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URANIUM-SERIES ISOTOPES AS PROXIES OF LATE PLEISTOCENE CLIMATE AND GEOCHRONOMETERS IN BOTTOM SEDIMENTS OF LAKE BAIKAL

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^{238}U, ^{234}U, and ^{230}Th concentrations in samples of Baikal bottom sediments from the submerged Akademichesky Ridge were measured by ICP-MS which is 100 times as fast as the traditional alpha spectrometry. These concentrations, and the respective activities A8, A4, and A0, show abrupt oscillations. The A4/A8 ratio varies more smoothly between 1.0 and 1.8 and correlates with the diatom record. A0 increases with depth in high-A4 intervals because ^{234}U decays to ^{230}Th ($\tau_{1/2}$ = 245.3 kyr). According to our geochemical model, excess ^{234}U (A4/A8 > 1) is supplied into Lake Baikal in the soluble form. This model, along with new data, was used to determine U-Th ages of six sediment intervals. In the suggested linear age-depth model for the core, the A4/A8 profile is similar to the SPECMAP record for the past 140 kyr. Fluxes of sediment components were estimated from sedimentation rates, water content, BiSi, and picnometric clay density. The clay flux during MIS 2, 3, 4 (controlled mostly by mountain glaciers) was four times as high as in the interglacials (MIS 5.5, 5.3, 5.1, and 1). The flux of authigenic uranium adsorbed by sediments from the Baikal water was almost zero during MIS 2 and 4, presumably because of strongly reduced Selenga discharge, the main source of dissolved uranium. The input of nutrients ceased for the same reason, and diatoms could not develop. Repeated cycles of aridization and the related discontinuity in river nutrient input may have been a major mechanism responsible for the formation of the unique assemblage of endemic organisms in Lake Baikal.

Climate proxy, uranium-series isotopes, activity ratios, ICP-MS, diatoms, Lake Baikal

INTRODUCTION

The upper section of bottom sediments in Lake Baikal is composed of diatomaceous silt tens of centimeters thick, underlain by dense blue clay. Even in the 1970s some workers believed that the blue clay was pre-Baikalian, i.e. had an age of few dozen million years (Goldyrev et al., cited from [1]), however more realistic estimates, e.g. from silica budget [2], moved the upper clay boundary to the Late Pleistocene. More evidence came from modern sedimentation rates estimated in different parts of Baikal from ^{210}Pb and ^{137}Cs to range between 0.05 and 1.2 mm/yr [3].

According to ^{14}C ages of sediments from a 4 m core from North Baikal, the boundary between the clay and diatom silt at 180 cm below sediment surface dates from the Early Holocene [4]. Bezrukova et al. [4] have for the first time found that the transition from diatom-barren clay to diatom-rich silt (diatom count $<10^4$ g^{-1} against 10^8 g^{-1}) records a dramatic change in the lake ecosystem. The diatoms were absent from the pelagial of Baikal during the Last Glaciation until the Holocene warming. It was proposed that diatoms could not develop because of high turbidity of water [4].

Longer cores (8–12 m) from sites of low sediment accumulation rates (submerged Akademichesky Ridge between the northern and central subbasins) showed intermittent diatomaceous silt and clay layers. It was suggested that all diatom-rich layers belong to interglacials, and all clay intervals, to glaciations [5–7]. However, this was a tentative inference because the ^{14}C ages below 15 kyr were not reliable [5, 7].

An important contribution to understanding of the Baikal record was done by Colman et al. [8]. Having assumed that the sediment accumulation rate was constant and equal to 4 cm/kyr (the same as in the Holocene), they found that the profile of BiSi in sediments of Lake Baikal correlates with SPECMAP [9] — a profile reflecting the changes in the volume of polar ice sheets over the past 220 kyr [9]. Spectral analysis of the BiSi record revealed variance at a periodicity corresponding to the Milankovitch cycles. However, the problem of dating could not be considered resolved as the basic assumption was arbitrary. Edgington et al. [10] confirmed the dates of [8] from uranium-series isotopes in the core (see below).

Subsequent studies of 200 m BDP-96 core which was dated by a few magnetic inversions have shown that the mean sediment accumulation rate on the Akademichesky Ridge was indeed constant and equal to 4–5 cm/kyr during the past 5 Myr [11–13].

Williams et al. [12] suggested a more detailed age-depth model for BDP-96 based on assumed synchroneity of peaks in the Baikal BiSi record and in the marine $\delta^{18}O$ curve. Spectral analysis revealed orbital periods of 100, 41, and 19 kyr. However, this correlation does not ensure accuracy of dating of every interval of the core. The profile of BiSi and SPECMAP cannot be absolutely synchronous — the response of the climate of Siberia to the tilt and precession of the axis of the Earth and to excentricity of the orbit, generally speaking, should not be simultaneous with the response of the ocean and polar ice sheets. The volume of polar ice cannot change as fast as response to insolation on the continent. The amplitude Fourier spectrum will not change if there will be a constant shift relative to every of the orbital frequencies, even if this shift will be different for different frequencies. In other words, Williams et al. [12] could not reveal the leads/lags in the Baikal record because they proceeded from the initial assumption of synchroneity.

Gavshin et al. [14, 15] have found that diatom-rich intervals of the sediments of Lake Baikal deposited in warm climates contain abnormally high concentrations of uranium. Edgington et al. [10] have found that layers of sediment rich in diatoms and uranium also contain significant amounts of unequlibrium ^{234}U: the ratio of the activities of ^{234}U (A4) and ^{238}U (A8) in them can be as high as 1.9. Diatom-barren intervals do not contain excess of ^{234}U. Activity of ^{230}Th (A0) is small in the upper layers, but increases with depth in layers having an excess of ^{234}U. Radioactive decay of ^{238}U proceeds according to the following simplified scheme, whitch does not include short-living isotopes [16]:

$$^{238}U \rightarrow {}^{234}U \rightarrow {}^{230}Th \rightarrow {}^{226}Ra \rightarrow$$

$$\tau_{1/2} = 4.51 \cdot 10^9 \text{ years} \quad \tau_{1/2} = 245.3 \text{ kyr} \quad \tau_{1/2} = 75.4 \text{ kyr}$$

The presence of excess ^{234}U and ^{230}Th suggested that it will be possible to apply the U-U (based on the A4/A8 ratio) and U-Th (based on A0/A4 ratio) geochronometers.

To explain the profiles of the isotopes of uranium and thorium, Edgington et al. [10] proposed a geochemical model according to which uranium is delivered to sediments of Lake Baikal from two sources: 1) rivers which bring dissolved uranium enriched in ^{234}U (A4 > A8, A4/A8 = const) which decays to ^{230}Th after burial; 2) terrigenic particles with equilibrium uranium with A4 = A8 = A0. The first source dominates in the interglacials, and the second one, during the glaciations. Edgington et al. [10] studied the same sediment as Colman et al. [8]. The sediment accumulation rate was estimated by three methods: from the distribution of A4/A8 (U-U geochronometer); from the distribution of A0/A4 (U-Th geochronometer); by correlation of the profile of total uranium with SPECMAP. The mean sediment accumulation rate for the last 230 kyr was ca. 3.5 cm/kyr.

Since 1996 our group attempted to improve the U-Th method of dating of sediments of Lake Baikal. The need for such a method stems from the above considerations and from the fact that all climate records, including the record from Lake Baikal [17], are complicated by signatures of pervasive millennial scale abrupt climate oscillations.

We hoped that analysis at a higher temporal resolution will improve the accuracy of the U-Th geochronometer and result in a better understanding of the connection between the concentrations of uranium-series isotopes in the sediments of Lake Baikal and the paleo-geochemical setting. Applicability of traditional alpha-spectrometry for this purpose is limited because it cannot provide the necessary throughput. We believed that it will be possible to perform the determination of isotopes by means of ICP-MS.

The first results of the applications of ICP-MS to determination of uranium and thorium in 13 intervals of sediments of Lake Baikal have been published earlier [19, 20]. The U-Th ages of two diatom-rich layers corresponding to MIS 7.1 and 5.5 were found equal to 202 and 128 kyr, respectively in an accord with global records and with ages of this stages in Antarctic ice from Vostok [21]. New algorithms were proposed for U-Th dating of sediments of Lake Baikal [19, 20, 22–24].

E.L. Goldberg et al. [25, 26] measured the distribution of many elements in the upper 30 m part of the drilling core BDP-96 by means of X-ray fluorescent analysis with synchrotron radiation. Using the Bruhnes-Matuyama boundary at 780 kyr [12] and "absolute" U-Th ages of sediments of MIS 7.1 and 5.5 [19, 20] as tie-points combined

with sliding-window spectral analysis, they obtained an orbitally tuned depth-age model which does not depend on a priori correlation with SPECMAP and found that maxima of BiSi in the sediments of Lake Baikal occur somewhat earlier than the peaks of $\delta^{18}O$ of SPECMAP. However the number of independently dated tie-points in the sediments of Lake Baikal is not yet sufficient to claim any leads or lags relative to astronomic forcing.

