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The formation conditions of subglacial Lake Vostok's accreted ice based on its stable water isotope composition

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Abstract. In this paper, we present a new dataset on the stable water isotopic composition (δD and $\delta^{18}O$) in a sequence of subglacial Lake Vostok's accreted ice (3538–3769 m) measured along three parallel ice cores. The high precision of the new data has allowed us to characterize the formation conditions of different sections of the ice. The whole lake ice interval may be divided into 3 zones: 1) "zone 0", 3538.8–3549.8 m, is under the strong influence of the local water formed from melted meteoric ice likely entering from under the glacier on the lake's west coast; 2) "zone 1" (accreted ice 1), 3549.8–3607.4 m, is experiencing significant variability due to the slightly different effective fractionation coefficient in the course of "water inclusions" in the ice matrix during the freezing process; 3) "zone 2" (accreted ice 2), 3607.4–3768.8 m, is under the influence of glacial melt water from the northern part of the lake and the hydrothermal flux from the lake's bottom. We defined the exact boundary between the accreted ice 1 and ice 2, which corresponds to a sharp isotopic excursion at a depth of 3607.4 m. In this work, we present for the first time data on the "^{17}O-excess" parameter in the lake ice and water, which allowed us to make a direct calculation of the equilibrium fractionation coefficient for oxygen 17 during water freezing.

Keywords: Lake Vostok, accreted ice, hydrology, water isotopes

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Introduction

April 2023 marked the 30th anniversary of the publication of Jeff Ridley's work with co-authors "Identification of subglacial lakes using ERS-1 radar altimeter" [1]. The publication of this article in 1993 ended the long history of the discovery of subglacial Lake Vostok. After three decades of first remote geophysical [2] and then direct comprehensive studies of lake ice and water samples [3], it still remains one of the least studied objects on our planet. The reason for this is, firstly, the impossibility of direct penetration into the lake from the currently operating 5G borehole [4], and secondly, the need to develop environmentally and biologically clean methods of accessing the lake and sampling lake water, which in terms of technical complexity and financial costs will be comparable to space missions.

Due to the current impossibility of direct studies of the lake, at this stage, the efforts of specialists are aimed at extracting all possible information from already available samples of accreted (i.e. frozen from the lake) ice (Fig. 1), as well as from the few (and partially contaminated with drilling fluid) samples of lake water. One of the main methods in this area has been and remains the analysis of the isotopic composition of hydrogen and oxygen. One of the first works summarizing the data available at that time

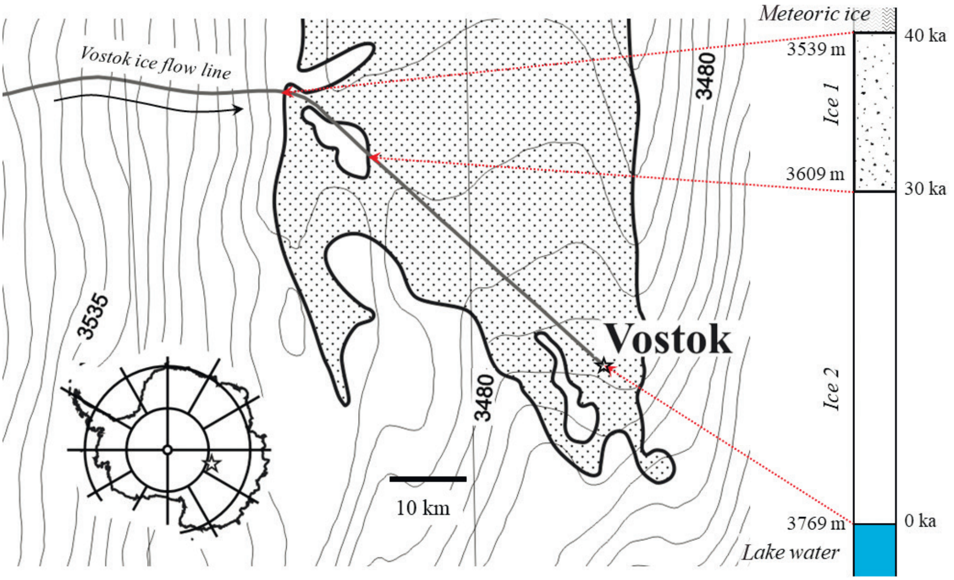

Fig. 1. Scheme of the formation of accreted ice in subglacial Lake Vostok.
The glacier crosses the southern part of the lake valley from northwest to southeast. While moving over the lake, a layer of ice freezes onto the base of the glacier, the entire thickness of which is divided into two intervals: 1) "lake ice 1" (3539–3609 m), formed in the strait between the western shore of the lake and the island (and, possibly, above the island) and containing visible mineral inclusions, as well as a relatively large amount of gas and chemical impurities; 2) "lake ice 2" (3609–3769 m), formed over the deep-water part of the lake and practically free of impurities. Adapted from [5] with small modifications.

Рис. 1. Схема формирования конжеляционного льда подледникового озера Восток.
Ледник пересекает южную часть озерной котловины с северо-запада на юго-восток. Во время движения над озером на подошву ледника намерзает слой льда, вся толща которого делится на два интервала: 1) «озерный лед 1» (3539–3609 м), сформированный в проливе между западным бортом озера и островом (и, возможно, над самим островом) и содержащий видимые минеральные включения, а также относительно большое количество газовых и химических примесей; 2) «озерный лед 2» (3609–3769 м), сформированный над глубоководной частью озера и практически не содержащий примесей.

on the isotopic composition of lake ice was the publication of Ekaykin and co-authors [5], in which a simple isotopic model of the lake was developed and it was shown that hydrothermal circulation plays an important role in the lake's hydrological regime. Further, in [3, 6], the isotopic composition of water was directly measured (which coincided with the results of calculations performed in [5]) and it was shown that ice formation generally occurs under equilibrium conditions, but at the same time the isotopic composition of ice experiences small fluctuations associated with the mechanism of ice formation and with variations in the isotopic composition of the water itself. The detailed reconstruction of these factors at that time was limited by the insufficient accuracy of the values of the isotopic composition profile of lake ice.

