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GEOCHEMISTRY

High-Resolution Record of Uranium Isotopic Composition of Paleo-Baikal Water during the Last 100 ka[1]

N. A. Zhuchenko, E. P. Chebykin, E. L. Goldberg, and O. G. Stepanova

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The study of bottom sediments of Lake Baikal attracts great interest as a tool for reconstruction of the paleoclimate in continental Asia. Several climate-sensitive indicators of variable paleoproductivity and vegetation of the lake, as well as provenances of the terrigenous material, have been found to date [1–3]. Uranium isotopes occupy a special position in this respect, because their contents in sediments of Lake Baikal correlate with the volume of river inflow. This correlation made it possible to reconstruct variations in climate humidity in East Siberia to reconstruct [4, 5]. Since a substantial excess of ^{234}U relative to ^{238}U was revealed in the present-day water and surficial sediments of Lake Baikal, Edgington et al. [6] proposed a geochemical model of supply and precipitation of uranium in sediments of this lake in order to carry out their direct dating. In activity units[2], the present-day activity ratio in the lake water is A4/A8 = 2 [5, 6]. The excess of the A4/A8 ratio over its equilibrium value (A4/A8 = 1) in sediments is related to the presence of authigenic uranium supplied from the water. Irrespective of the mechanism of precipitation of the dissolved uranium in sediments, the authigenic uranium must inherit the isotopic composition of this element dissolved in water at the moment of burial. Thus, based on the measurement of the isotope ratio of authigenic uranium in sediments and its correction for decay, one can determine the initial ratio $\beta = (A4_{aut}/A8_{aut})_{t=0}$ at the moment of burial and this ratio corresponds to the isotopic composition of uranium dissolved in the lake water. Conversely, if the U/U ratio in water is known, this value may be used for calculation of the initial nonequilibrium state of authigenic uranium in the sediments. The $\beta = (A4_{aut}/A8_{aut})_{t=0}$ value should be known for the correct U/U and U/Th timing of sediments [7]. In oceanic water, this ratio has remained constant over the last 500 ka (A4/A8 = 1.14 ± 0.03 [8]). By analogy with the ocean, Edgington et al. [6] postulated that this ratio is also retained in the Baikal water (β = const = 2) irrespective of climate variations. However, the breach of this condition during the transition from warm to cold climates has been revealed from indirect experimental data [9, 10]. Direct systematic measurements of uranium disequilibrium in paleolake waters have not been carried out until now. Therefore, the long-term variability or constancy of this ratio in Baikal waters remains an open issue.

The objective of this study is to obtain a high-resolution record of the authigenic uranium ratio $\beta = (A4_{aut}/A8_{aut})_{t=0}$ for sediments and water of Lake Baikal over the last 100 ka and to provide evidence for variability of this ratio as a response to climate variation in contrast to the situation with oceanic water [7, 8].

The isotopic measurements were performed with sediments from Core VER-99-1 st2 GC taken from the slope of the Akademicheskii Ridge located between the central and the southern depressions of Lake Baikal. The core description and high-resolution records of bulk uranium isotopes in sediments are given in [5]. The authigenic uranium content in sediments was measured by the following new technique. To measure the $A4_{aut}/A8_{aut}$ ratio in sediments, it is not necessary to extract the whole authigenic uranium. It is sufficient to extract only a part of the authigenic uranium by processing a minimal amount of the terrigenous matrix. The authigenic uranium was extracted from sediments with a 1% NH_4HCO_3 solution. In certain time intervals (5, 10, 15, 20, 25, and 60 min; 1, 2 days), we took an aliquot of suspension and immediately centrifuged it. Then, a supernatant was analyzed for uranium isotopes and some other elements with a VG PlasmaQuad 2 ICP-MS quadrupole spectrometer (Institute of Limnology, Irkutsk) and an ELEMENT 2 high-resolution spec-

[1] Dedicated to the Memory of Academician P.I. Chalov.

[2] Abbreviations used hereafter for activity: ^{234}U, ^{238}U, and ^{232}Th—A4, A8, and A2, respectively.

Limnological Institute, Siberian Division, Russian Academy of Sciences, ul. Ulan-Batorskaya 3, Irkutsk, 664033 Russia; e-mail: gold@econova.nsk.su

trometer with magnetic scanning sector (Institute of the Earth's Crust, Irkutsk). The isotope $A4_{extr}/A8_{extr}$ ratio and the bulk U and ^{232}Th contents, as well as contents of K, Ti, La, and Ce (elements of clastic material), were measured in extracts. At the stage of technique development, the U and Th isotopes were also measured in residues and bulk sediments. The measurements were performed using a certified mixture of artificial ^{229}Th and ^{236}U isotopes for monitoring U and Th losses on chromatographic columns. The GSO 7521-99 (UEKhK) uranium isotope standard was used to correct the effects of mass fractionation. The accuracy of the isotope ratio and concentration determinations was not worse than 0.5% and 2%, respectively.