The first purpose of the present study was to improve the technique of ICP-MS analysis in order to increase its productivity and to provide the necessary accuracy and precision in mass determination of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th. This was necessary as a step towards high resolution "absolute" dating. The second purpose was U-Th dating of a few layers of the core. The third purpose was to explain the uranium signal as a proxy of climate-driven geochemical changes of watershed of Lake Baikal. We present experimental data for a 608 cm section at a resolution of 1–2 cm and their interpretation.

MATERIALS AND METHODS

Sampling. Bottom sediments were sampled on the top of the submerged Akademichesky Ridge (station 2) in 1996 and 1999. The VER-96-1 st 2PC core, 530 cm of total length, was retrieved by advanced hydraulic piston coring (68 mm i.d.) at 53°33′04″ N — 107°54′53″ E under 400 m of water; the 450 cm long VER-99-1 st 2GC core was obtained by gravity coring (aluminum corer, 100 mm i.d.) at 53°33′03″ N — 107°54′53″ E in a water depth of 430 m. The cores were split along into halves, divided into 1 cm (gravity core) and 2 cm (piston core) sections, placed into plastic containers and stored at 4 °C.

Preparation of samples. After taking subsamples for diatom analysis and determination of biogenic silica as described in [6], five-gram samples were dried at 105 °C to constant weight for determination for water content and ground in agate mortar. Analytical-grade HNO_3, $LiBO_2{\cdot}2H_2O$, HCl, and $FeSO_4{\cdot}7H_2O$ were tested prior to analysis and found free from U and Th.

Extraction of sediments with HNO_3. U and Th were measured in nitric acid extracts of dried sediment (2 g) obtained by digestion in 8M HNO_3 (3×6 ml) in a constantly agitated 15 ml polypropylene tube at 85 °C. The first extraction lasted 2 hours and the following ones were half-hour long. The solution was centrifuged to remove the undissolved residue, the extracts were united, supplemented with certified ^{229}Th and ^{236}U spikes (0.2 ml, 10 ppb each), evaporated to dryness and redissolved in 3 ml 8M HNO_3; 1 ml was loaded onto an ion-exchange column.

Complete dissolution [27]. 0.7 g sediment specimens were mixed with 2.4 g $LiBO_2{\cdot}2H_2O$ in graphite-glass crucibles and ignited in a muffle furnace for 20 min at 1000 °C. The crucibles were placed into a lidded ceramic box, and argon was supplied inside the box through a hole to prevent them from burning. The pearl was left for a week for dissolution in a 15 ml polypropylene tube in 10 ml 8M HNO_3. Then the extract was centrifuged and the supernatant was carefully separated from the silica precipitate. The sediment was rinsed twice with 5 ml 8M HNO_3, the supernatants were united and supplemented with a 100 µl spikes solution of ^{229}Th and ^{236}U, 10 ppb each, evaporated to dryness and redissolved in 4 ml 8M HNO_3; 3 ml was loaded onto an ion-exchange column.

Ion-exchange separation. Extracts (3 ml) were applied on a polypropylene column with 2 ml of Biorad AG1-X8 anionite pre-washed with 10 ml 8M HNO_3. Elution was performed with 4 ml 8M HNO_3 followed by 30 ml 0.4M HCl. The united eluate was evaporated to dryness and residue dissolved in 4 ml 3% HNO_3. To ensure accuracy, yields of elements after chromatography were determined by isotopic dilution. Extracts prior to chromatography were supplemented by artificial isotopes ^{229}Th and ^{236}U (RIMEX, St. Petersburg). Both artificial isotopes were at first studied by ICP-MS. The preparation of ^{236}U was isotopically pure. The preparation which was nominally ^{229}Th contained only 6.67% of this isotope. 93.33% of thorium consisted of ^{232}Th. Traces of ^{230}Th ($^{229}Th/^{230}Th = 69$), ^{239}Pu and isotopes having masses 240 and 241 were also present. A stock solution of artificial isotopes was prepared. This solution was calibrated using standard solution of ^{232}Th and ^{238}U (Thermo Jarrell Ash Corporation). The calibrated stock solution was added to every sample prior to chromatography.

Mass spectrometry. Measurements were performed with a VG PlasmaQuad II PQs instrument (VG Elemental, UK) in the Corporate Analytical Center at the Limnological Institute (Irkutsk), in repeated cycles "standard—washing—7 samples—washing—standard", 3 min for a sample, at an uptake rate of 1 ml/min. Some specimens were measured in the Peak Jumping and some in the Scanning Mode. Before the experiment the eluates (see above) were diluted in 3% HNO_3 (1:50–100 "diluted solutions" or 1:1.75 "concentrated solutions"), or not diluted, depending on the concentration of the analyzed isotopes.

U and Th were determined in bottled Baikal water [28] taken from a 500 m depth 1.7 km offshore in Listvenichny Bay. 4.5 l of this water was filtered through 0.1 µm caprone filters; 100 mg $FeSO_4{\cdot}7H_2O$ were dissolved in every 1.5 l bottle, and 2 ml of concentrated NH_4OH added. After 16 hours, the $Fe(OH)_3$ precipitate was collected by decantation, followed by filtration and dissolution in 5 ml 8M HNO_3. The solution was evaporated to dryness and redissolved in 1 ml 8M HNO_3. U and Th were separated by anion-exchange chromatography (see above) and the isotopes were determined by ICP-MS.

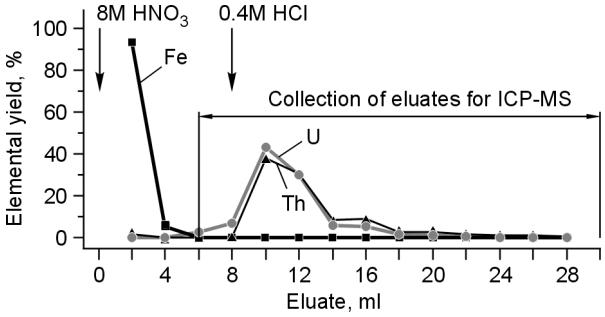

Fig. 1. Elution of U and Th nitrate complexes in a 2 ml column with AG-1 X8 anion-exchange resin.

RESULTS AND DISCUSSION

Correlation of cores. We investigated two cores retrieved at different times on the Akademichesky Ridge in Lake Baikal, one by a piston and the other by gravity coring. The gravity core has an undisturbed surface. The corer penetrated to a depth of 450 cm and reached the layer deposited during MIS 5.3 (see below). The piston core reached the depth corresponding to MIS 7 but lacked the top section. Although the two coring sites had very close geographic positions, the sediment accumulation rates differed significantly. The diatom assemblages in the cores were identical to those described earlier for the Akademichesky Ridge [6, 29]. Hence, the two cores were correlated against the diatom species in the overlapping section (300–450 cm in the gravity core and 100–200 cm in the piston core) with tie points at half-widths of the peaks of *Aulacoseira baicalensis*, *Stephanodiscus grandis*, and *Cyclotella minuta*. The depths of the tie-points were plotted in coordinates Z_{pc}–Z_{gc} (depths in the piston and gravity cores, respectively) and the linear regression $Z_{pc} = a + bZ$ was calculated. All data below are presented against the depths Z, real or calculated, in the section sampled by the gravity corer.

Chromatography. The concentrations of ^{234}U and ^{230}Th in the Baikal sediments are too low to be determined by ICP-MS in extracts directly. Hence U and Th were enriched using anion-exchange chromatography of their nitrate complexes [30]. There is no need to separate the two elements from each other. Therefore, diluted HCl was applied to the column as soon as major elements had been removed by elution with nitric acid. A typical chromatogram is shown in Fig. 1.

Samples extracted with nitric acid. In the first series of experiments, U and Th were extracted with hot 8M HNO_3 under an assumption that the two elements will be extracted quantitatively [10]. The first ICP-MS analyses were made in the Peak Jumping Mode: ion currents were measured at a few selected *m*/*e* settings instead of scanning continuous spectra, with seven settings within every expected isotope peak, along with settings in "blank" intervals at *m*/*e* = 227, 228, 240, and 241 for background subtraction. The Peak Jumping Mode was applied to the first 350 cm of the gravity core (Fig. 2).

However, the Peak Jumping Mode does not always provide the required accuracy and precision. Real peaks have a non-Gaussian geometry; moreover, real records sometimes exhibit more than one maximum within the interval nominally belonging to one mass. Therefore, the choice of fixed *m*/*e* settings may cause systematic errors due to drift of the calibration for mass.