In this article, we present a new, most accurate to date stacked (based on 3 parallel cores) vertical profile of the isotopic composition of the accreted ice of subglacial Lake Vostok and analyze it from the point of view of the conditions of its formation. In addition to oxygen 18 and deuterium, we are also publishing data on the concentration of oxygen 17 in lake ice for the first time and discussing the prospects for using this parameter in future studies of the hydrological regime of the lake.

Methods

To construct a stacked profile of the isotopic composition of lake ice lying in the basal part of the glacier under the Vostok station in the depth range of 3538–3769 m, 10 cm samples were used from the cores of parallel hole branches 5G-1 (in the depth range of 3538–3611 m), 5G-2 (3601–3769 m), and 5G-3 (3538–3608 m and 3715–3769 m).

Isotope measurements were performed in the Climate and Environmental Research Laboratory of the AARI using Picarro L2120-i and L2140-i laser analyzers according to the methodology developed by us and previously published [7]. As a working standard, the VOS-4 standard was used, which was made from surface snow collected near Vostok station and calibrated relative to the IAEA standards VSMOW-2, SLAP and GISP. The isotopic values of VOS-4 are –439.7±0.3 ‰ for δD, –56.81±0.02 ‰ for $\delta^{18}O$ and –30.41±0.01 ‰ for $\delta^{17}O$. The working standard is measured every 5 samples. About 10 % of randomly selected samples are measured repeatedly in order to determine the reproducibility of measurements. For a single sample measurement, the random measurement error is 0.046 ‰ and 0.21 ‰ for, respectively, $\delta^{18}O$ and δD.

To construct a stacked series for all cores, the depths of cores 5G-2 and 5G-3 were reduced to a depth of 5G-1, and the values of the isotopic composition of ice for all three cores were reduced to the values of the isotopic profile of lake ice to a depth of 3611 m, obtained at the Laboratoire des Sciences du Climat et de l'Environnement (Saclay, France) based on 1 m samples and published in [8].

The standard error of the values of the stacked series of isotopic composition of lake ice was determined as the standard deviation of the values of the isotopic composition of ice at a given depth in individual cores, divided by the square root of the number of observations, and amounting to 0.038 ‰ and 0.17 ‰ for, respectively, $\delta^{18}O$ and δD.

Oxygen measurement 17 is performed using a different technique on the Picarro L2140-i device. For one measurement cycle, which lasts 3 days, only 5 samples are measured. Each sample is poured into 3 vials, and the resulting 15 vials are randomly placed on the tray. At the beginning, in the middle and at the end of the series, the VOS-4 standard is set. First, the first standard is measured 20 times to stabilize the device, and then each vial is measured 20 times. The first 5 measurements are ignored, and the last

15 measurements are averaged. Thus, for each sample we obtain 3 independent values of isotopic composition, each of which, in turn, is obtained by averaging 15 measurements. These three values are compared to make sure that the standard deviation of the ^{17}O-excess values (^{17}O-excess = $(\ln(\delta^{17}O/1000+1) - 0.528 \ln(\delta^{18}O/1000+1))\cdot 10^6$) does not exceed the limit of 5 per meg (5 units per million). If the sample meets this criterion, the average value of its isotopic composition is calculated; if not, it is sent for additional measurement.

Results

In Fig. 2*a* the profile of the isotopic composition ($\delta^{18}O$) of lake ice is shown. Unlike atmospheric ice, accreted ice is characterized by extremely low variability of isotopic values in depth: 1 standard deviation of oxygen 18 values in the upper part of the profile (in the so-called "lake ice 1" [3], up to a depth of 3608 m) is 0.2 ‰, and in the lower part of the profile it is 3 times less (0.06 ‰). Despite such low variability of the isotopic composition, its fluctuations in the upper part of the profile are significant. In the lower part of the profile ("lake ice 2"), the variability of isotopic values is only 1.6 times higher than the measurement error. Apparently, there are no significant short-period fluctuations in the isotopic composition.

Figure 2*b* shows the profile of the dxs parameter (which is defined as dxs = $\delta D - 8\delta^{18}O$ [9]). This parameter is widely used in interpreting the isotopic composition of atmospheric ice as an indicator of the intensity of kinetic isotopic processes during evaporation of water in a moisture source and during precipitation from ice clouds [10]. It is not convenient for studying isotopic fractionation during the freezing of water, since the regression coefficient of the "freezing line" (the line connecting the points of the isotopic composition of water and the formed ice) in typical Earth conditions is always less than 8.

Because of this, in [5] we proposed using the parameter dxs4 = $\delta D - 4.02\delta^{18}O$ (Fig. 2*c*). The coefficient 4.02 is the slope (regression coefficient) of the "freezing line" (i.e., the line connecting the points corresponding to water and ice formed by freezing this water in the diagram δD *vs* $\delta^{18}O$) for water having an isotopic composition that is the same as the water in the subglacial Lake Vostok. The regression coefficient of the freezing line k can be calculated using the following formula:

$$k = [(\delta D_w + 1000)/(\delta^{18}O_w + 1000)]\cdot[(\alpha_D - 1)/(\alpha_{18} - 1)], \quad (1)$$

where w stands for the isotopic composition of water, and α_D and α_{18} are the coefficients of isotopic fractionation during the freezing of water for deuterium and oxygen 18, respectively. The equilibrium values of α_D and α_{18} are 1.0208 and 1.003 [8], but their real (effective) values may be lower. However, no matter how the fractionation coefficients change, they change in parallel for deuterium and oxygen 18 — thus, the value of the right part in formula (1) – and therefore the value of the coefficient k — always remains unchanged. At a very high freezing rate, the fractionation coefficients are equal to 1 — in this case, the isotopic composition of ice is equal to the isotopic composition of water, and equation (1) does not make sense.