The $A4_{aut}/A8_{aut}$ ratio of authigenic uranium in sediments was determined from the $A4_{aut}/A8_{extr}$ ratio in extracts after correction for contamination with the terrigenous component. The contamination was estimated from concentrations of ^{232}Th and some other clastogenic elements in extracts. The first estimate was obtained from relationships

$$A4_{aut}/A8_{aut} = \frac{A4_{extr}/A8_{extr} - \omega}{1 - \omega}, \quad (1)$$

$$\omega = (^{232}Th_{extr}/3)/^{238}U_{extr}, \quad (2)$$

where ω is the fraction of terrigenous uranium in extracts. The a priori value $^{232}Th/^{238}U = 3$ in the terrigenous matrix was used as the clarke value for clays [11]. This method allows us to estimate the $A4_{aut}/A8_{aut}$ ratio for each separate extract. The uncertainty of determination shows a direct correlation with the content of terrigenous uranium in the extract. In the second method, a priori knowledge of the $^{232}Th/^{238}U$ ratio in terrigenous matrix is not required and isotopic data on a series of several extracts are used. According to the isochron method based on the sequential leaching of a sample, the $A4_{extr}/A2_{extr}$ versus $A8_{extr}/A2_{extr}$ relationship in a series of extracts from the same sample should be described by a straight line with the tangent of the slope equal to the true $A4_{aut}/A8_{aut}$ ratio in the studied sample [7]. Figure 1 shows examples of such isochrons based on extraction with 4% and 1% NH_4HCO_3 solutions from one sample taken at the horizon of 197 cm (in total, 500 samples were analyzed). One can see perfect linear relationships ($R^2 = 0.9997$). In accordance with the isochron method [7], the $A4_{aut}/A8_{aut}$ ratio of the studied sample is estimated at 1.304 ± 0.009 (for extraction with 1% solution) and 1.316 ± 0.010 (for extraction with 4% solution). These values do not differ within error limits from the value of 1.300 ± 0.013 obtained for this sample from formulas (1) and (2).

The experiments also demonstrated the following regularity: if the authigenic uranium is extracted from Baikal sediments with 1% NH_4HCO_3 solution at an optimal duration of 20–60 min, the share of terrigenous uranium in the extracts does not exceed 0.3%. Moreover, the errors in determination of the $A4_{aut}/A8_{aut}$ value related to the terrigenous contamination are minimal. Precisely these optimal conditions were used to obtain a high-resolution record of $A4_{aut}/A8_{aut}$ at 500 horizons of the sediment core.

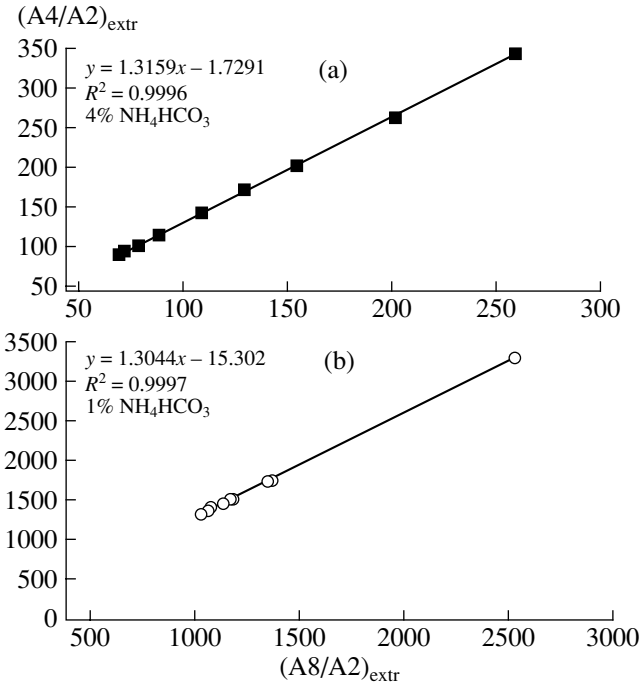

Fig. 1. Isochrons of sediments at the horizon of 197 cm (age 45 ka) in $(A4/A2)_{extr}$–$(A8/A2)_{extr}$ coordinates for a series of sequential extraction with (a) 4% and (b) 1% NH_4HCO_3 solutions. The tangent of the slope of straight lines is equal to the true $A4_{aut}/A8_{aut}$ ratio in the studied sample [7].