Having realized this complication, we used scanning mode with nitric acid extracts of samples over the interval of the core between 350 and 450 cm, as indicated in Fig. 2. We consider these data as more reliable. Note that both modes provide a higher accuracy in measurements of isotope ratios, compared to absolute concentrations.

Analysis of ignited samples. Necessary precautions. Additional experiments with diatom-rich and diatom-barren sediments showed that digestion with hot 8M HNO_3 always provided a 98–99% yield of U but occasionally only a 90% yield of Th. This could compromise the U-Th geochronometer. Therefore, the samples from the gravity core between 320 and 450 cm and all piston core samples (Fig. 2, right sides of the profiles) were fluxed together with $LiBO_2$ in graphite-glass crucibles to achieve better dissolution [27] and extraction of total uranium and thorium.

Special attention was given to background correction. Signal intensities in the blank intervals (where no signal was expected, *m*/*e* = 227, 228, 240, 241) appear to depend on the matrix composition. The background signals of the eluate-free blank solutions of dilute acid in these intervals were twice as low as for real samples. To provide reliable determination of ^{230}Th and ^{234}U peaks, we subtracted the mean signals in the bracketing blank intervals (*m*/*e* = 227, 228, 240, 241). This bracketing correction technique improves the accuracy and precision of analysis and, moreover, makes it much faster than the usual routine which requires careful rinsing of ionization chamber

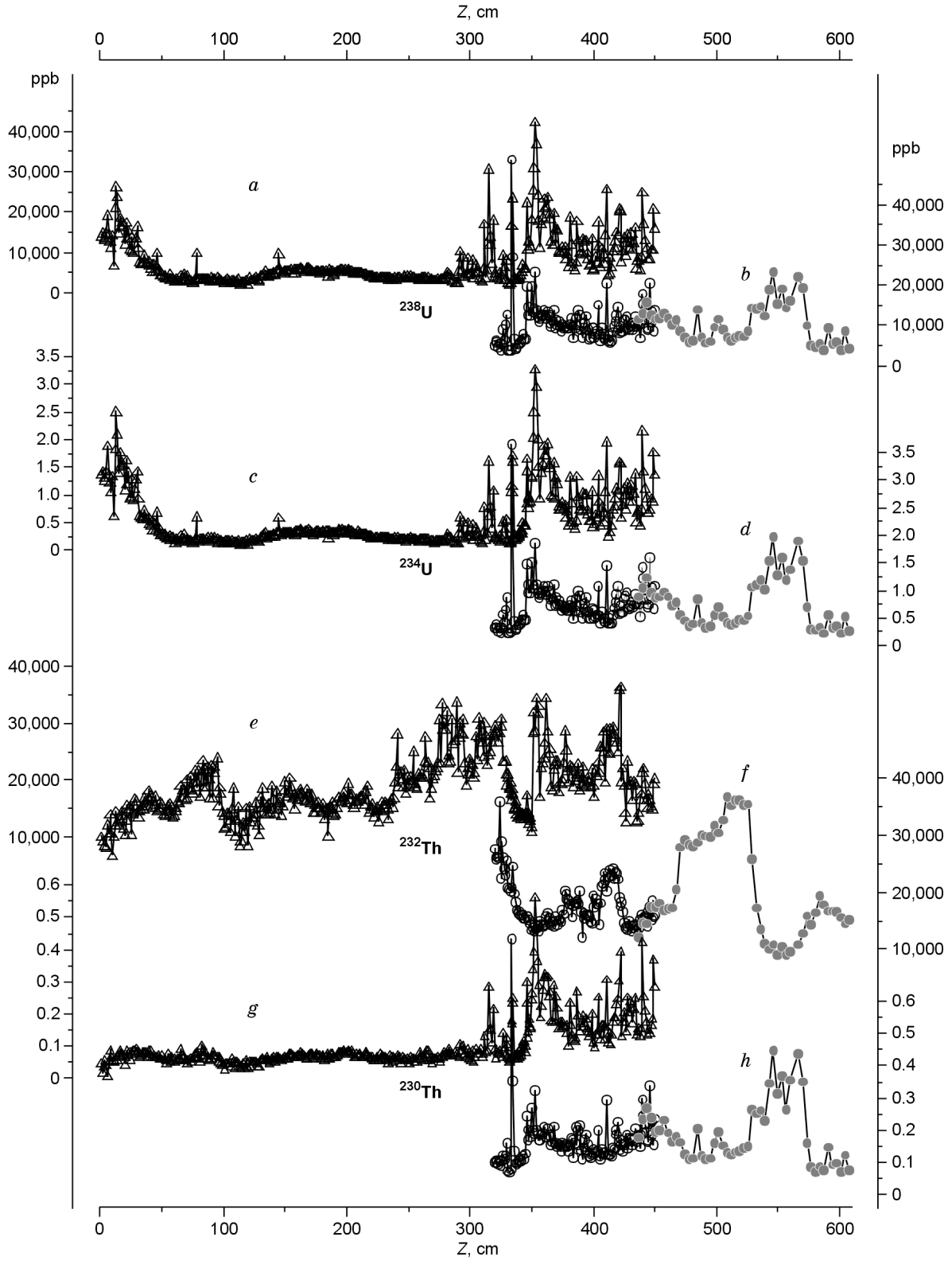

Fig. 2. Concentrations of U and Th isotopes in sediments of Lake Baikal measured by ICP-MS. Profiles *a*, *c*, *e*, and *g* refer to extracts obtained by treatment with 8M HNO_3; 1–350 cm in the Peak Jumping Mode, and 350–450 cm in the Scanning Mode. Profiles *b*, *d*, *f*, and *h* refer to samples decomposed by ignition with $LiBO_2$ (gray circles); piston core, Scanning Mode.

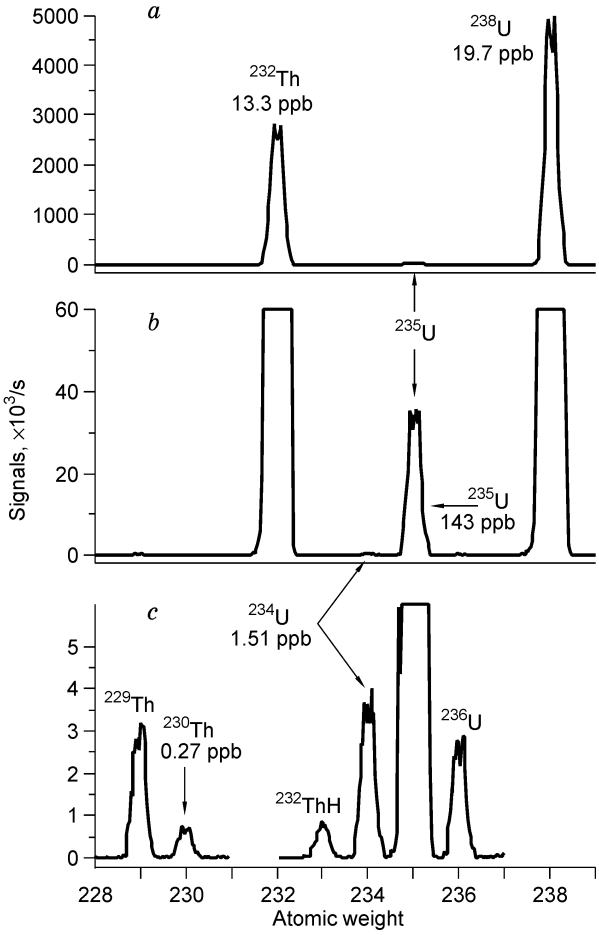

Fig. 3. Mass spectra of a typical effluent fraction. *a* — diluted and *b*, *c* — concentrated eluates. ThH is thorium hydride ion.

between samples with pure nitric acid to achieve the "true" blank. The protocol which we used was as follows: "standard—rinsing with HNO_3—seven unknowns—rinsing—standard", etc. This protocol is highly efficient (3 min per sample) and superior to rinsing after each sample, because samples differ from one another much less than from pure HNO_3. The concentrations of different isotopes vary over a range of 4–5 orders of magnitude, and simultaneous measurement of major and minor isotopes would lead to a large counting error due to the dead time of the detector. To avoid dead-time correction errors which might deteriorate the analytical quality, we measured major and minor isotopes in diluted and in more concentrated solutions, respectively.

The ^{230}Th signal (Fig. 3) was most often at least ten times as high as the background. The ^{230}Th concentrations were corrected using spikes of ^{229}Th, and those of ^{234}U and ^{235}U using spikes of ^{236}U (see Materials and Methods). The concentrations of ^{238}U were calculated from those of ^{235}U using the known ratio $^{238}U/^{235}U = 137.79$. Possible separation of U and Th during chromatography was corrected using the $^{236}U/^{229}Th$ ratios of the added spikes. The $^{238}U/^{232}Th$ ratio measured in diluted solutions and corrected for separation was used to calculate ^{232}Th. Thus we obtained data for the interval Z = 320–608 cm (right side of the profiles in Fig. 2).