Thus, a notable feature of the dxs4 parameter is that it does not change during the freezing process of water (i.e. it is the same for water and for the ice formed from it) and, moreover, its value does not depend on effective fractionation coefficients, but only on the isotopic composition of the freezing water.

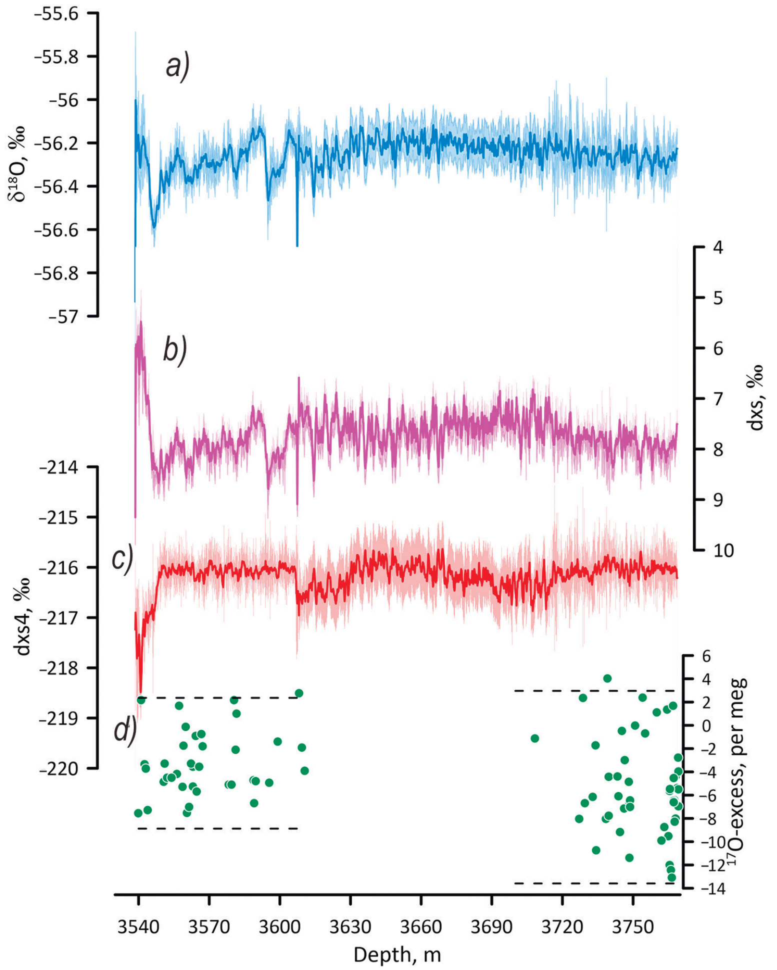

Fig. 2. Stacked isotopic profile of the subglacial Lake Vostok's accreted ice: *a)* — concentration of oxygen 18; *b)* — dxs parameter (dxs = $\delta D - 8\delta^{18}O$); *c)* — dxs4 parameter (dxs4 = $\delta D - 4.02\delta^{18}O$); *d)* — ^{17}O-excess parameter ($^{17}O\text{-excess} = (\ln(\delta^{17}O/1000 + 1) - 0.528\ln(\delta^{18}O/1000 + 1))\cdot 10^6$).

In Figs. 2*a–c*, the shading shows the uncertainty (±2σ). In Fig. 2*d* the dash lines show 96 % of the ^{17}O-excess values distribution (±2σ)

Рис. 2. Сводный изотопный профиль конжеляционного льда подледникового озера Восток: *a)* — содержание кислорода 18; *b)* — параметр dxs (dxs = $\delta D - 8\delta^{18}O$); *c)* — параметр dxs4 (dxs4 = $\delta D - 4{,}02\delta^{18}O$); *d)* — параметр ^{17}O-excess ($^{17}O\text{-excess} = (\ln(\delta^{17}O/1000 + 1) - 0{,}528\cdot\ln(\delta^{18}O/1000 + 1))\cdot 10^6$).

На рис. 2*a–c* заливкой показаны пределы погрешности (±2σ). На рис. 2*d* пунктиром показаны пределы значений ^{17}O-excess, в которые укладывается 96 % распределения (±2σ)

Accordingly, if the value of dxs4 changes in the lake ice, this indicates that the isotopic composition of the water from which this interval of lake ice was formed is changing.

Figure 3*b* shows the values of deuterium concentration (δD) as a function of $\delta^{18}O$, and Figure 4 shows a diagram of the dependence of dxs4 on $\delta^{18}O$ for lake ice.

Fig. 2*d* shows the values of the ^{17}O-excess parameter. 42 measurements were performed in Lake ice 1, the average value of this parameter was –4.2±0.6 per meg (a confidence interval equal to ± 2 errors of the average is given). 59 measurements were performed in Ice 2, the average value of ^{17}O-excess was –4.8±0.7 per meg. Thus, lake ice of both types does not differ in terms of relative concentration 17. It is obvious that the variability of this parameter in depth (if any) is significantly less than the measurement error. Therefore, it is not possible to establish a connection between this parameter and other characteristics of the lake ice.

We also measured the oxygen 17 content in the "icicle" frozen on the drill bit during the first opening of the lake (see Fig. 2 in [6]), the isotopic composition of which corresponds to the isotopic composition of the surface water layer in the southern part of Lake Vostok. The value of ^{17}O-excess in this sample is –15±2 per meg.

Discussion

Characteristics of the conditions of lake ice formation in various sections of the ice flow line passing through the borehole at Vostok station.

In order to characterize the conditions of lake ice formation at different depth intervals, we divided the isotope profile into homogeneous sections based on data on the ratio of oxygen 18 and deuterium isotopes (Fig. 3*b*) and on the variability of the dxs4 parameter (Fig. 2*c* and Fig. 4), see Table.

The obtained results show, first of all, that the traditional division of lake ice into 2 layers ("ice 1", with mineral inclusions, presumably formed over the strait near the western shore of the lake, and "ice 2", without mineral inclusions, presumably formed over the deep part of the lake (Fig. 1)) is too simplified, at least in terms of isotopic composition. At least we can talk about three layers, two of which, in turn, are also divided into sections that differ in isotopic composition.

