter redistribution in the sediments and to the formation of new minerals, aggregates and micro-layers. Time estimation of climate change periodicity depends on the locality of utilized analysis methods and on the ability of the methods to determine an element presence form in the sediments.

The purpose of this research is determination of mineralogical, geochemical, physical and chemical conditions of concentration and dispersal as well as evaluation of distribution patterns and periodicities (due to paleoclimatic conditions of sedimentation) for uranium and phosphorus in the benthal sediments of the Baikal Lake. Fragments of the lake sediment columns taken from the axial part of the Akademicheskiy Ridge in Lake Baikal (stations coordinates St 8-107 56 25E; 53 32 15N - and St11 – 108 00 05E; 533351N)

View from space of Lake Baikal and the position of well number 8 and number 11 in the structure of the underwater ridge Academic

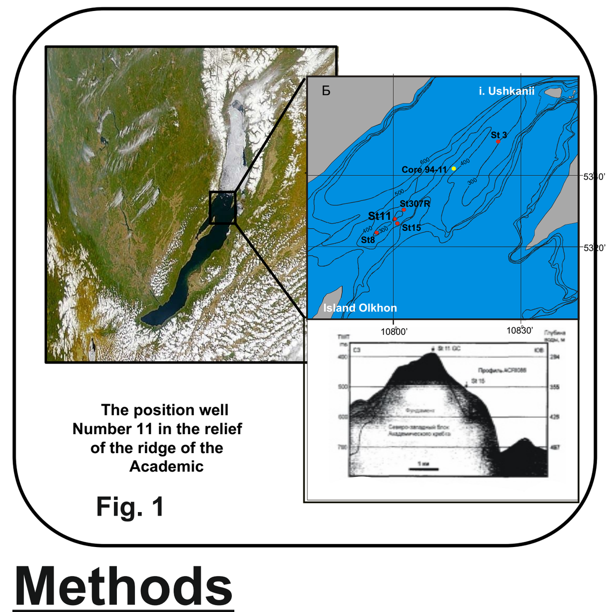


Fig. 1

Methods

Fragments of the lake sediment columns were studied using complex of local analysis methods, such as: n, f - and n, β-autoradiography, SR-XFA, EMP(an electron microprobe), SEM(scanning electron microscope) and TEM(transmission electron microscopy). The specific feature of the examined sediments is the presence of phosphorus-iron-manganese formations with stratified, concretionary and flocculation structures in them. An integrated approach has allowed a detailed investigation of the distribution of U and P, as well as a number of related elements (U, Y, As, Sr, Ca, Fe, Mn, Ti, etc.) in the fragments of the bottom sediments columns. The distributions of U and P in the authigenic component of sediments along the whole columns length (with the step of 12 micron) have been studied by the autoradiography method. Layer-by-layer sediment columns scanning with the step of 100-200 microns were performed using SR-XFA which also allowed to determine the concentration of such elements as: Y, As, Sr, Ca, Fe, Mn, Ti and others.

The core of bottom sediments of Lake Baikal (Academic Ridge, St8 (left), St11 (right))

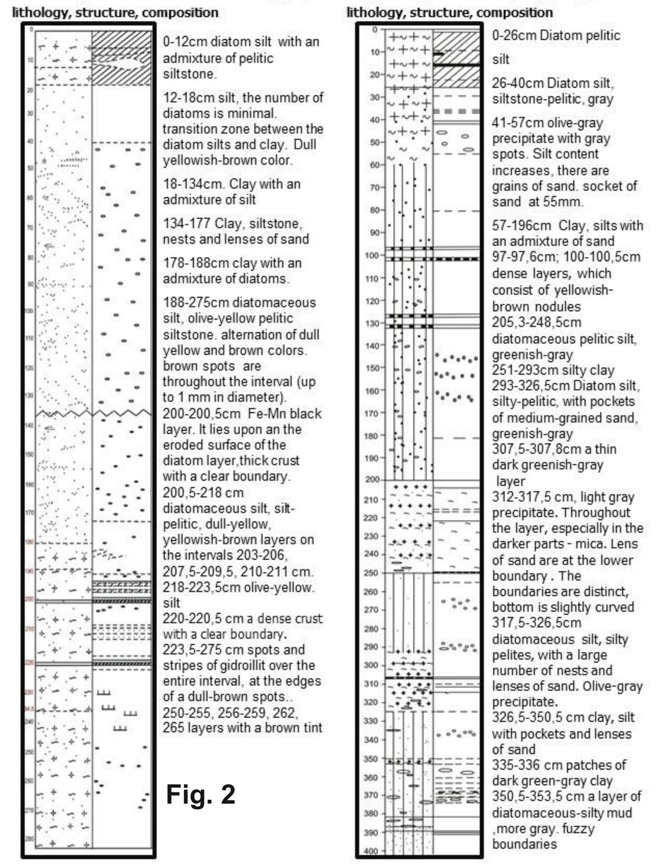


Fig. 2

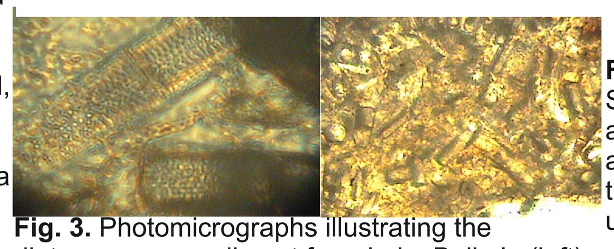


Fig. 3. Photomicrographs illustrating the diatomaceous sediment from Lake Baikal: (left) St 11, thin-section, interval 123-125 cm; microscope JENEVAL, transmitted light; (right) St8, thin-section, interval 215-216 cm; SEM LEO