Correlation of the profile of diatom abundance with that of A4/A8 profiles. Profiles of diatom abundance, of ^{238}U, and of A4/A8 ratios are compared in Figure 4. The ^{238}U profile, as well as those of ^{234}U and ^{230}Th (Fig. 2) exhibit sharp peaks (discussed below). The A4/A8 profile is smoother and generally correlates with the diatom record.

U-Th dating. Concentrations of ^{230}Th and ^{234}U determined by ICP-MS in ignited samples were recalculated into corresponding activities A0 and A4 for samples between Z = 320 and Z = 610 cm (Fig. 5) using the known decay constants of $\lambda_0 = 9.193 \cdot 10^{-6}$ yr^{-1} and $\lambda_4 = 2.826 \cdot 10^{-6}$ yr^{-1} [31, 32], respectively. Figure 5 also shows the profile of terrigenous ^{232}Th.

Dating was based on the geochemical model [10] implying that excess ^{234}U is delivered into Lake Baikal in a dissolved form by rivers (mainly the Selenga River), and the sediment contained no ^{230}Th at the time of

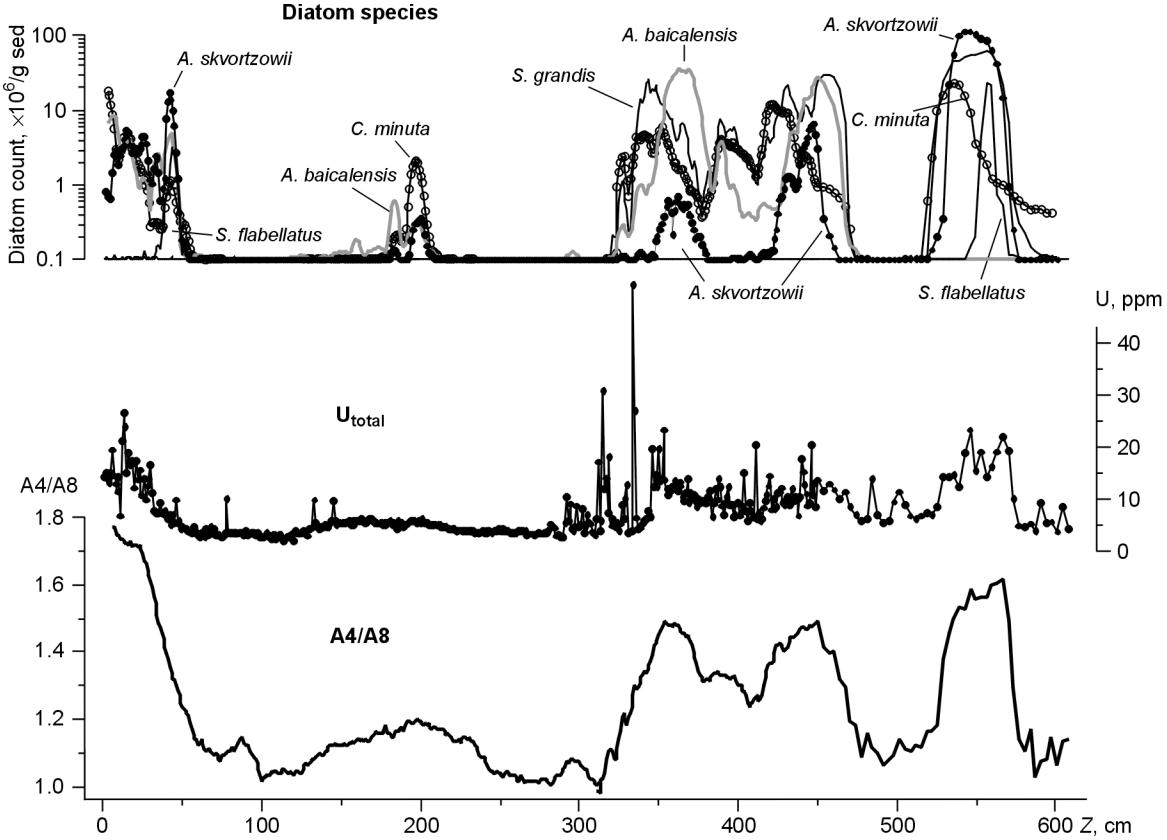

Fig. 4. Profiles of diatom species (logarithmic scale), and of ^{238}U and A4/A8.

burial. According to the same model, about 30% of dissolved uranium supplied into Lake Baikal is adsorbed on settling particles and becomes buried [10]. Besides the authigenic uranium absorbed from water, with excess ^{234}U (A4 > A8), the suspended particles themselves contain some terrigenous uranium in which ^{238}U, ^{234}U, and ^{230}Th are in secular equilibrium (i.e., $A8_{ter} = A4_{ter} = A0_{ter}$). After burial the sediments remain a closed system relative to U and Th, and concentrations of these isotopes only change due to radioactive decay ($^{238}U \rightarrow {}^{234}U \rightarrow {}^{230}Th \rightarrow {}^{226}Ra$, see Introduction). The time dependence of the A0/A4 ratio is given by the $R(t)$ function dependent on the initial A4/A8 and on the decay constants of ^{230}Th and ^{234}U, or the U-Th geochronometer [19, 20, 22].

In the present study we assumed for the purpose of dating that the ratio of the activities of adsorbed ^{234}U and ^{238}U $A4^0_{aut}/A8^0_{aut}$ at the moment of burial was equal to 2. Our ICP-MS results give a value of A4/A8 = 2.05 for U dissolved in the water of Lake Baikal, in an accord with the data of alpha-counting [10]. The ^{232}Th signal in the filtered Baikal water is about twice as low as ^{235}U, i.e, [^{232}Th]≈2.1 ppt; ^{230}Th was not detected (<0.8 ppq).

Figure 6 shows the function $R(t)$ at $(A4_{aut}/A8_{aut})_0 = 2$. The real $(A4_{aut}/A8_{aut})_0$ ratio is variable and was apparently slightly lower at cold/warm transitions [20]. However, the dependence of $R(t)$ on $(A4_{aut}/A8_{aut})_0$ is weak [19, 20, 22]. For example, the age calculated with $(A4_{aut}/A8_{aut})_0 = 1.7$ differs from that calculated with $(A4_{aut}/A8_{aut})_0 = 2$ as little as 2.6%. Since the ratio was never below 1.6 during MIS 5.5 and 7.1 [20], we assumed that $(A4_{aut}/A8_{aut})_0$ was constant and equal to 2 for warm intervals (Fig. 5).

Correlation with global climate. In the present study we determined the areas under the profiles of A0 and A4 over the 6 intervals as shown in Fig. 5. To find the function $R(t)$ and the ages, it was necessary to subtract the background — activities of terrigenic U and Th. We assumed that this background is low, equal to concentrations found for intervals with low concentrations of ^{232}Th, constant and equal to 50.8 Bq/kg, i.e., to the experimental values of A0 and A4 at 340 and 600 cm. After subtraction of the background the function R(t) was calculated, and U-Th ages were found.

The data obtained, along with the age at Z equal to 0, and age equal to 15 cal. kyr at Z = 42 cm (age of the peak of *Stephanodiscus flabellatus* [7, 33]) were used as a basis for the linear age-depth model shown in Fig. 7.

The age dependence of $(A4/A8)_0$ of Baikal sediments was in an accord with the changes in global climate, as revealed by comparison with the time course of insolation for July at 60° N [34] and the SPECMAP profile