The upper 11 m of lake ice (adhering to the accepted classification, we will call this layer "lake ice 0") differ very much from the underlying ice thickness by a large range of isotopic values and an unusual ratio between oxygen 18 and deuterium (red, orange and yellow sections in Fig. 3*a*, 3*b* and 4). We believe that in this zone there is the influence of local glacial meltwater (and probably hydrothermal waters) coming from under the glacier near the western side of the lake.

To illustrate this hypothesis, in Fig. 3*c* we have shown the isotopic composition of the main components of the hydrological system of Lake Vostok — the isotopic composition of the water freezing under the Vostok station (determined by the isotopic composition of the above-mentioned "icicle"), the isotopic composition of glacial melt water coming from the northern part of the lake (according to [5]), as well as the probable isotopic composition of meltwater, which could come from under a glacier near the western shore of the lake (corresponds to the average isotopic composition of atmospheric ice core 5G in the range 3500–3530 m).

Regarding the isotopic composition of the lake water, it is vital to distinguish between the isotopic composition of water freezing under a glacier in the area of Vostok station (this is shown in Fig. 3*c*) and the isotopic composition of "resident" lake water. The difference between them is due to the fact that the melted glacial water coming from the northern part of the lake does not completely mix with the resident (lying deeper) lake water [5]. Whereas the isotopic composition of the freezing water was measured directly from the isotopic composition of the water sampled after the unsealing of the lake [6], the isotopic composition of the resident water, on the contrary, is not known and can only be

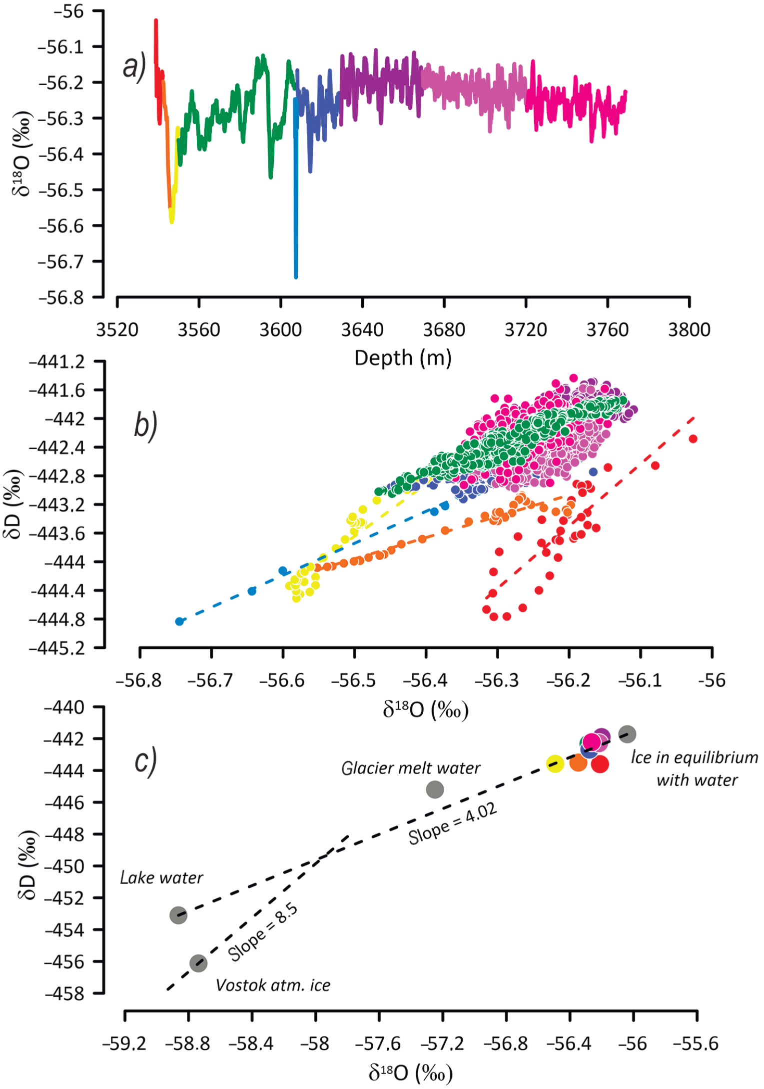

Fig. 3. Uniform segments of the lake ice’s isotopic profile and the relationship between different components of Lake Vostok.

a — uniform segments of the lake ice thickness defined on the base of the oxygen 18/deuterium relationship (Fig. 3*b*) and the dxs4 parameter (Figs. 2*c* and 4); *b* — the relationship between oxygen 18 and deuterium; *c* — the isotopic composition of the different components of Lake Vostok’s hydrological cycle: the coloured circles are the mean values of the different segments isotopic profile of lake ice; the grey circles are the isotopic composition of the lake water; the isotopic composition of ice in the equilibrium with this water (the slope of the line connecting these two points is 4.02); the isotopic composition of the melt glacier water entering the lake in its northern part according to [5]; the isotopic composition of the lower part of the meteoric ice in the 3500–3530 m interval of the 5G ice core; and the local Meteoric Water Line with a slope of 8.5.