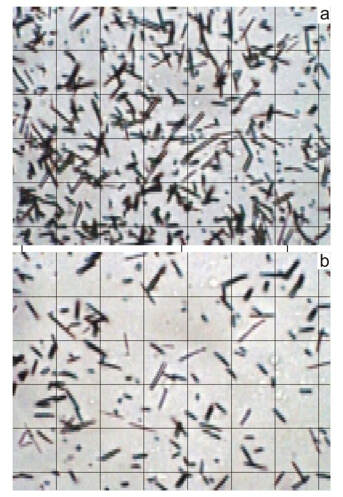


Fig. 4. Typical U-235 fission track distribution in a fluorofloopite, reflecting dispersed uranium distribution.(diatomaceous sediments of Lake Baikal, St8) The lateral length of the small grid square is 12.5 μm. a) The distribution of uranium in the diatomite, b) in the clay medium.

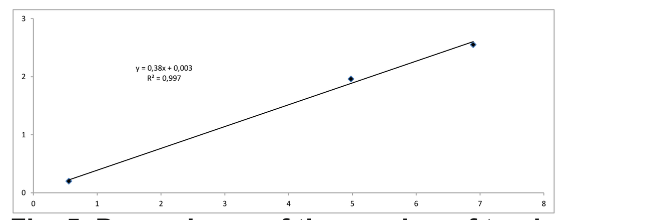


Fig. 5. Dependence of the number of tracks on uranium concentration(calibration curve), see table 1

Table 1 Data for construction of calibration curve.

Standard glass	Density(g/cm^3)	C_u(ppm)	N of tracks[a]	$N^{1/2}$(%)	track density (tracks/mm^2)	$(A^{1/2})_m$	K	track density (tracks/mm^2)[b]
Basalt	2.75	0.2	720	3.7	555	4.75	0.95	584
Andesite 1	2.56	1.96	875	3.4	4978	4.66	1	4978
Andesite 2	2.56	2.55	1454	2.6	6893	4.66	1	6893

Remarks: $\sqrt{A_m}$ $-$ reduced atomic weight: $\sqrt{A_m} = \frac{1}{\sum \frac{p_0}{\sqrt{A_0}}}$; $\overline{A_m}$ $-$ atomic weight of matirial; A_0 $-$ atomic weight of oxide; p_0 $-$ weight fraction of additive oxides; $K = \frac{\sqrt{A_m}\rho_{st}}{\sqrt{A_{st}}\rho_m}$;

A_{st} $-$ atomic weight of standart,
ρ_{st} and ρ_m $-$ density of standart and material (Badyin, 1969)

For the calculation of the uranium concentrations in siliceous and clayey constituents, sediments K was set equal to 1(ρ=2.56 g/cm³). Quantitative determination of uranium in accessory minerals could not be conducted because of the high track densities.

[a] Measured number of tracks on different areas (for basalt: 1.297 mm^2; andesite1: 0.72 mm^2; andesite2: 0.0864 mm^2)

Table 2. Contribution to total density of U and Th fission tracks in reactor WWR (C_{Th}/C_U=1)

Conditions of neutrons activation	Contribution in relative units Th-232	U-234	U-235	U-238	Th*(%)
Thermal neutrons	3		1040	17	0.3
Cd-filter	2		60	8	12.5
B_4C-filter	8		12	8	28.6
Contents of U and Th isotopes in natural materials and fission cross-section of thermal neutrons					
Isotopic composition wt%	100	0.0057 ±0.002	0.7204 ±0.0007	99.2739 ±0.0007	
Fission cross-section, barn	$<2*10^{-6}$	0.65	586±7	$<5*10^{-6}$	

Remarks: Tabulation was made from data of Flerov and Berzina(1979). Our samples were activated in the Research reactor Tomsk, Institute Nuclear Physics in TPU with thermal neutrons flux of $2*10^{12}$ neutrons/cm²sec.

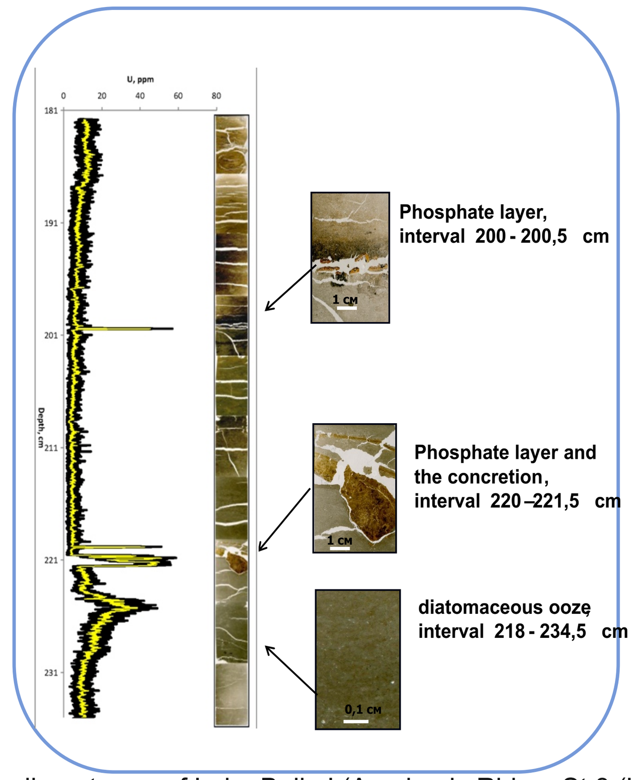
* Contribution of fission tracks induced by Th-232 (n,f) reaction.

