

GAS HYDRATES FORMATION

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FORMATION OF CLATHRATE HYDRATES  
OF HYDROCHLOROFLUOROCARBON 141B  
IN THE DEEP BOREHOLE AT VOSTOK STATION (ANTARCTICA)  
IN THE COURSE OF THE UNSEALING OF SUBGLACIAL LAKE VOSTOK

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We have presented the results of a study of core samples which were recovered from a deep borehole after the second unsealing of subglacial Lake Vostok in 2015 (borehole 5G-3, in which a mixture of kerosene and HCFC-141b densifier was used as the drilling fluid). The intensive mixing of the subglacial water and the drilling fluid resulted in the formation of a solid plug that filled the volume of the borehole and blocked the access to the lake. We have demonstrated that this solid plug consists of kerosene, ice and clathrate hydrate of HCFC-141b. The obtained data suggest that the drilling fluid presently used at Vostok should be replaced, at least in the bottom section of the hole, by another fluid which does not react with subglacial water.

*Lake Vostok, drilling, gas hydrate, Freon HCFC-141b*

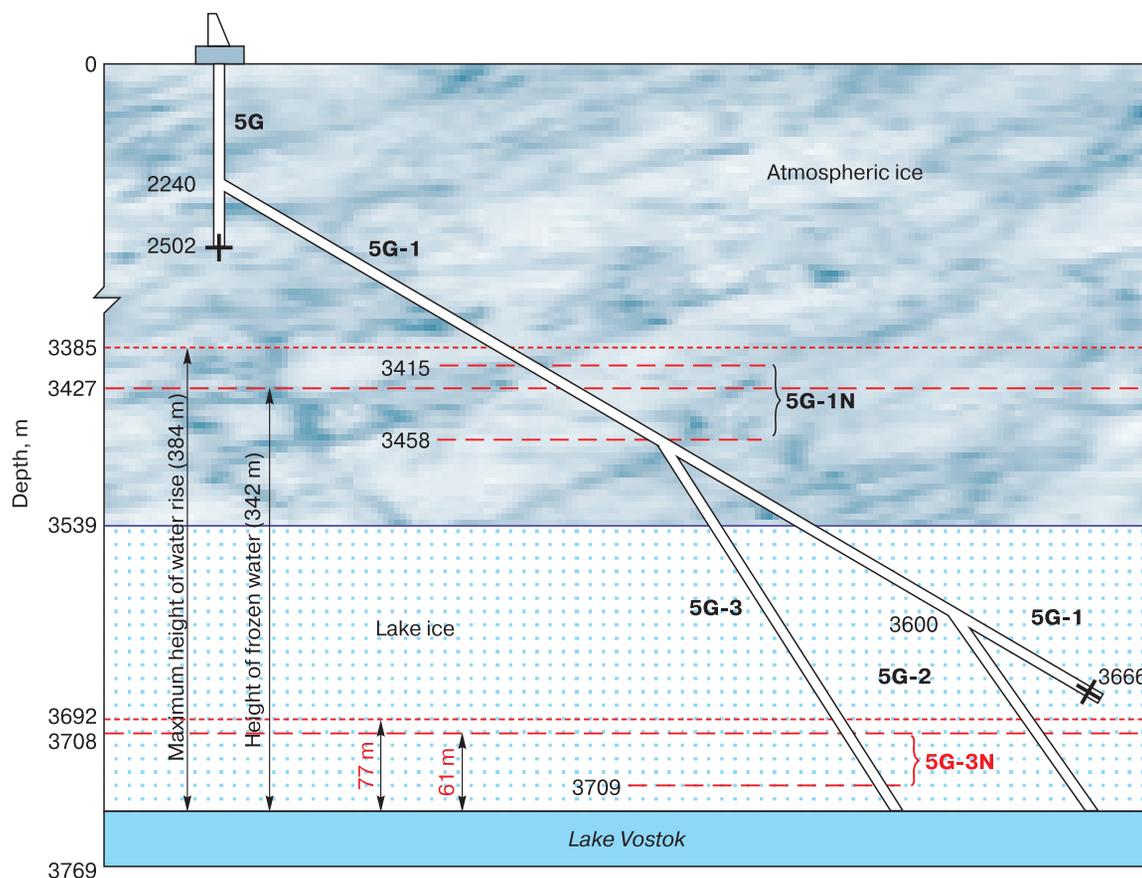
INTRODUCTION

The study of the cryosphere and of the ice cover of Antarctica has invariably attracted the attention of the scientific community (see, for example, [Abramov *et al.*, 2011]). The many years' project of deep drilling of the Antarctic glacier at the Russian Vostok station, which made a fundamental contribution to the study of the Paleolithic on the Earth [Petit *et al.*, 1999], has been recently associated with conducting a comprehensive study of Lake Vostok, the largest subglacial lake on the Earth discovered in this region of Antarctica at the end of the 20<sup>th</sup> century [Kapitsa *et al.*, 1996]. It is planned to penetrate into the lake in order to take samples of water and of bottom sediments using the borehole 5G-3, which reached the lake surface in January 2015 (Fig. 1). Development of the technology of direct studies of the subglacial lake is aggravated by a number of factors, the major ones of which are the small diameter of the access borehole (135–140 mm in its lower end) and the detrimental, from the environmental viewpoint, composition of the borehole fluid filling the borehole to prevent its compression due to ice deformation. At Vostok Station, a mixture of aviation kerosene TC-1 (the freezing point  $-60$  °C, density  $810$  kg/m<sup>3</sup> at  $0$  °C) and of