Figure 2a shows the high-resolution record of the measured $A4_{aut}/A8_{aut}$ ratio in Baikal sediments over the last 100 ka. Figure 2b exhibits the calculated $\beta = (A4_{aut}/A8_{aut})_{t=0}$ ratio in sediments at the moment of their burial. This value is inherited from waters of the lake. Thus, the calculated ratio reflects the initial disequilibrium of uranium isotopes in Baikal paleowater. The correction was introduced in accordance with the U/U geochronometer using the following formula:

$$\beta = (A4_{aut}/A8_{aut})_{t=0} = (A4_{aut}/A8_{aut} - 1)\exp(\lambda_4 t) + 1, \quad (3)$$

where λ_4 is the ^{234}U decay constant and t is the age of the horizon. The depth–age scale of the studied column is given in [4, 5].

As can be seen from Figs. 2a and 2b, in contrast to the uranium isotope ratio in oceanic water, the uranium isotope ratio in sediments and paleowaters of the lake did not remain constant through time [7]. Hence, the assumption of invariance of this ratio accepted in the model of supply and precipitation of uranium in Lake Baikal [6] is incorrect. Furthermore, indicators of lake productivity, such as the content of diatom algae and sponge spicules, as well as the water content in sedi-

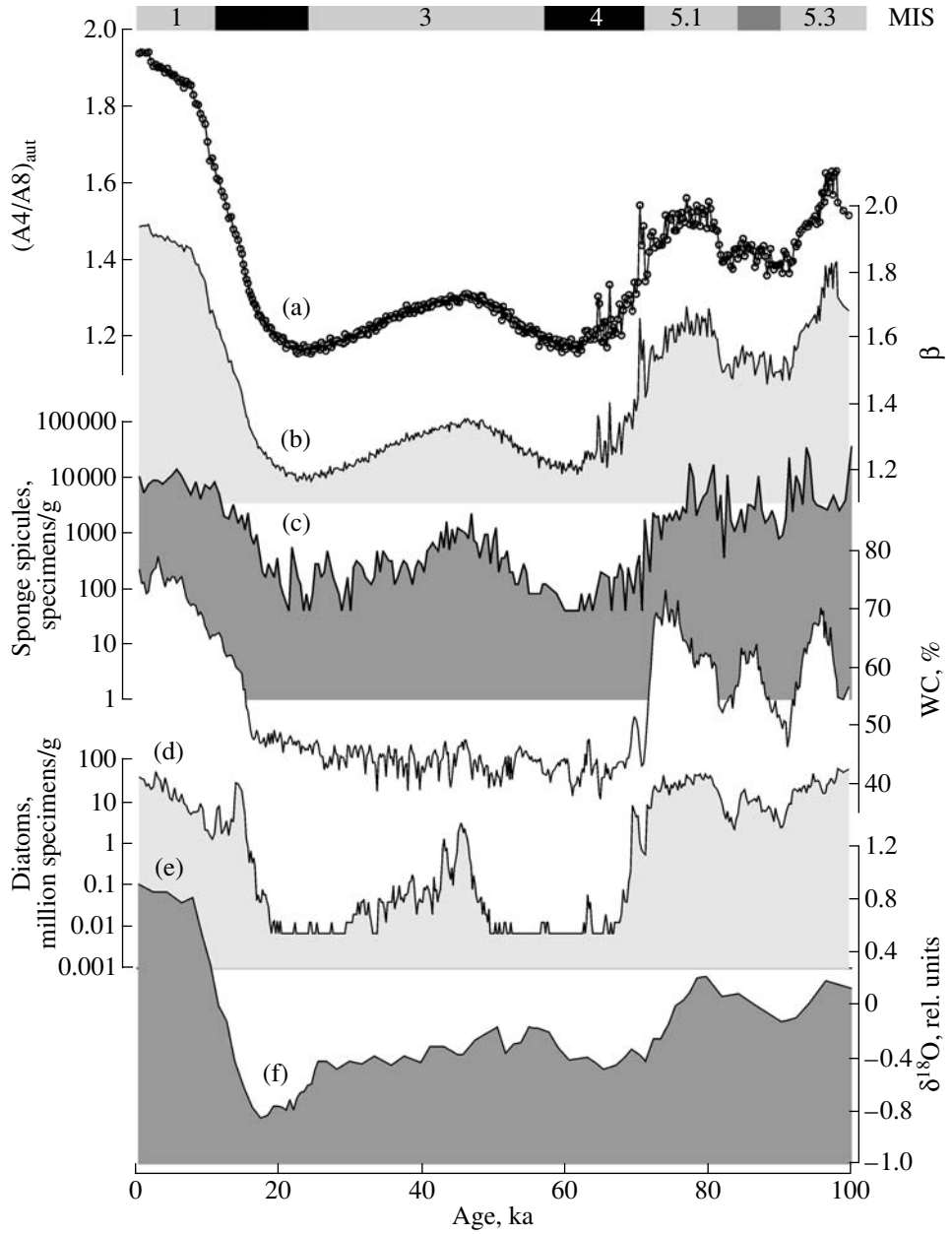

Fig. 2. Paleorecords of Core VER-99-1 st-GC from Lake Baikal on a U–Th geochronological scale [4, 5, 10]. (a) Isotope ratio of authigenic uranium in sediments $A4_{aut}/A8_{aut}$; (b) isotope ratio of uranium in lake water at the moment of sediment burial $\beta = (A4_{aut}/A8_{aut})_{t=0}$; (c) content of sponge spicules in sediments (logarithmic scale); (d) water content in sediments (WC), % [5, 10]; (e) content of diatom frustules in sediments [5, 10] (logarithmic scale); (f) $\delta^{18}O$ in benthic foraminifers as an indicator of the volume of global ice sheets. MIS is the marine isotopic stage [12].

ments, which is correlated with the biogenic silica content, is perfectly correlated with the uranium isotope ratio of paleowater (Figs. 2c–2e). This fact and good correlation of the obtained record for Lake Baikal with global volumes of ice sheets (Fig. 2f, [12]) suggest that the response of the uranium isotope ratio in water is caused by global climatic variations (Fig. 2) despite a small asynchronism of the regional response. During global warm interstades characterized by high productivity of the lake, deviation from uranium isotopic equilibrium in water was maximum. As in the present-day Lake Baikal, the β value during these periods was equal to 1.9–2.0 [5, 6, 10]. During global glaciations, the degree of disequilibrium of U isotopes decreased, and β is approximately 1.15–1.17. It is evident that variability of the β value should be taken into account in the models designed for the direct U–Th dating of the Baikal sediments.