Results

The distribution of uranium was studied by neutron-induced fission autoradiography via U-235 (n, f). The distribution of phosphorus was studied by neutron activation autoradiographyvia P-31(n,β)P-32. P-32 is a β emitter(100%) with a half-life of 14.5 days and a maximum energy of the beta particles of 1.707 MeV , graphs are presented below;

The station number 8, the interval 181.8 - 234.5 cm

The station number 11, 0-50 cm



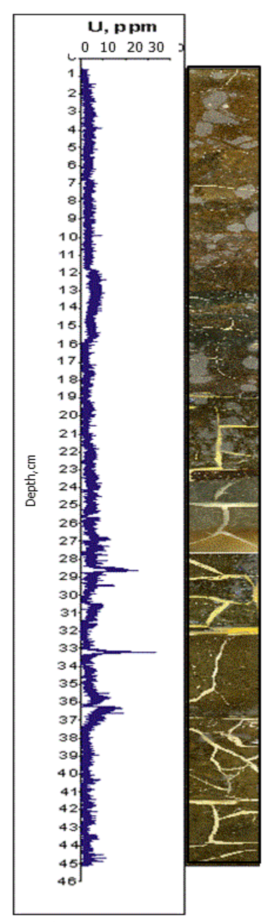


Fig. 7. Sediment core of Lake Baikal (Academic Ridge, St 8 (le St11 (right) showing distribution of diffuse uranium by (n, f)-autoradiography data. Those parts corresponding to inclusions and mineral particles with high uranium concentration, and als those part with increased content of diffuse uranium were not used

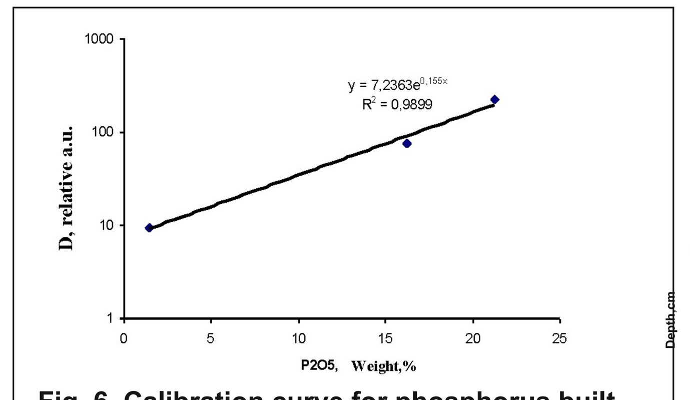


Fig. 6. Calibration curve for phosphorus built using the internal standard methodology. D-blackening intensity for selected points on the autoradiograms measured in average relative units.

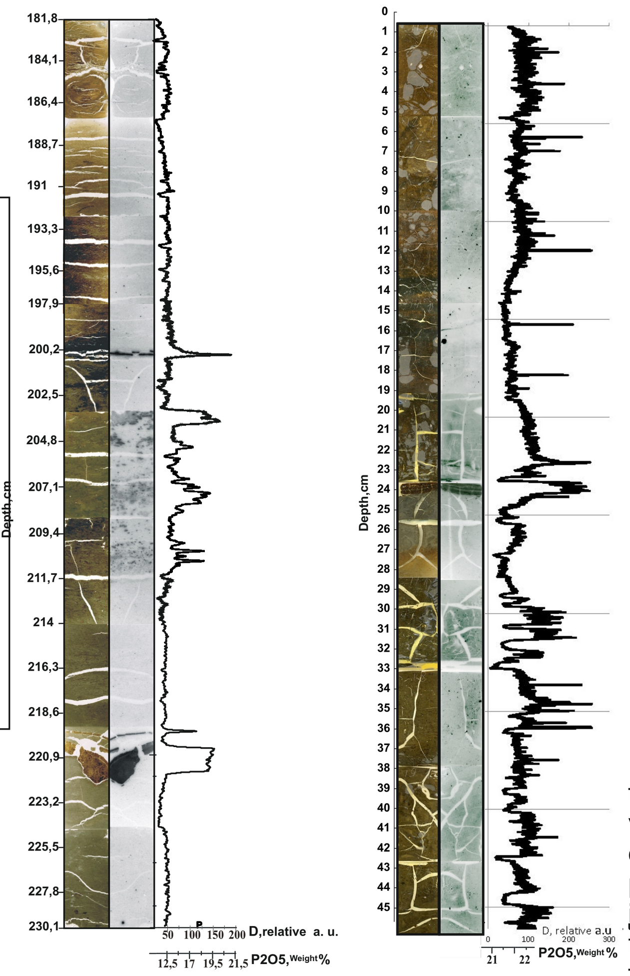


Fig. 8. Core of bottom sediments of Lake Baikal St8 (left) and St11 (right) showing the distribution of diffuse phosphorus by(n, β)-autoradiogram; parts corresponding mineral particles with high phosphorus content, and parts with increased contents of diffuse phosphorus were not used(left); were used(right). a - thin section, b-(n, β)-autoradiogram