HCFC-141b densifier (CCl<sub>2</sub>F–CH<sub>3</sub>, the freezing point  $-103$  °C, the boiling point  $32$  °C, density  $1283$  kg/m<sup>3</sup> at  $0$  °C) in the proportion of approximately 5:1 is used [Tchistiakov *et al.*, 1994].

To carry out the first unsealing of Lake Vostok, the specialists from the St. Petersburg Mining Institute (now the St. Petersburg Mining University) and from the Arctic and Antarctic Research Institute (AARI) proposed a simple technique which minimized the risk of polluting the subglacial lake. It presupposed channeling the lake water into the borehole by creating a negative pressure difference between the drilling fluid and the water on the lower surface of the glacier at the moment of the ice break in the lake. After freezing of the water filling the borehole, it was planned to conduct repeated drilling for core sampling to be used in further studies.

This technology, with insignificant deviations from the original version [Verkulich *et al.*, 2002] was applied twice at Vostok Station in 2012 and in 2015 [Vasilyev *et al.*, 2012]. However, it was found out during the drilling works aimed at the ice break and during repeated drilling, that in the zone of mixing of the drilling fluid and of the lake water, a solid plug of a



**Fig. 1. A layout of the shafts of the deep borehole 5G at Vostok Station (the status quo at 08.02.2015).**

The borehole depth is indicated on an arbitrary scale, the borehole inclination is exaggerated: in reality, the deviation angle from the vertical line does not exceed  $6^\circ$ . The explanations are in the text.

white color was formed, which partly or fully filled the borehole, preventing tripping of the sampling devices into the lake water. Previously, the substance with similar signs was discovered in the bore mud lifted from the borehole at Kohnen Station (Queen Maud Land, Eastern Antarctica), after the borehole opened the thin layer of the subglacial water. The study of the sample of this bore mud by the methods of synchrotron diffractometry and of Raman's spectroscopy showed that it was composed of particles of ice and of clathrate hydrate of HCFC-141b [Murshed *et al.*, 2007]. It is to be noted that in the borehole that was drilled at Kohnen Station in order to obtain an ice core for paleoclimatic research [EPICA..., 2006], the same drilling fluid was used as that applied at Vostok Station.

In this paper, the results of studying the white material lifted from the deep borehole drilled at Vostok Station are discussed. The data obtained are of significant interest in the context of developing the technology of direct investigation of the subglacial Lake Vostok.