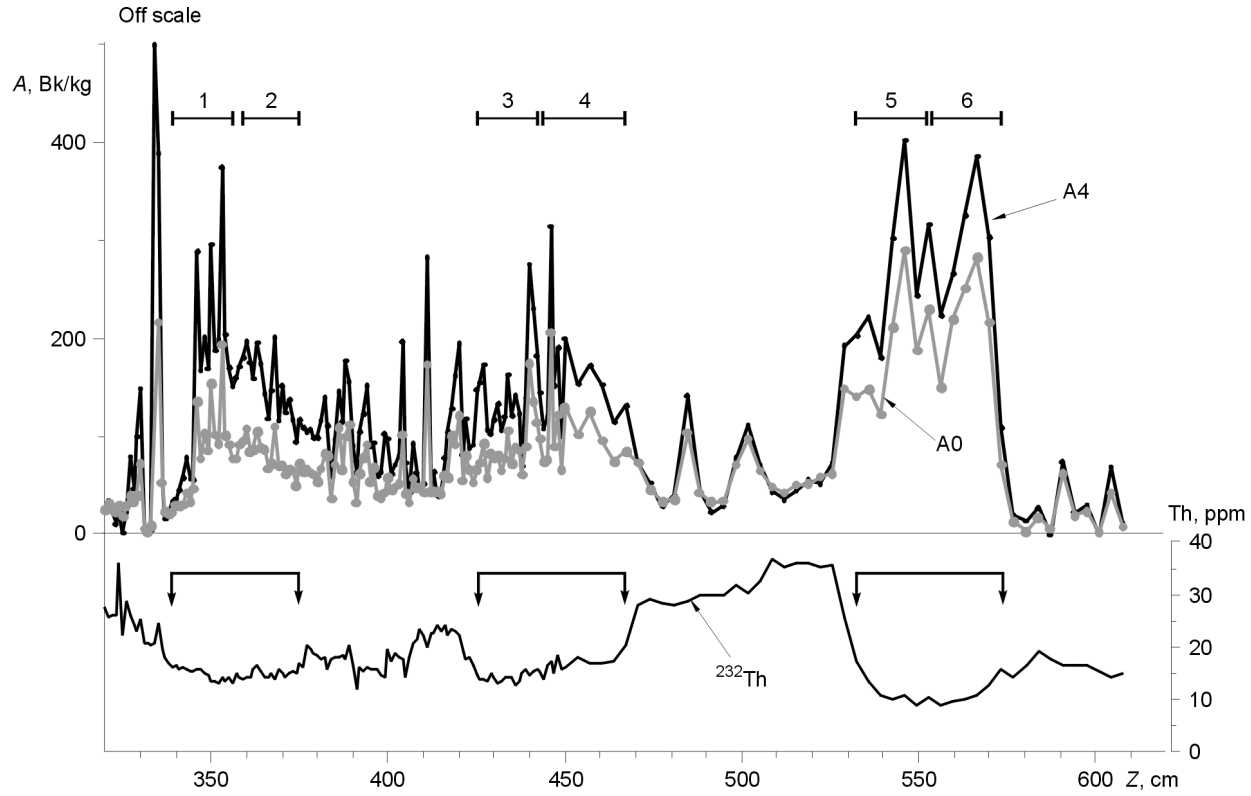

Fig. 5. A0 and A4 profiles (corrected for background of 50.84 Bq/kg for both isotopes) and ^{232}Th concentrations.

[9] (Fig. 7). New data confirm the earlier U-Th ages of the sediments of Lake Baikal deposited during MIS 5.5 [19, 20]. Independent ages for MIS 5.3 and 5.1 given in Fig. 7 have been obtained for the first time. Discussion of the shift of the $(A4/A8)_0$ relative to the SPECMAP and that of the insolation is beyond the scope of the present paper because the age-depth model is not sufficiently accurate.

It will be noted that it was attempted earlier to date Baikal sediments by means of the U-Th geochronometer on the basis of a different geochemical model [35]. However, the ages published in this paper are wrong. For example, it is claimed that the age of the sediment in the BDP-96-2 core at a depth of 4.4 m is equal to 52–63 kyr. Data of diatom analysis unequivocally place the sediment at 4.4 m in BDP-96-2 to MIS 5.5 [8, 10–13, 17, 19, 20, 23, 26, 33], i.e., to 120–130 kyr BP, twice as old, as suggested in [35]. The reason of the discrepancy is that during the extraction of phases with strong alkali and acid U and Th are redistributed between the phases, contrary to the starting assumption of the model.

Fluxes of sediment components. We estimated the fluxes of sediment components for the past 100 kyr from the known constant mean sediment accumulation rate of 4.6 cm/kyr (Fig. 7), water content (*WC*), biogenic silica (BiSi), the known density of biogenic silica of 2.07 g/cm^3 [36], and the specially measured average picnometric density of the Pleistocene clay of Lake Baikal of 2.63 g/cm^3.

The mass of 1 cm of wet sediment (m) over 1 cm^2 of the bottom is the sum of the constituent masses of rock (clay), biogenic silica, and water. Let the volume of the three components be V_r for solid rock of clay particles, V_{BiSi} for BiSi, and $V_{\mathrm{H_2O}}$ for water, respectively. Evidently,

$$m = 2.63\ V_r + 2.07\ V_{\mathrm{BiSi}} + V_{\mathrm{H_2O}},$$

$$V_r = V_{\mathrm{BiSi}} + V_{\mathrm{H_2O}} = 1,$$

$$2.07\ V_{\mathrm{BiSi}}/(2.63\ V_r + 2.07\ V_{\mathrm{BiSi}}) = \mathrm{BiSi},$$

$$V_{\mathrm{H_2O}}/m = WC.$$

The obtained values of m, V_r, V_{BiSi}, and $V_{\mathrm{H_2O}}$ were used to calculate the masses of components for each centimeter Z over 1 cm^2 of sediment which, along with linear sedimentation rates and concentrations, were further

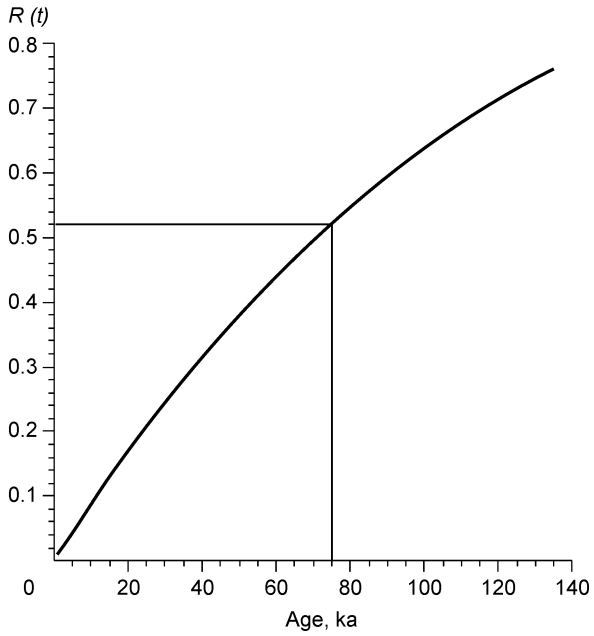

Fig. 6. $R(t)$ for $(A4_{aut}/A8_{aut})_0$ = const = 2 [19, 20, 22].

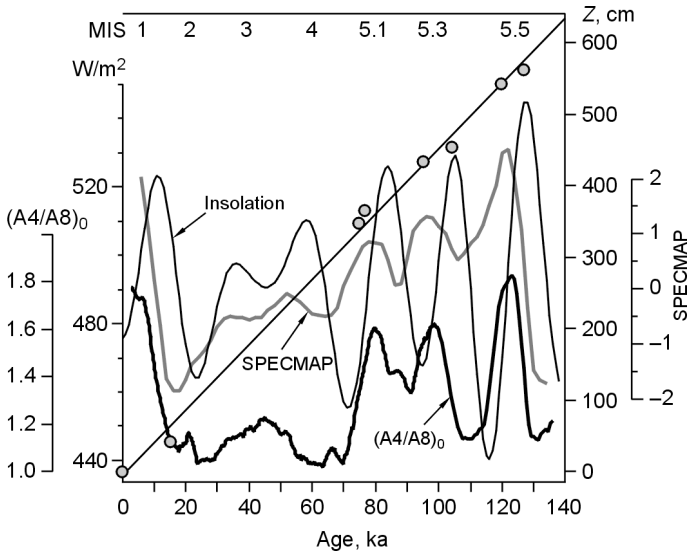

Fig. 7. Linear age-depth model based on U-Th dating. Linear function was calculated by the least squares method for six indicated U-Th ages, zero age at Z = 0, and 15 cal. kyr at Z = 42 cm (gray circles). Linear regression: $y = 4.567x - 5.575$; $R^2 = 0.995$. $(A4/A8)_0$ profile calculated from the measured (A4/A8) profile on an account for the decay of excess ^{234}U and corresponding to A4/A8 at the time of burial. SPECMAP profile from ref. [9] and insolation at 60° N from ref. [34].

used for the estimation of fluxes of sediment components (Fig. 8). The clay flux during MIS 4 (Zyryanka glacial), MIS 3 (Karga interstadial), and MIS 2 (Sartan glacial) was much higher than in the Holocene and during MIS 5.1 and 5.3. Note that it remained high during MIS 3 but diatoms still persisted (see the diatom flux in Fig. 8). The invariability of clay flux during MIS 4, 3, and 2 means that glaciers in the mountains around the lake did not disappear in Karga time (MIS 3), contrary to the earlier statements that the Karga interstadial was warmer than the Holocene [37]. In fact, a much warmer climate in the Holocene than in MIS 3 is indicated by a low clay flux and the absence of mountain glaciers around Lake Baikal. Moreover, the presence of diatoms during MIS 3