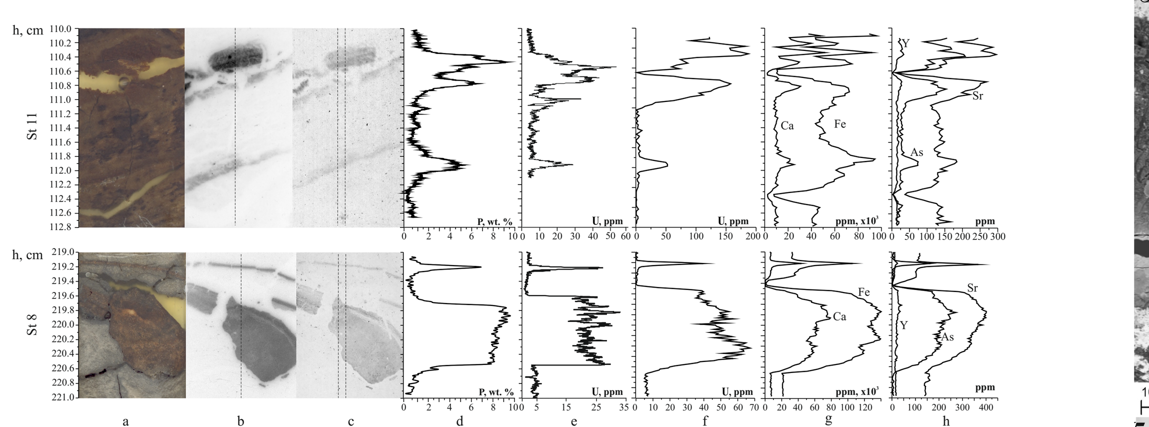


Fig 9 Autoradiographs and distribution profiles of elements in sediment cores from the Academician Ridge of Lake Baikal: (a) thin section; (b) (n, β) - autoradiograph; (c) (n, f) - autoradiograph; (d) phosphorus distribution by the autoradiography method; (e) uranium distribution by the autoradiography method; (f) uranium distribution by SR-XFA; g) Ca, Fe distribution by SR-XFA; (h) Y, Sr, As distribution by SR-XFA. Sections of sediment cores consist of clay-diatomaceous material with phosphate layers (upper row) and predominantly diatomaceous material with layers and concretions of phosphate; h, cm depth below sediment surface

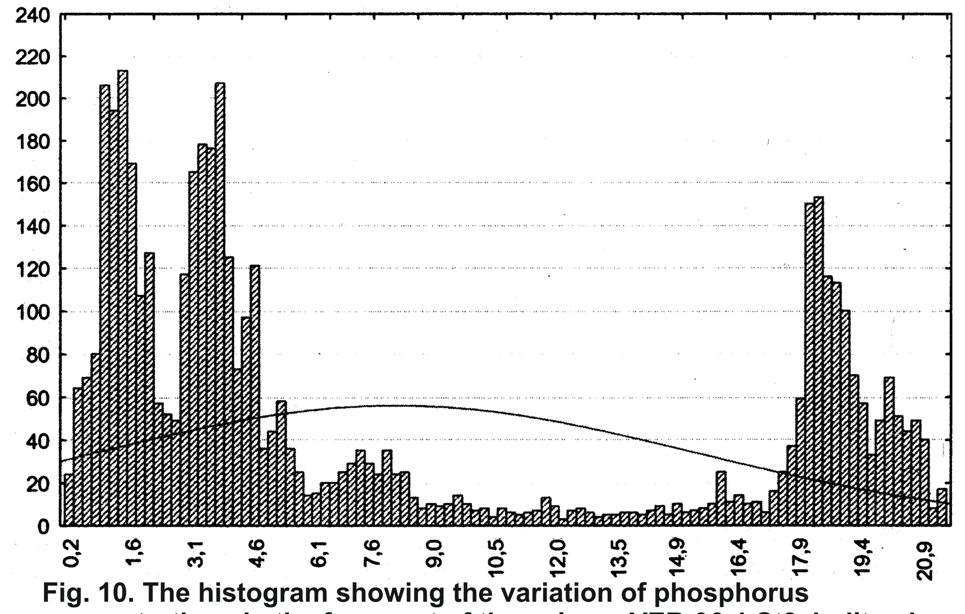


Fig. 10. The histogram showing the variation of phosphorus concentrations in the fragment of the column VER-96-1 St8, built using data of the activation and β-autoradiograms analysis. The y-axis - frequency of occurrence, the x-axis - concentration of phosphorus in weight.%