The same colours in Figs. 3*a*, 3*b* and 3*c* depict the same segments of the isotopic profile

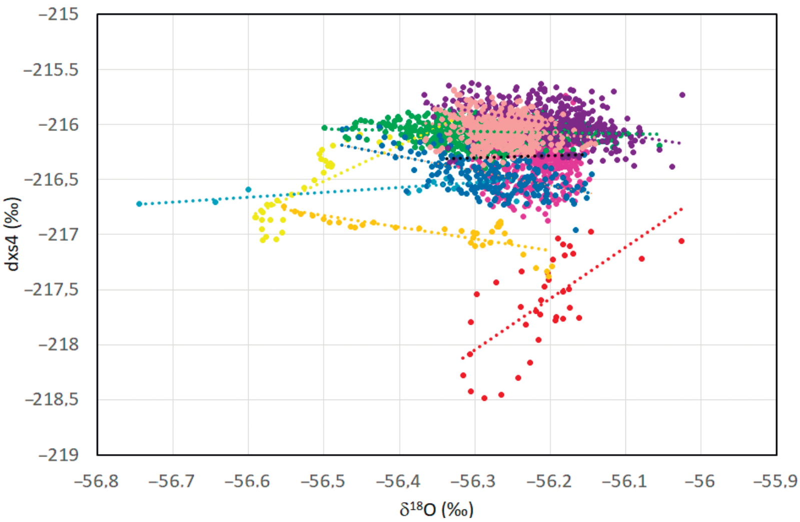

Fig. 4. The dxs4/δ^{18}O for the lake ice. The colours of the segments correspond to the colours in Fig. 3

Рис. 4. Диаграмма dxs4/δ^{18}O для озерного льда. Цвета интервалов соответствуют аналогичным цветам на рис. 3

estimated approximately based on existing ideas about the hydrological regime and the mass balance of Lake Vostok.

Figure 3*c* does not show the isotopic composition of the hydrothermal waters – its value is not known for certain, but, in any case, in this diagram the corresponding point is located to the right of the isotopic composition of the lake water [5].

The isotopic composition of the freezing lake water may change 1) due to a change in the ratio of resident lake water and glacial/hydrothermal melt water, and 2) due to a change in the isotopic composition of glacial/hydrothermal melt water. In the first case, the oxygen 18 / deuterium ratio in the freezing lake water will be close to 4 for meltwater coming from the northern part of the lake (see Fig. 3*c*). In the case of the arrival of local meltwater from under the western shore of the lake, the oxygen 18 / deuterium ratio can be almost any due to the proximity of its isotopic composition to the lake water. In the second case, the oxygen 18 / deuterium ratio in the freezing lake water will be close to 8. In the case of the influence of hydrothermal waters, this ratio should be significantly less than 4 [5].

Рис. 3. Однородные сегменты изотопного профиля озерного льда и соотношение между различными изотопными компонентами озера Восток.

a — изотопно однородные участки толщи озерного льда, выделенные на основе данных о соотношении кислорода 18 и дейтерия (рис. 3*b*) и параметра dxs4 (рис. 2*c* и 4); *b* — зависимость между концентрацией кислорода 18 и дейтерия; *c* — изотопный состав различных компонент гидрологического цикла озера Восток: цветные кружки — средние значения изотопного состава однородных участков показанных на рис. 3*a* и 3*b*; серые кружки — изотопный состав озерной воды, определенный по «сосульке», намерзшей на буровой снаряд после первого вскрытия озера; изотопный состав льда, который находится в равновесии с этой озерной водой (эта точка соединена с предыдущей линией с коэффициентом регрессии равным 4,02); изотопный состав талой ледниковой воды, поступающей в озеро в его северной части по [5]; изотопный состав нижней части атмосферного льда керна 5Г в интервале 3500–3530 м и локальная линия метеорных вод с коэффициентом регрессии 8,5.

Одинаковые цвета на рис. 3*a*, 3*b* и 3*c* показывают одни и те же участки изотопного профиля

Table

Characteristics of homogeneous sections of the vertical profile of the isotopic composition of the Lake Vostok accreted ice

Таблица

Характеристики однородных интервалов вертикального профиля изотопного состава конжеляционного льда озера Восток

Zone	Depth interval, m		δD, ‰	δ^{18}O, ‰	dxs4, ‰	Slope (regression coefficient)	
	Top	Bottom				δD/ δ^{18}O	dxs4/δ^{18}O
0–1	3538.8	3542.3	–443.6	–56.22	–217.65	**8.5±0.9**	**4.5±0.9**
0–2	3542.3	3545.8	–443.5	–56.35	–217.0	**3.0±0.2**	**–1.1±0.2**
0–3	3545.8	3549.8	–443.6	–56.49	–216.5	**7.3±0.3**	**3.3±0.3**
1	3549.8	3606.8	–442.3	–56.28	–216.1	**3.92±0.05**	–0.1±0.05
“Peak 3608”	3606.8	3608.1	–443.3	–56.39	–216.6	**4.2±0.3**	0.1±0.3
2–1	3608.1	3629.3	–442.7	–56.28	–216.4	**2.2±0.2**	**–1.8±0.2**
2–2	3629.3	3693.3	–442.0	–56.20	–216.1	**2.7±0.2**	**–1.3±0.2**
2–3	3693.3	3720.3	–442.4	–56.23	–216.3	**3.9±0.4**	–0.1±0.4
2–4	3720.3	3768.8	–442.2	–56.26	–216.0	**3.5±0.1**	**–0.6±0.1**

Note. Bold text highlights statistically significant regression coefficients.
Примечание. Жирным шрифтом выделены статистически значимые коэффициенты регрессии.

Taking this into account, let’s consider in more detail each of the sections of the isotope profile (the specified colour refers to the colour with which the sections are painted in Fig. 3; isotopic characteristics for each section are shown in the Table).

The interval 3535.8–3549.8 m (“lake ice 0”) differs from the underlying ice column, first of all, by a very strong change in the parameter dxs4 (Fig. 2*c*), which indicates a significant change in the isotopic composition of freezing water during the formation of this ice column. Another notable difference between this interval is that the values of its isotopic composition in the diagram δD *vs* δ^{18}O (Fig. 3*b*) have a large spread and lie away from the array of points of the isotopic composition of ice below 3549.8 m. At the same time, according to the slope between δD and δ^{18}O, this interval is clearly divided into 3 zones (Fig. 3*b*):

Zone 0–1 (red, 3538.8–3542.3 m):

A strong change (by more than 2 ‰) in the values of dxs4 (Fig. 4) indicates an intensive change in the isotopic composition of the freezing water. The ratio of oxygen 18 and deuterium is $\delta D = 8.5\ \delta^{18}O + 44.8$. This is very close to the local meteoric water line for the lower part of the atmospheric ice at Vostok (3500–3530 m), and in general we interpret the variability of the isotopic composition of the ice in this zone as a manifestation of the strong influence of local glacial melt water, which can dominate the freezing mixture.