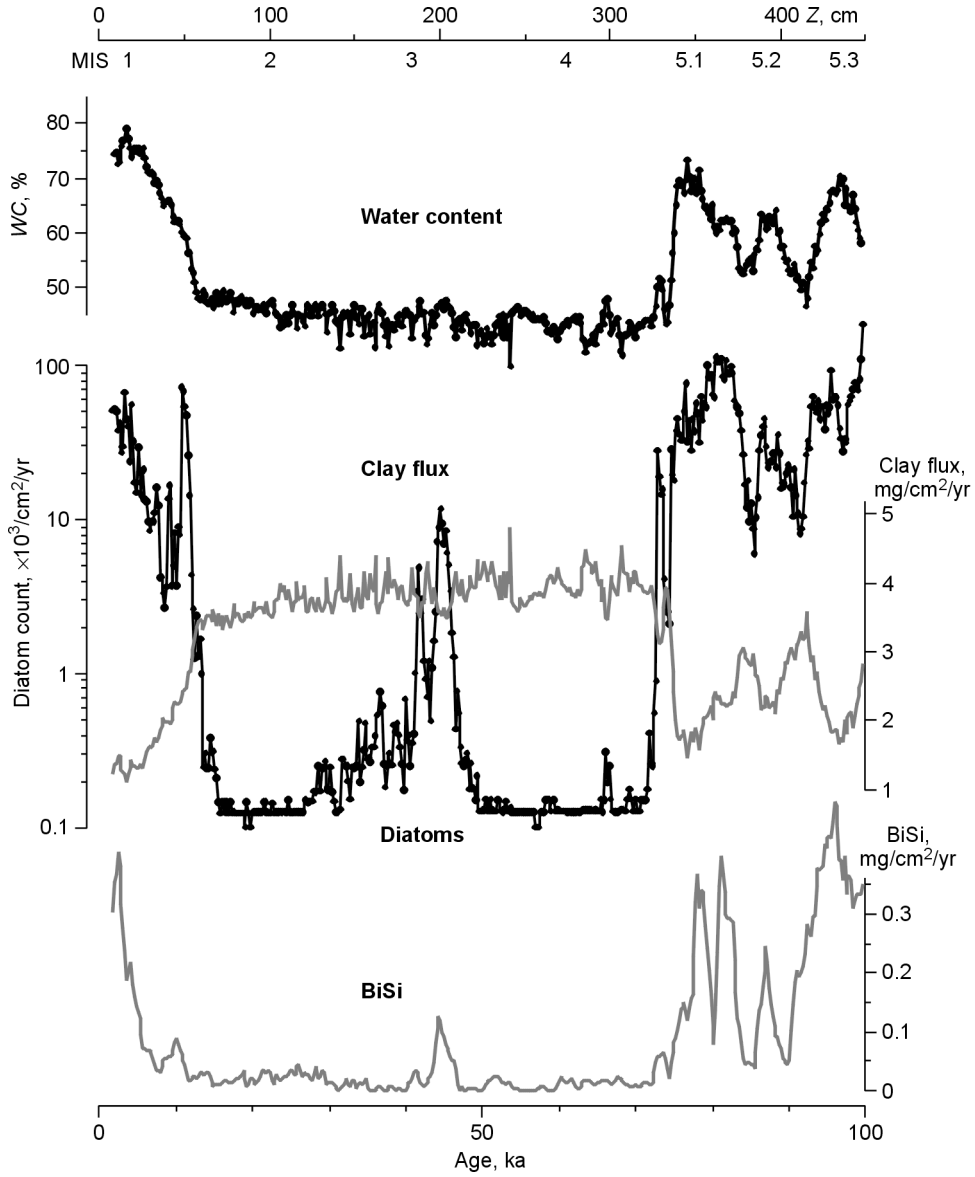

Fig. 8. Water content (*WC*) and fluxes of clay, biogenic silica, and diatoms in sediments of gravity core.

in spite of the high clay flux disproves the earlier hypothesis [4] that diatoms disappeared during glacials mainly because of water turbidity.

Authigenic and terrigenous uranium. According to the model in [10], all uranium with A4/A8 > 1 was supplied to Baikal in the soluble form. With the assumption that the A4/A8 ratio for dissolved uranium in the Baikal water was inherited by its settling authigenic fraction, the U activities at the moment of burial were

$$A4^0 = (A4_{ter} + A4_{aut})_0, \quad (1)$$

$$A8^0 = (A8_{ter} + A8_{aut})_0, \quad (2)$$

$$A4^0_{aut}/A8^0_{aut} = 2. \quad (3)$$

The subscripts (ter) and (aut) denote the terrigenous and authigenic components, respectively. Then, for simplicity, we assume as in [10] that the initial disequilibrium of the soluble uranium has been constant and equal to 2, though the true ratio apparently varied during MIS 5.5 and 7.1 from 2.1 at interglacial peaks to 1.6 at interglacial/glacial transitions [20]. However, this has very little significance for the inferences below. Dating was likewise based on $(A4_{aut}/A8_{aut})_0$ = const = 2 in warm climates, as a first approximation (see above).

^{238}U has a long half-life, and therefore $A8 = A8^0$. Excess ^{234}U decays approaching the secular equilibrium with $^{238}U_{aut}$. Then,

$$A4^0 - A8 = (A4 - A8)/\exp(-\lambda_4 \cdot t), \quad (4)$$

$$A4^0 - A8 = A8^0_{aut}, \quad (5)$$

$$A8^0_{ter} = A8 - A8^0_{aut}. \quad (6)$$

Using equations (5) and (6), experimental A4 and A8, the linear depth-age model (Fig. 7) and the mass sediment accumulation rates, we reconstructed the profiles of the fluxes of authigenic and terrigenic U (Fig. 9). It is seen that the profile of the flux of U_{ter} is generally similar to that of the flux of terrigenic ^{232}Th. The small difference in these profiles can be explained by increased delivery of Th-rich terrigenic material into the lake during the glacials.

The activity ratio $(A4_{aut}/A8_{aut})_0$ is the measure of the excess of ^{234}U relative to secular equilibrium with ^{238}U. Excess ^{234}U in natural water was discovered in the 1950s and explained by Chalov and Cherdyntsev [37]. ^{234}U is a daughter of ^{238}U. The atom of ^{234}U formed by decay of ^{238}U can, due to recoil, shift from the crystal lattice of the uranium-containing mineral into interstitial space where it becomes more available to leaching. Therefore, $(A4_{aut}/A8_{aut})_0$ in the water of many rivers and lakes is much above the unity: $(A4_{aut}/A8_{aut})_0$ is equal to 2–2.1 in the Selenga River, to 2 for uranium dissolved in modern Lake Baikal, and to 1.28–1.4 for uranium dissolved in the tributaries of North Baikal [10].

Note that the profiles of $(A4_{aut}/A8_{aut})_0$ and U_{aut} flux show a good correlation (Fig. 9). Discussion of this correlation is beyond the scope of the present paper, but the finding is interesting, because it is simpler to measure the $(A4/A8)_0$ ratio than U_{aut} flux.

Integrate profiles and paleo-geochemistry of the watershed of Lake Baikal. Data from Fig. 9 were used to calculate integrate accumulation profiles from Z = 450 to 0 cm, the last 100 kyr (Fig. 10). The fine-grained terrigenous material deposited from 70 to 15 kyr (70 Gtons, or 25 km^3 of solid rock) was composed mainly of "glacier flour", clay-sized particles produced by mechanic disintegration of rocks by glaciers [4, 6, 39–42] and of a size which allowed them to reach the underwater Akademichesky Ridge separated from the shore by deep troughs.

At present the snow line in the Baikal region approaches the highest tops of the mountains surrounding Lake Baikal, at about 2300 asl [43] where sometimes snow persists in summers. During the Zyryanka and Sartan glacials, valley glaciers formed in the mountains around North Baikal. The thickness of their ice was up to 400 m. Glaciers reached the shoreline and were discharged directly into the lake [44]. The snow line in the LG was 1100 m below the present level, about 800 m above the water surface of Lake Baikal. Climate models show that highest July air temperature in the glacial maximums was ~6 °C lower than it is now (25 °C) [45]. Our data indicate that the Karga climate was warmer than those of the Sartan and Zyryanka times, but much colder than the climate in the Holocene, as suggested by fast clay deposition at MIS 3 (Figs. 8, 10), evidence for the existence of glaciers in the highlands. The estimate for the rock volume reworked by glaciers during 100 kyr into clay-sized material (25 km^3) appears reasonable as the maximum area of glaciers around North Baikal was about 1000 km^2 [44], i.e., rocks were eroded by glaciers at a mean rate of 0.25 mm/yr.

Accumulation of sediments in Lake Baikal in the Pleistocene apparently occurred at two typical rates: faster one, reflecting erosion by glacier during glacials and a slower one which was the case in warm climates, when the mountains around Baikal were free from glaciers, and the dominating contribution to sediment accumulation was provided by diatoms. The constant rate of erosion by glaciers which repeatedly occupied the slowly changing mountain landscapes may account for the surprisingly stable mean linear sedimentat accumulation rate in the Pleistocene (4–5 cm/yr over the last 1.8 myr) [11, 12].