Energy dispersive X-ray spectra of different parts of diatomaceous sediments

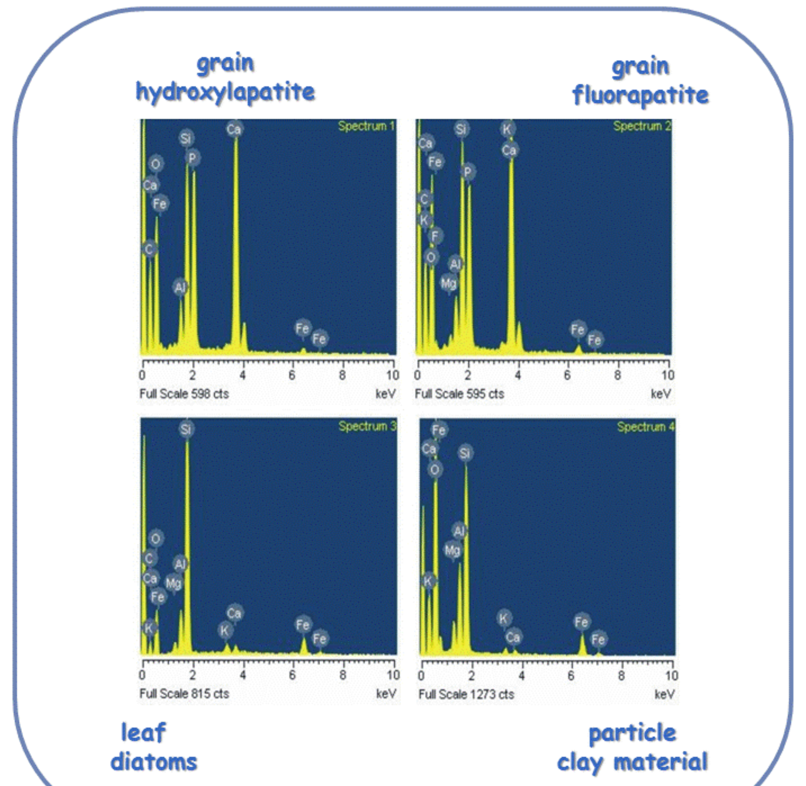


Fig. 11. The Ca/P ratios shown in the first and second spectra are close to normal for apatite. It was established that the Ca/P ratio is not constant and its value varies within a single sample. Analysis of the spectra indicates that the inner part of the diatom covered by the silica shell undergoes to a process of phosphatization and also that the dominant material in the phosphatized diatoms is calcium-deficient hydroxyapatite. In rare cases, there are phosphates in which the ratio of phosphorus and calcium approaching a deficient-free apatite. In a few cases the phosphates with the ratio of calcium and phosphorus corresponds to hydroxyapatite were found. Thus, in the bottom sediments of Lake Baikal, there are layers of authigenic phosphorites which are formed with the active and direct participation of diatoms. These phosphorites are concentrators of uranium and other related elements (As, Mo, Sb, Sr, F, Rb, Ni, Ba, Cu, Ca).

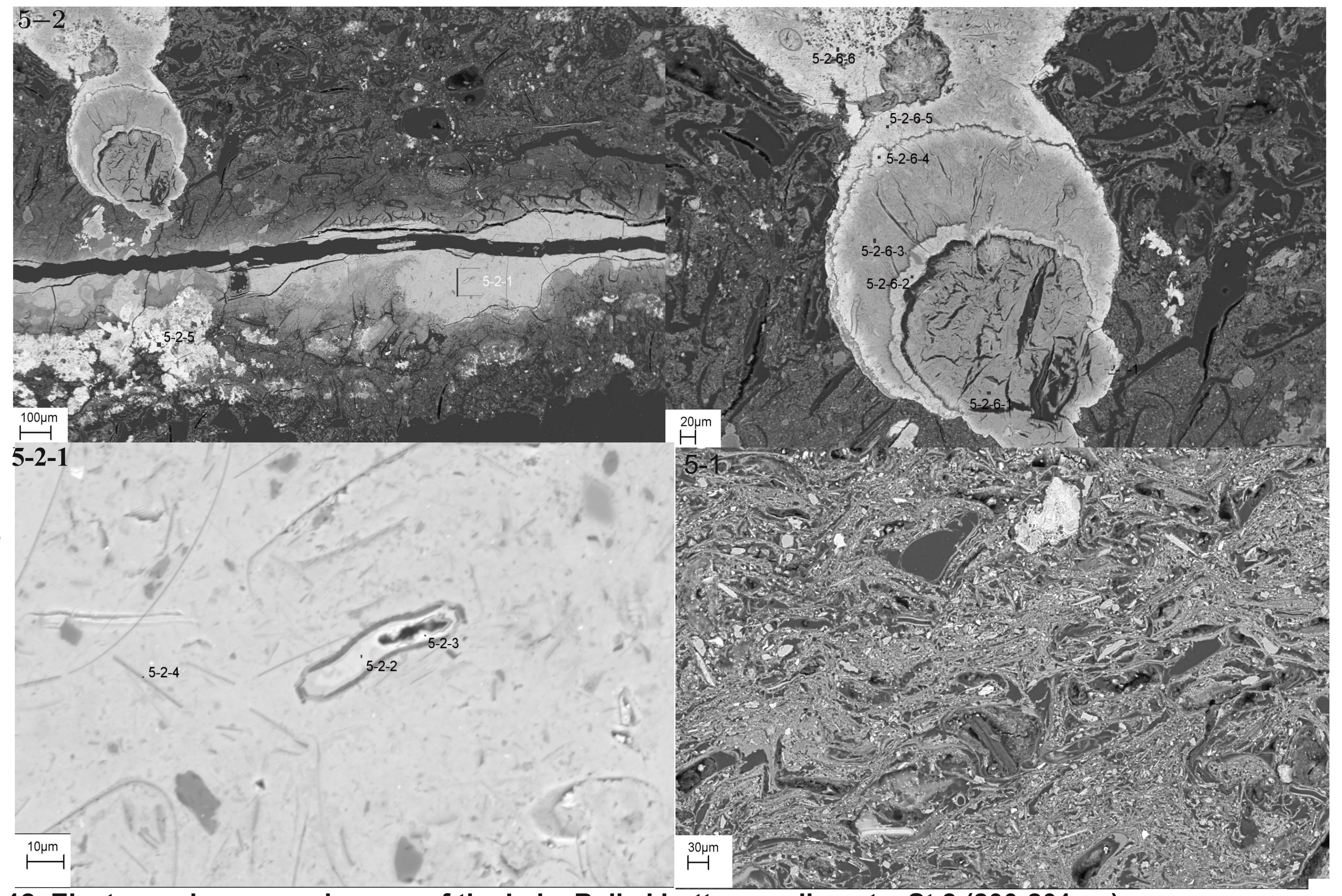


Fig. 12. Electron microscope images of the Lake Baikal bottom sediments, St 8 (200-201cm)