The average isotopic values of ice in this zone are –56.22 ‰ for oxygen 18 and –443.6 ‰ for deuterium (Table).

Zone 0–2 (orange, 3542.3–3545.8 m):

Dxs4 is also noticeably changing here (by almost 1 ‰, Fig. 4), but at the same time $\delta D = 3.0\delta^{18}O - 276.5$. Such a low regression coefficient of the oxygen 18 / deuterium line may indicate the influence of hydrothermal waters, but, apparently, this section of ice is simply a transition between zones 0–1 and 0–3.

Zone 0–3 (yellow, 3545.8–3549.8 m):

This section is similar to ice 0–1, but with a noticeably lighter (by 0.27 ‰) isotopic composition of oxygen 18. The ratio between oxygen 18 and deuterium is $\delta D = 7.3\delta^{18}O - 31.7$.

It can be assumed that the influence of resident lake water is greater in the freezing mixture. On the other hand, the shift of section 0–1 relative to section 0–3 and the underlying ice thickness in oxygen 18 with a constant deuterium content (Fig. 3*b*) may also indicate that there is more hydrothermal water admixture in zone 0–1 compared to all the other ice sections.

Zone 1 (green, 3549.8–3606.8 m):

This section, in fact, is "lake ice 1". The isotopic composition varies quite widely, but dxs4 remains unchanged (Fig. 2*c* and 4). The freezing line is described by the equation $\delta D = 3.92\delta^{18}O - 221.8$. This section of ice is the only one whose isotopic composition's formation mechanism is known for certain. It is formed from lake water that is homogeneous in composition, and variations in isotopic composition are due to changes in the effective fractionation coefficient due to different volumes of trapped water inclusions ("pockets" [3]). Since aqueous inclusions freeze after being incorporated into the ice matrix, their isotopic composition does not change after freezing. Thus, the larger the proportion of these pockets, the lower the effective fractionation coefficient, and the closer the isotopic composition of ice is to the isotopic composition of the freezing water.

The available isotope data make it possible to calculate the volume of these water pockets fairly accurately. In particular, the maximum decrease in the values of the isotopic composition at a depth of 3595.1 m can be explained by the volume fraction of aqueous inclusions, which is 11 %.

The average isotopic values of ice in this zone are –56.28 ‰ for oxygen 18 and –442.3 ‰ for deuterium.

Further, the blue colour in Figures 3 and 4 shows the "isotopic peak of 3608 m", which will be discussed in more detail in the next section.

Ice below 3608.1 m ("lake ice 2") is characterized by the apparent absence of short-period fluctuations in isotopic composition (Fig. 2*a*), as well as by low values of the regression coefficient of the freezing line (< 4, Fig. 3*b* and Table). At the same time, according to the nature of the dxs4 variability (Fig. 2*c* and 4), this section can be divided into several zones:

Zone 2–1 (blue, 3608.1–3629.3 m):

This interval is characterized by a low dxs4 value compared to the above and below ice layers (Fig. 2*c*). The ratio between oxygen 18 and deuterium is $\delta D = 2.1\delta^{18}O - 322$. Such a low regression coefficient may indicate a change in the proportion of hydrothermal waters in the freezing mixture. At the same time, the isotopic composition of ice within a given area first decreases, then increases – this may be due to a change in the volume of water pockets, which are practically not found in the underlying ice layers [3].

Zone 2–2 (purple, 3629.3 – 3693.3 m):

Starting from this section, significant short-period variations in isotopic composition are completely absent. According to the ratios of δD *vs* $\delta^{18}O$ and dxs4 *vs* $\delta^{18}O$, this zone is similar to the previous one (Table), but at higher (respectively, by 0.08 and 0.3 ‰) values of $\delta^{18}O$ and dxs4 (Fig. 2*c*, 3*b* and 4), which indicates a slight change in the proportion of hydrothermal waters in the freezing mixtures.

Zone 2–3 (magenta, 3669.3 – 3720.3 m):

The dxs4 parameter practically does not change here, despite the fact that the isotopic composition of the ice decreases markedly with depth. The immutability of the dxs4 values is explained by the fact that the regression coefficient between oxygen 18 and deuterium is close to 4 here (3.9, Table). This could be explained by a change in the fractionation coefficient, but this is unlikely, since there are practically no water pockets in this zone. It follows from Figure 3*c* that such an isotopic composition may be due to a change (decrease with depth) in the proportion of glacial melt water from the northern part of the lake.

Zone 2–4 (pink, 3720.3–3768.8 m):

This section is characterized by a weak (but significant) negative correlation between dxs4 and δ^{18}O (a slight increase in dxs4 with a decrease in the values of δ^{18}O), and the ratio between oxygen 18 and deuterium is $\delta D = 3.5\delta^{18}O - 247.3$. The isotopic composition of this zone is similar to the previous one in deuterium, but slightly lighter (by 0.03 ‰) for oxygen 18. All this generally suggests that the proportion of meltwater from the northern part of the lake continues to decrease in this area, but the contribution of hydrothermal waters is also slightly lower than in the previous section.

In Fig. 5, we have shown the average values of the isotopic composition of different sections of ice, as well as the isotopic composition of ice, which is in isotopic equilibrium with the freezing lake water.