The integral profiles obtained (Fig. 10) highlight the "missing link" between the known diatom signal of warm climates [4] and the geochemistry of the watershed of Lake Baikal: deposition of authigenic uranium in the sediments of Lake Baikal was almost zero during MIS 4 and 2 (Zyryanka and Sartan glacials in Siberia). In our opinion the main reason was a lower discharge of the Selenga River, as compared with that in the Holocene and in the Last Interglacial. It seems reasonable that cold and dry climates inhibited the supply of soluble uranium and nutrients from the watershed.

Precipitation in the catchment basin of Lake Baikal increased abruptly (within less than 300 years) by 2–2.5 times about 15 kyr BP and reached the Holocene level, as inferred from the geochemistry of sediments of the lake [46]. The catchment basin of Selenga River may have been then a "mammoth steppe", a typical landscape of the mid-latitude plains in cold and dry Pleistocene climates [47], in which soils were alkaline, Ca-rich, and apparently bound the silicate anion. A change in the Northern Atlantic circulation in the beginning of Boelling warming (about 14.7 cal. kyr BP) caused a higher humidity in tropics, the formation of bogs, and an abrupt increase in atmospheric methane [48]. It is probable that much greater amounts of moisture from the North Atlantic started

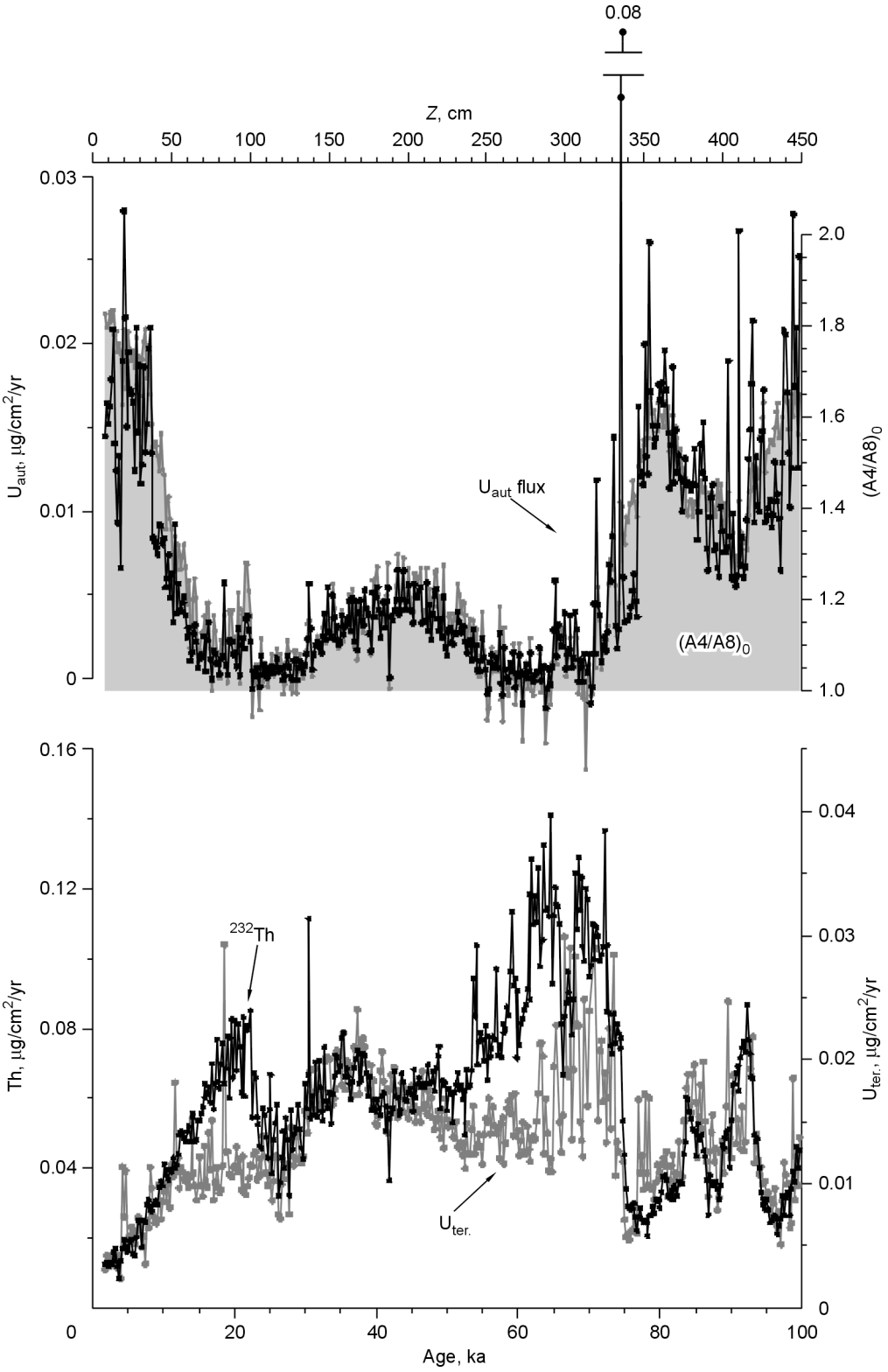

Fig. 9. Measured ^{232}Th flux and theoretical $^{238}U_{ter}$ and $^{238}U_{aut}$ fluxes, and reconstructed $(A4/A8)_0$ profile (Fig. 7).

to arrive to East Siberia; the mammoth steppe degraded, soils were acidified, and the leached nutrients (Si, P, etc.) penetrated into Baikal.

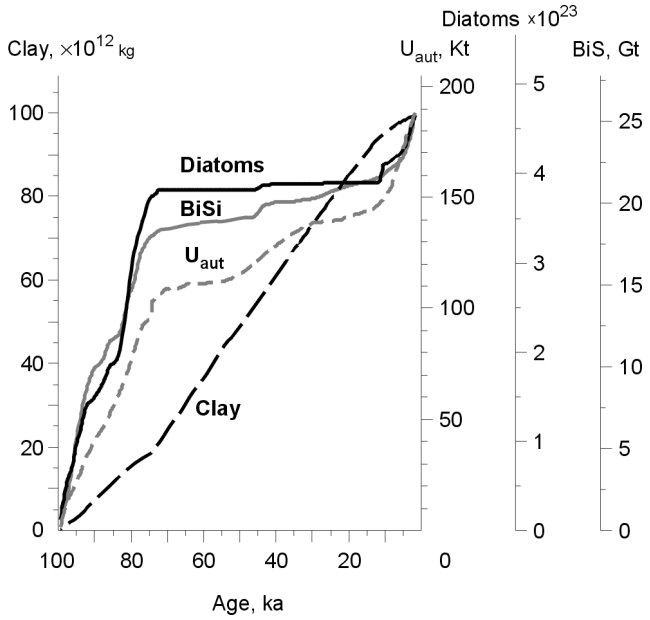

Fig. 10. Accumulated diatoms, biogenic silica, authigenic uranium, and clay in Lake Baikal for past 100 kyr, found as integrals of fluxes (Figs. 8, 9) calculated for gravity core samples multiplied by the surface area of Lake Baikal (31,500 km^2).

The fluxes of sedimentation of BiSi and diatoms behaved generally in the same way as that of U_{aut} (Fig. 10): their accumulation rates approached zero during MIS 4 and 2 and were much lower during MIS 3 than in MIS 5.3–5.1 and in the Holocene.

Note that the integral flux of authigenic uranium changes smoothly, whereas the BiSi and diatom profiles show a prominent step in the middle of MIS 3 (Fig. 10). This can be easily accounted for by the suggested model which relates the climate humidity and the flux of nutrients, as diatoms are unable to compete successfully with Si-free plankton algae at the concentrations of dissolved SiO_2 below 0.5 mg/l [49].

The growth of U_{aut} (e.g., during MIS 3) is smooth. Presumably, delivery of dissolved silica also grows smoothly, but diatoms started to develop only when silica concentration surpassed a limit of 0.5 mg/l. Accordingly, on the onset of a dry climate diatoms disappeared sooner than the flux of soluble uranium ceased.

High-frequency oscillations. ^{234}U and ^{230}Th in the Baikal sediments vary strongly (Figs. 2 and 5) and show numerous sharp peaks, e.g., twenty two congruent A0 and A4 peaks in the interval Z = 450–320 cm (100–70 kyr) (Fig. 5). These oscillations can be due to the pervasive millennial-scale abrupt climate fluctuations that occur at an irregular periodicity of 0.5–2.5 kyr [18] and manifest themselves in abrupt humidity changes on different continents. Whatever the cause of the high-frequency oscillations of ^{234}U and ^{230} Th (Fig. 5) and their relationship with the millennial-scale climate oscillations, the deposition of both authigenic and terrigenous uranium (and total Th) is subject to significant variations. This makes dating more difficult. A closer consideration revealed that high-frequency fluctuations also involve $A4_{ter}$ and $A8_{ter}$. The earlier algorithms [19, 20, 22], which would allow dating every centimeter of the core if there were no high-frequency fluctuations, have been no success so far. We failed to obtain reliable ages for MIS 3, let alone the low-U sediments of MIS 2 and 4. We are going to try chemical separation of authigenic ^{234}U and ^{230}Th from their terrigenous counterparts to reduce this terrigenic background.