5-2-Overall photo for the main Fe-Mn crust. It is possible to see that the crust is made of separate parts of iron and manganese.

5-2-6-Analytical data for the manganese nodule zones. Points of the analysis are shown on the photo.

5-2-1-Analytical data for the iron crust; Here shown the points where the tests were made.

5-1-averaged analysis for the host sediment (0.6 by 0.6 mm)

№ dots	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO	ΣFeO	BaO	total
5-1	2,01	13,52	70,19	0,00	2,32	1,62	0,38	6,71	0,00	98,85
5-2-1	0,48	1,80	21,08	16,00	0,25	3,87	0,25	56,28	0,00	100,00
5-2-2	0,00	0,00	28,66	2,50	0,00	1,43	0,00	67,40	0,00	100,00
5-2-3	0,00	0,00	19,86	20,15	0,00	4,20	0,00	55,54	0,00	99,75
5-2-4	0,37	0,00	19,58	20,34	0,17	5,34	0,26	53,16	0,78	100,00
5-2-5	1,46	0,00	0,00	0,64	0,60	3,74	81,73	1,70	10,13	100,00
5-2-6-1	0,96	6,24	27,70	0,77	0,49	2,90	47,28	4,43	7,39	99,50
5-2-6-2	0,79	1,44	5,09	1,88	0,30	2,36	69,19	2,64	15,83	99,53
5-2-6-3	1,95	4,53	12,57	0,95	0,85	2,80	61,05	5,30	9,63	99,61
5-2-6-4	2,21	1,68	4,05	0,98	1,06	2,77	73,33	2,88	10,86	99,82
5-2-6-5	1,24	1,02	17,64	0,76	0,39	2,78	64,73	2,43	8,84	99,83
5-2-6-6	1,71	0,00	2,24	0,82	0,54	3,37	78,74	1,67	10,27	100,00

Table 3. The results of chemical analysis of the phosphate layer (St 8) and microconcretions (wt%) Microconcretions with compounds having in their composition barium(up to 15.83 wt.% BaO) were detected for Lake Baikal for the first time

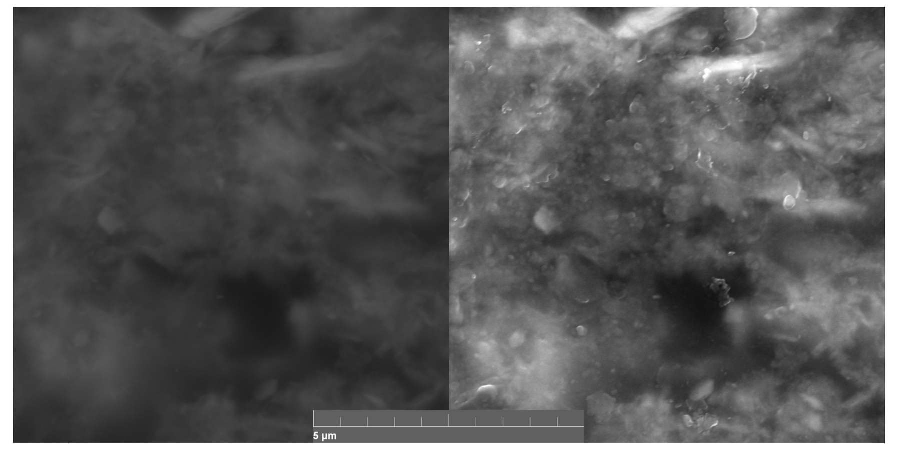


Fig 12.a. Electron microscopic images of the bottom sediments of Lake Baikal, St 8

Unconsolidated sediments characterized by low P and Ca (± K) content and high content of Mg, Al, Si and Fe.

	Means	Std.Dev.	Total	Si	Al	Fe	Mg	Ca	Na	K	P	Cl	O
Total	35,05	4,52	1	0,04	-0,10	0,73	0,07	0,70	-0,09	-0,09	0,61	-0,36	0,96
Si	6,19	2,12	0,04	1	0,52	-0,61	0,14	-0,44	0,52	0,55	-0,70	0,02	0,01
Al	1,72	0,44	-0,10	0,52	1	-0,49	0,53	-0,26	0,74	0,46	-0,61	0,12	-0,18
Fe	9,00	2,87	0,73	-0,61	-0,49	1	-0,09	0,75	-0,47	-0,53	0,91	-0,30	0,68
Mg	0,38	0,15	0,07	0,14	0,53	-0,09	1	-0,04	0,12	0,25	-0,18	0,11	-0,02
Ca	1,05	0,25	0,70	-0,44	-0,26	0,75	-0,04	1	-0,23	-0,26	0,82	-0,33	0,69
Na	0,21	0,21	-0,09	0,52	0,74	-0,47	0,12	-0,23	1	0,35	-0,53	0,08	-0,17
K	0,42	0,19	-0,09	0,55	0,46	-0,53	0,25	-0,26	0,35	1	-0,48	0,08	-0,07
P	2,17	0,80	0,61	-0,70	-0,61	0,91	-0,18	0,82	-0,53	-0,48	1	-0,35	0,62
Cl	0,18	0,04	-0,36	0,02	0,12	-0,30	0,11	-0,33	0,08	0,08	-0,35	1	-0,32
O	13,72	1,85	0,96	0,01	-0,18	0,68	-0,02	0,69	-0,17	-0,07	0,62	-0,32	1