This figure confirms the strong difference between zone 0, on the one hand, and zones 1 and 2, on the other. The regression coefficient of the line connecting the average values of sections 1 and 2 is 5.44. That is, the difference between different sections of the profile is explained by both a change in the effective fractionation coefficient (the proportion

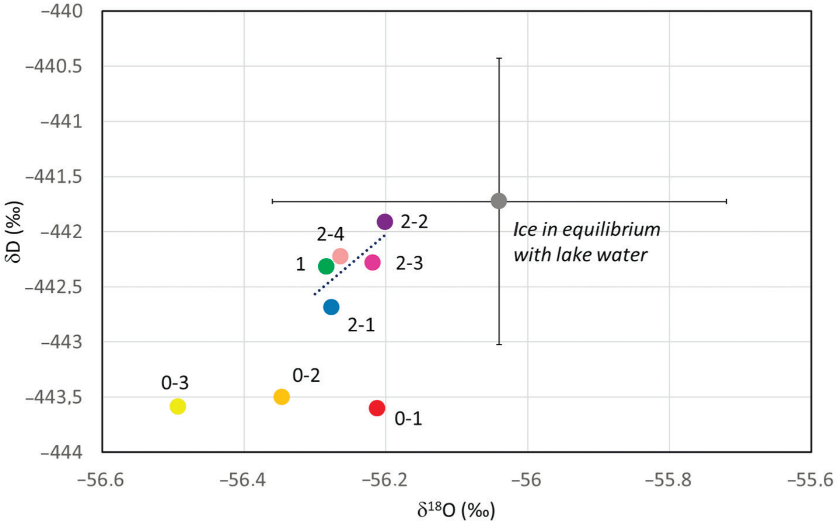

Fig. 5. The isotopic composition of the different lake ice segments, as well as the isotopic composition of the ice in equilibrium with the freezing lake water.

The error bars are ± 2 standard errors of mean. The colours of the points correspond to different ice segments in Figures 3 and 4. The dotted line denotes the linear regression for the isotopic composition of lake ices 1 and 2

Рис. 5. Изотопный состав различных участков озерного льда, а также изотопный состав льда, который находится в изотопном равновесии с замерзающей озерной водой. Пределы погрешности показывают ±2 ошибки среднего.

Цвет точек соответствует цвету разных участков льда на рис. 3 и 4. Пунктирной линией показана линейная регрессия для изотопного состава озерного льда 1 и 2 of water inclusions) and the influx of glacial melt water (and, possibly, a change in the isotopic composition of the latter).

Figure 5 also suggests that the lake ice may not be in complete equilibrium with the freezing lake water (the fractionation coefficient is 90–95 % of the equilibrium one). However, given the relatively large error in our estimates of the isotopic composition of the freezing lake water, and therefore ice in equilibrium with this water, we cannot judge this reliably.

If we assume that the lower part of the ice is in equilibrium with the lake water, then the isotopic composition of zone 2–4 can determine the isotopic composition of the water freezing directly under Vostok station: it is equal to –59.09 ‰ for oxygen 18 and –452.61 ‰ for deuterium.

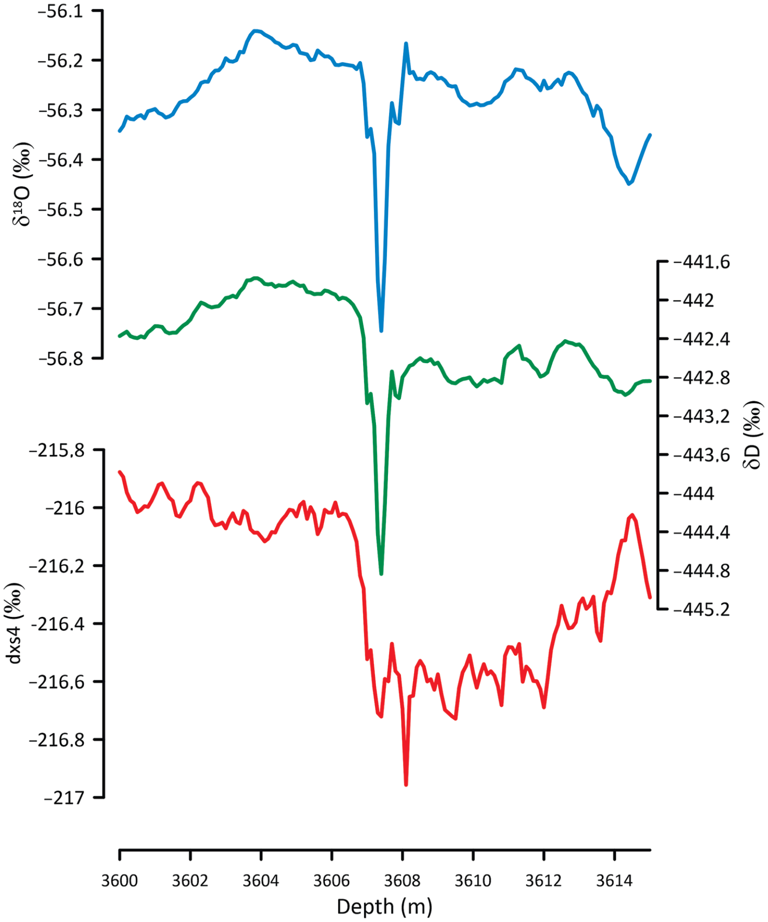

Fig. 6. The isotopic composition of lake ice in the interval 3600–3615 m.

From top to bottom: concentration of oxygen 18, concentration of deuterium and the dxs4 parameter

Рис. 6. Изотопный состав озерного льда в интервале 3600–3615 м.

Сверху вниз: содержание кислорода 18, содержание дейтерия и параметр dxs4

The nature of the unique peak of the isotopic composition of lake ice discovered at a depth of 3608 m

Figure 6 shows the isotopic composition of lake ice in the interval 3600–3615 m.

At a depth of 3607.4 m (or rather, in the range 3606.9–3608.0 m) we see a strong decrease in the values of the isotopic composition, which has been called the "isotopic peak 3608". We strongly believe that this peak is not an artefact associated with measurement problems, as it occurs in all three cores (5G-1, 5G-2 and 5G-3).

Within this peak, $\delta^{18}O$ changes by 0.75 ‰ and drops to the minimum values for the entire lake ice (Fig. 3*a*). The regression coefficient of the regression line for the ice interval containing the peak is 4.5 (Fig. 3*b* and Table). This clearly indicates a sharp change in the effective fractionation coefficient, which could be caused either by a large water inclusion or a change in the freezing rate of water (a lower fractionation coefficient corresponds to a higher freezing rate).