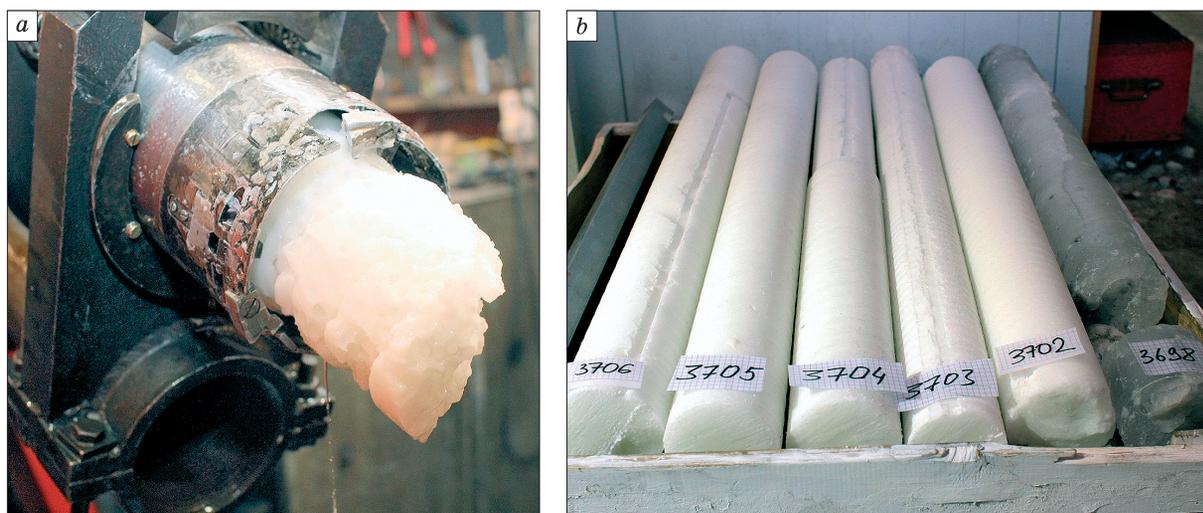
#### THE DRILLING WORKS AND THE PRELIMINARY FIELD STUDIES

The first unsealing of Lake Vostok was performed on February 5, 2012. Borehole 5G-2, which is one of the offshoots of the deep borehole 5G, reached the surface of the subglacial lake at the depth of 3769.30 m (Fig. 1). The figure shows the level of the maximum rise of water and the height of the column of frozen water in the boreholes 5G-2 and 5G-1 (black) and 5G-3 (red) after the first and second unsealing procedures of Lake Vostok. The sections of boreholes 5G-1 (3415–3458 m) and 5G-3 (3697–3709 m), from which cores of frozen lake water and of hydrate material were obtained by repeated drilling, were indicated as 5G-1H and 5G-3H, respectively. The lake water entered the borehole under pressure of not less than 0.3 MPa, which completely ruled out the possibility of the drilling fluid penetrating into the subglacial lake. At the time of the first unsealing, the level of the fluid in borehole 5G was at the depth of 30–40 m from the glacier surface. The rise of the fluid column in the drive pipe as far as the hole mouth

was unable to ensure complete compensation of the pressure of the lake water at the glacier base. In this situation, the pressures were fully levelled by replacing the less solid drilling fluid with more solid lake water, resulting in the water in the hole rising higher than planned and filling first the entire borehole 5G-2 as far as its coupling with borehole 5G-1, and then the lower section of borehole 5G-1 (Fig. 1). A significant amount of the drilling fluid (up to 2.5 m<sup>3</sup>) was ousted from the borehole and flew out from its mouth [Vasilyev et al., 2012].

It was discovered during repeated drilling of borehole 5G-1 a year after the unsealing of the subglacial lake that water originally rose to the height of 384 m from the lake surface, i.e., it was at the depth of 3385 m from the glacier surface. Then its level dropped to 3427 m, under which the borehole turned out to be completely filled with frozen lake water (Fig. 1). Above the surface of the frozen water, in the range of the depths of 3415–3427 m, the borehole was partly (30–40 %) filled with solid foam-like substance of the bright white color, differing from ice, which rose to the surface as core fragments with uneven porous surface (Fig. 2, a). In accordance with the similarity of the look of this substance to that of the white sludge which rose from the borehole at Kohnen Station [Murshed et al., 2007], an assumption was made that it also contained a hydrate of Freon HCFC-141b, so, the unusually looking core extracted from the borehole at Vostok Station was conditionally named “hydrate” [Lipenkov et al., 2013]. Later the increased concentration of Freon in the white substance was corroborated by the results of the chemical analysis of this material [Alekhina et al., 2014].