Table 4. Correlation matrix of the elemental composition of the 26

Table 5.

Name of cycle	Period(years)
Oceanic Tidal cycle[1]	6-to-9; 1000-to 2000
"Schwab" cycle ; "Hale" cycle *"Gleissberg "cycle; "Suess" cycle(*solar cycle)	11; 22; 87; 210
In carbon-14[2]	105, 131, 232, 385, 504, 805, 2,241
"Milankovitch" cycles (Orbital forcing)	21,000, 40,000, 100,000, 400,000

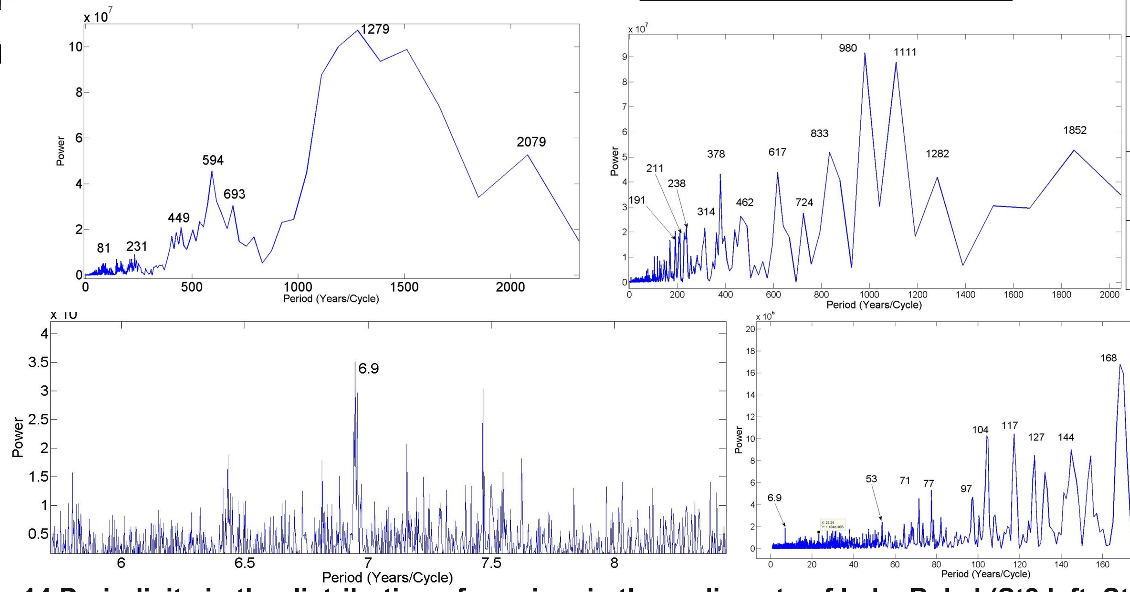


Fig. 14.Periodicity in the distribution of uranium in the sediments of Lake Bakal (St8 left, St 11 right) identified byFourier transform

We identified periodicity in the distribution of uranium (st8 and st11), using Fourier analysis. The rate of the sediment formation is 0.027 mm/year, step of the autoradiography analysis is equal to 12.5 microns, the time resolution of autoradiography analysis was equal to 0.463 years. Columns of bottom sediments correspond to the time interval: st8 (16 632 years from 67,400 to 84 000 years ago) and st11 (from now until 16,887 years ago). In addition with millennial cycles, there are also cycles with a small period of about 7 years (found in both columns).