Extinction of fauna at 74.5 kyr BP. The profile of $(A4/A8)_0$ compared with the behavior of three diatom species in the 60–100 kyr interval (Fig. 11) shows a prominent U_{aut} peak at Z = 334 cm (74.5 kyr BP). This section, if present throughout the Baikal bottom, stores 5.2 ktons of uranium, i.e., 42% of total U dissolved in modern Lake Baikal (0.54 μg/l ^{238}U [10] × 23,000 km^3 volume of Lake Baikal). A thin (5.5 mm) layer of iron-calcium phosphorite found at this depth [50] contains 7% P, against the 0.15% background, and, if continuous throughout Baikal, stores 9.3 Mtons P, which is 37 times as high as soluble inorganic phosphorus in the water of modern Lake Baikal (253 ktons). We believe that this U-P anomaly may record an episode of mass extinction of aquatic organisms.

The value of $(A4/A8)_0$, roughly proportional to the flux of authigenic U to the Baikal bottom (Fig. 9), can be interpreted as a measure of the flux of nutrients. Figure 11 shows that $(A4/A8)_0$ reduced to ≈1.35 at 75 kyr

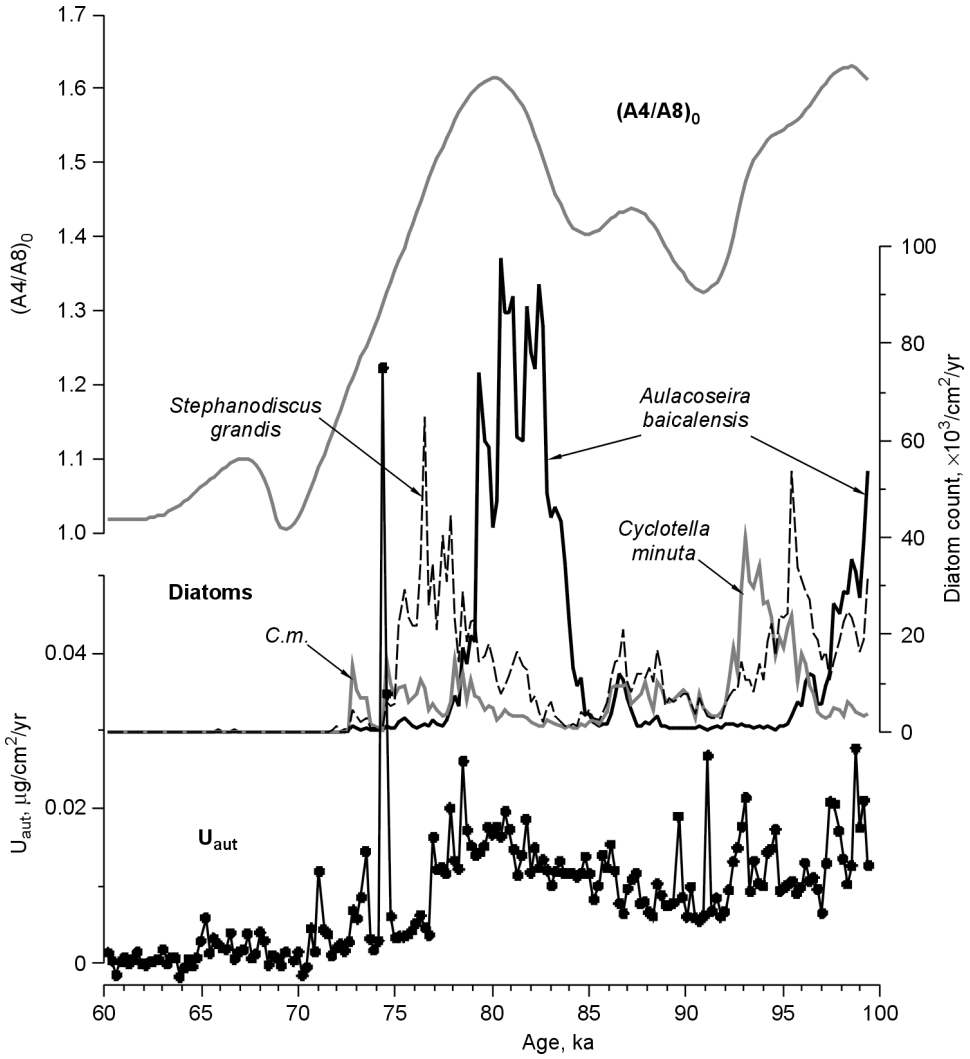

Fig. 11. U_{aut} profile compared to diatom fluxes and $(A4/A8)_0$.

BP. This decrease was followed by a sharp drop in the flux of buried diatoms, which, according to our hypothesis, was a consequence of a decrease in the flux of nutrients. The absence of diatoms, the main primary producent, in turn, caused starvation and extinction of animals in Baikal and burial of phosphorus. Finally, the sediments deposited at that period adsorbed almost all soluble uranium from the lake water.

After the extinction, authigenic uranium may have been accumulated for different reasons, e.g., as a result of its high affinity to hydroxylapatite [51] or to organic matter [24]. Perhaps, soluble six-valent uranium at the water-sediment interface was reduced by organic matter to insoluble four-valent U. The extinction hypothesis is supported by the behavior of different species of diatoms, sensitive indicators of the trophic state of lake ecosystems. It is seen in Fig. 11 that, within the interval presented, there were two episodes of decrease of $(A4/A8)_0$. At highest $(A4/A8)_0$, *Aulacoseira baicalensis* dominated twice. Subsequent decrease in $(A4/A8)_0$ was twice accompanied by dominance of *Stephanodiscus grandis*, followed by *Cyclotella minuta*, and, finally, diatoms disappeared. A possible relationship between the flux of nutrients and diatom abundance in sediments of Lake Baikal and the Black Sea was pointed out by V.M. Gavshin et al. [52].

We have to consider an alternative explanation of the mass extinction of biota in Lake Baikal, particularly, the formation of a permanent ice cover. Ice, if present all year round, would block the supply of oxygen. This scenario would easily explain both the extinction of aquatic organisms and deposition of uranium. However, it is very unprobable for the following reasons. First, Lake Baikal is inhabited by several thousands of oxygen-breathing animal species which are known to have originated in the Miocene, Pliocene, and Pleistocene — far ahead of the mass extinction episode, as suggested by data of molecular biology [53]. Second, paleogeographic reconstructions

have shown that the ice cover was not permanent even in the LG: The open water period at that time was 5.5–6 months, and now it lasts for 7–8 months [54].

CONCLUSIONS

The present paper for the first time describes a high-resolution (~200 years) record of uranium-series isotopes in the sediments of Lake Baikal for the past 140 kyr and U-Th absolute dating of sediments deposited during MIS 5.1 and 5.3. The $(A4/A8)_0$ profile for the past 140 kyr correlates well with the SPECMAP record within the limits of the suggested age-depth model.

A deficiency of nutrients at low input of river water, indicated by low $(A4/A8)_0$, caused extinction of diatoms and a decrease in total primary production, followed by extinction of pelagic fauna. According to our data, an extinction episode in Lake Baikal in the beginning of the Zyryanka glacial, 74.5 kyr BP, was accompanied by burial of a large amount of authigenic uranium.

This hypothesis provides a simple explanation for rhythmic appearance and disappearance of diatoms in the sediments of Lake Baikal throughout the Pleistocene (0.01–1.8 Myr BP). The delivery of nutrients decreased during Pleistocene glacials, and pelagial became an aquatic desert, similar to the open ocean. Flora and fauna migrated to estuaries and to shallows where the supply of nutrients remained sufficient for the survival of small populations. The shallow-water ecosystems became geographically isolated, and each one evolved independently. After every warming, a few species could succeed to colonize the pelagial. This success depended not only on the Darwinian fitness but also on the effect of the founder, i.e., the winners were the species which came first.

Note that *Stephanodiscus grandis* first appeared in the middle Pleistocene and disappeared forever during MIS 4; *Aulacoseira baicalensis*, the most important extant endemic diatom species in Lake Baikal, first appeared during MIS 5.3, and never occurred over the time interval of the preceding 2 Myr [13] (see also Fig. 4). Therefore, the alternating wet and dry climate cycles in the Pleistocene may have been a major driving force in the nascence of the unique complex of endemic aquatic organisms of Lake Baikal.

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