At the same time, a sharp change in the dxs4 parameter is also observed in this section of ice (Fig. 2 and Fig. 6), which indicates that the isotopic composition of the freezing water was different above and below the peak. Surprisingly, the isotopic composition was approximately the same in oxygen 18, but differed in deuterium (Fig. 6). This behaviour can only be explained by a change in the proportion of hydrothermal water in the freezing mixture (it is higher below the peak), since all other processes would lead to a parallel change in both isotopes.

The peak width is 110 cm, but taking into account molecular diffusion, it can be assumed that the initial peak width (before diffusion smoothing) was significantly smaller, the first tens of centimetres. This suggests that the event that caused the occurrence of this peak was extremely abrupt — very short in time and/or very small in space.

We consider the most likely explanation of the observed pattern to be the contact of lake ice with the water of the deep-water part of the lake after passing over the island (Fig. 1). In this case, it is "peak 3608" that can be considered to be the boundary between lake ice 1 and lake ice 2, and we can also assume a break in ice formation at the end of section 1.

It is interesting to note that the layer of large mineral inclusions previously found in the core of 5G-1 [11] lies at a depth of 3606.3–3606.5 m, i.e. almost at the very bottom of zone 1, approximately 1 m above the isotope peak. These inclusions could not be captured by ice except through direct contact between the glacier and the underlying rock. This generally does not contradict the idea that the isotope peak was formed after the passage of the glacier over the island (Fig. 1).

Oxygen 17 in the lake ice and the lake water

^{17}O-excess is a relatively new parameter that has only recently entered the practice of isotope studies [12, 13]. It has already been successfully used in paleoclimatic reconstructions based on ice core data [14, 15], but its application in hydrology is still limited by insufficient understanding of oxygen 17 fractionation during processes such as water freezing [16] and isotope exchange between water and rocks.

In this paper, for the first time, we present data on the value of ^{17}O-excess in the ice (4.8±0.7 per meg) and in the water (–15±2 per meg) of Lake Vostok. Since, as shown in the previous sections, this water and ice are likely to be in isotopic equilibrium, this gives us the opportunity for the first time to determine the equilibrium fractionation coefficient for oxygen 17 when water freezes.

Fractionation coefficient for oxygen 17:

$$\alpha_{17} = \alpha_{18}{}^{m}, \qquad (2)$$

where α_{18} is the fractionation coefficient for oxygen 18, and m is the exponent equal to 0.529 for equilibrium processes and 0.518 for kinetic processes [13]. Since the freezing of water in Lake Vostok occurs under equilibrium conditions, it can be expected that the value of m will be close to 0.529, and in this case the ^{17}O-excess of ice would be equal to –12.5 per meg. In order to get a value of ^{17}O-excess in the lake ice equal to –5 per meg, the value of m must be equal to 0.5315.

The same conclusion was drawn earlier when measuring the isotopic composition of water frozen in the 5G-1 borehole after the first unsealing of the lake in 2012 (the data have not been published).

The value of m obtained by us significantly exceeds 0.529, but it nevertheless fits into the range of 0.501–0.553 obtained in other experimental studies [16].

Conclusion

As a result of the research that was conducted, we were able to characterize in detail the ratio of various factors that played a role in the formation of different sections of the accreted ice of the subglacial Lake Vostok. It is shown that the division of ice into two zones — "ice 1", with mineral inclusions, and "ice 2", without mineral inclusions — is too simplified. At least 3 zones should be distinguished, two of which, in turn, are divided into shorter homogeneous sections. The isotopic composition of these sections is determined by a different ratio of four different factors: 1) a change in the effective fractionation coefficient due to the capture of water pockets; 2) the contribution of local melted atmospheric waters from the western shore of the lake; 3) the contribution of melted atmospheric waters from the northern part of the lake; 4) the contribution of hydrothermal waters.

For the first time, we were able to measure the value of the ^{17}O-excess parameter in lake ice and in lake water and, thus, experimentally determine the equilibrium fractionation coefficient for oxygen 17 during the freezing of the lake water.

In the future, we plan a more comprehensive analysis of the lake ice, taking into account all available data on isotopic, gas, mineral and chemical compositions. It is also necessary to continue theoretical and experimental studies on the geochemistry of oxygen 17 during processes such as freezing/melting and isotope exchange with rocks, which will clarify the contribution of various sources of Lake Vostok water to its mass balance.

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Условия формирования конжеляционного льда подледникового озера Восток по данным о его изотопном составе

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Аннотация. Представлен новый набор данных по составу стабильных изотопов воды (δD и $\delta^{18}O$) в толще конжеляционного льда подледникового озера Восток (3538–3769 м), измеренных по трем параллельным ледяным кернам. Высокая точность новых данных позволила охарактеризовать условия формирования различных участков этого льда. Весь интервал озерного льда можно разделить на три зоны: 1) «зона 0», 3538,8–3549,8 м, находится под сильным влиянием местных вод, образованных растаявшим атмосферным льдом, вероятно, поступающим из-под ледника на западном берегу озера; 2) «зона 1» (озерный лед 1), 3549,8–3607,4 м, испытывает значительные колебания изотопного состава вследствие различий эффективного коэффициента фракционирования при замерзании водных включений в ледяной матрице; 3) «зона 2» (озерный лед 2), 3607,4–3768,8 м, находится под влиянием талых ледниковых вод, поступающих из северной части озера, и гидротермального потока со дна озера. Впервые определена точная граница между озерным льдом 1 и льдом 2, которая соответствует резкому изотопному выбросу на глубине 3607,4 м. Приводятся данные о параметре ^{17}O-excess в озерном льду и воде, что позволило провести прямой расчет равновесного коэффициента фракционирования кислорода 17 при замерзании воды.

Ключевые слова: изотопный состав, гидрология, конжеляционный лед, озеро Восток

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