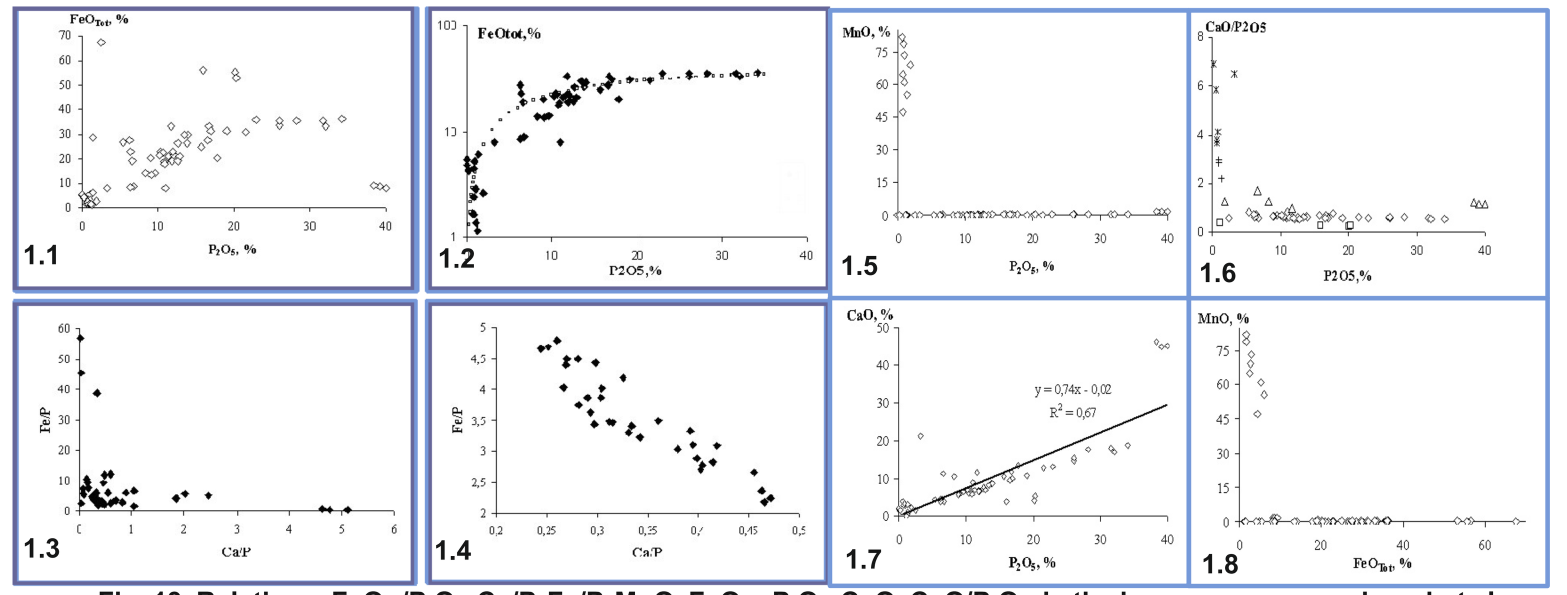


Fig. 13. Relations FeO_{tot}/P_2O_5, Ca/P, Fe/P, MnO, FeO_{tot}, P_2O_5, CaO, CaO/P_2O_5 in the iron-mangamese-phosphate layers and nodules from the sediments of Lake Baikal,(Academic Ridge, St8 и St 11)

Acquired data used to build correlation graphs for different elements. FeO/P2O5 ratio shows that in addition to the apatite (Fig. 1.1, bottom right) and vivianite (Fig. 1.1, upper left corner) we could see intermediate compound also

. This conclusion was confirmed by plotting the data on the graph within Fe/P - Ca/P coordinates (fig 1.3-1.4). . Fig. 1.4 is a more detailed view of Fig. 1.3.If we will remove from consideration the points corresponding to the apatite and vivianite from the graph 1.1 (Fig. 1.2) we can see that the ratio of FeO and P2O5 follows the Langmuir distribution. This kind of distribution indicates the sorption process of phosphorus accumulation on the Fe hydroxide particles. This is also confirmed by Fig. 1.5 which shows that the accumulation of phosphorus is directly related to the Fe deposition, and almost has no correlations with the Mn accumulation.

On the graph 1.7 a direct correlation between the CaO - P2O5 established. This correlation probably indicates a preferred formation of phases which has phosphorus and calcium in the composition. On the graph built using the FeO - MnO coordinates (1.8) the separation of iron and manganese is established.

Conclutions

The (n, f)-autoradiography method allowed the study of uranium distribution in sediments of Lake Baikal within the Academicheskiy Ridge. Three main types (groups) of concentrators were established for U and P: 1) - terrigenous (clastogenic) - thorite, monazite, apatite, ilmenite, magnetite; 2) - authigenic - clay minerals, diatoms, phosphorus "flakes", iron-manganese-phosphatic layers; 3) - diagenetic - iron-manganese-phosphatic nodules, area enriched by Fe and Mn (evidence of the redox conditions variation). The same three groups of concentrators have been also identified for the most of major, minor and trace elements.

The following factors can influence the uranium concentration in sediments: (1) influx of new materials; (2) diagenetic processes, taking place as a result of sediment consolidation and liquid separation from the sediment; (3) change of oxidizing–reducing conditions; (4) organic material; (5) phosphate depositions; and (6) change of environmental conditions, i.e. climatic changes.

A number of possible mechanisms can account for phosphate accumulation in Baikal sediments:(1)phosphorus sedimentation as a result of mixing of warm and cold waters (upwelling effect) with active participation of biota and with enrichment in phosphorus of pore water and its further deposition; (2)biogenic phosphorus accumulation during sedimentation and its further redistribution in the sediment as a result of oxidization–reduction and transition diagenetic processes; (3)accumulation of P as organic matter deposited along with sediment; the gradual increase of P then reflects climatic variations; (4)bulk burial of phosphorus-bearing biota enriching the pore water with phosphorus; and (5)sorptive accumulation of phosphorus and calcium by colloidal iron hydroxides from the Ca–P–Fe phase

The regular periodicity in the distribution of antigenic uranium in the sediment core were identified by statistical methods (Fourier analysis). These uranium concentrations oscillations periodicities are determined by oscillations in the sedimentation conditions. Some of periods of the observed periodicities match with known periods of solar activity cycles and cycles associated with the actions of tides in the oceans. We can conclude that the distribution of diffused uranium in the sediments of Lake Baikal, reflects not only the diagenetic changes have occurred with sediment, but also(importantly) paleoclimatic conditions of sedimentation.

Acknowledgements

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