It is reasonable to assume that uranium disequilibrium in lake water depends on processes in its drainage

basin. At present, the U isotope ratio is equal to 2.15–2.30 in water of the Selenga River (the main tributary to the lake) and ~1.3 in water of the northern tributaries [5, 6, 13]. The isotope ratio and U contents were not determined in other tributaries that supply about 22% of water to the lake [6]. Thus, the uranium isotope ratio measured in the lake water depends on the proportions of uranium flows that enter into the lake from different sources, such as the Selenga River, other tributaries, and the streams formed by thawing of glaciers. The river inflow into Lake Baikal abruptly decreased during periods of global glaciations and coolings [4, 5]. The inflow from semiarid Mongolia (Selenga River) should have been decreased most appreciably. Even during the present-day relatively humid period, up to 75% of atmospheric precipitation is evaporated within its drainage basin [14]. If we assume according to the basic concept elaborated by Chalov [15] that disequilibrium of uranium isotopes in river water does not depend on climate but is largely controlled by the mean composition of the drained rocks, it is reasonable to refer the established decrease in β during glacial periods to the abruptly diminished contribution of the Selenga River to the water budget of the paleolake up to the complete cessation of its inflow at the peaks of global glaciations (cf. [4]). The estimation of the paleolake water budget is beyond the scope of this communication. However, some qualitative implications are already evident from consideration of Fig. 2. As can be seen, the contribution of the Selenga River to the lake budget at the optimum of the Karginsky period (24–59 ka ago) was approximately two or three times less than the present-day inflow. During the interstadial substage MIS 5.3, this contribution was approximately the same as in the current period and further decreased in the next interstadial substage 5.1. During global glaciations MIS 4 and MIS 2, the contribution of the Selenga River was minimal, and the supply of water to southeastern Siberia and northern Mongolia progressively diminished.

The minimum β value (1.15–1.17) recorded for peaks of glaciations MIS 2 and MIS 4 (Fig. 2b) suggests that a source of water with a U/U ratio below ~1.17 existed at that time. At present, such sources are unknown in the drainage basin of Lake Baikal and all known sources are characterized by higher ratios. However, it may be inferred that the tributaries yet unstudied or the water supplied by thawing of glaciers might have been such sources, assuming a rather reasonable uranium concentration in these waters.

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