The second time the lake surface was reached was on January 25, 2015 by the borehole 5G-3 at the depth of 3769.15 m. That time, the researchers were able to exercise full control over the motion of the fluids in the borehole shaft. The lake water rose to the height of 61 m above the lake surface, which was close to the estimated value (Fig. 1), whereas the rise of the drilling fluid was stopped at the distance of 45 m from the borehole collar. As a result of repeated drilling that started 5 days after the second unsealing of the lake, it was found that a 10-meter long supposedly hydrate plug was formed above the freezing water in the borehole, which completely filled the borehole in the depth range of 3697.57–3708.12 m. This time, the core lifted from the borehole was indiscrete solid white material without visible pores but fully permeated with kerosene (Fig. 2, b). Immediately above the plug, a layer of congelation ice 92 cm thick was discovered, in the central part of which unfrozen water remained near the borehole axis. As the auger containing the core was lifted to the colder section of the borehole, the water froze, which resulted in formation of a crevice and in partial destruction of the core (the right side of the core was destroyed, as seen in Fig. 2, b). The volume of the amount of the congelation ice in the borehole was about 15 L, which approximately corresponds to the amount of water which could flow from the sections of the auger system after its outflow from the column of the lake water which rose in the borehole. The fact that the water that flew out from the auger system stayed on the plug surface suggests that the plug got formed immediately after the water rise stopped and water stopped getting mixed with the drilling fluid.



**Fig. 2. Hydrate cores extracted from the deep holes of Lake Vostok.**

*a* – a core from borehole 5G-1N, lifted from the depth of 3419 m after the first unsealing of Lake Vostok; *b* – cores from borehole 5G-3N (the range of depths 3697.57–3708.12 m), lifted after the first unsealing of Lake Vostok; the last right trough contains a core of secondary congelation ice with a longitudinal crevice extracted from the depth of 3696.65–3697.57 m (immediately above the hydrate plug).

Preliminary studies of the core of the plug formed in borehole 5G-3 were conducted in the glaciology laboratory of Vostok Station. The density of the white substance was measured by weighing and evaluating the volume of the core pieces which had an almost ideal cylindrical shape (Fig. 2, *b*). The mean density of the core was  $(927 \pm 5) \text{ kg/m}^3$ . Thus, the material investigated proved to be heavier than pure ice and the drilling fluid but lighter than water; so, after being formed on the boundary between water and the drilling fluid, it stays there, without polluting the lake water and without ascending up the borehole.

The mass concentrations of different components that formed the white material were measured in a 20-cm long piece of core from the depth of 3700.8–3701.0 m. The sample volume was  $1496 \text{ cm}^3$ , its mass was 1391 g, and the aggregate density was  $930 \text{ kg/m}^3$  (all the values of the component density were obtained for the temperature  $-15^\circ\text{C}$ ). The mass of the kerosene saturating the aggregate was determined after melting the sample and partial breakdown of the melt components (kerosene–water–Freon). The concentrations of kerosene and of HCFC-141b in their mixture were determined by the data on the mixture density at a given temperature [Tchistiaikov *et al.*, 1994]. The kerosene mass was 540 g, which corresponded to its mass fraction in the aggregate, equal to approximately to 39%. Thus, the mass of the solid phase of the aggregate was 851 g, while its mean density was  $1015 \text{ kg/m}^3$ . Based on the assumption that the density of the solid phase of the white material exceeded that of pure ice ( $919 \text{ kg/m}^3$  [Bader, 1964]) due to the presence of the clathrate hydrate of HCFC-141b with the density of  $1061 \text{ kg/m}^3$  [Mursheed *et al.*, 2007], mass fractions of ice and of Freon hydrate were calculated, which amounted to 18% and 43%, respectively. Using more accurate data on the density of HCFC-141b hydrate obtained during this study ( $1078 \text{ kg/m}^3$  at  $-15^\circ\text{C}$ , see below), these fractions are 22 and 39%, respectively.

An experiment was conducted in the field laboratory to freeze the mixture of kerosene, clathrate hydrate, and water. It turned out that, when intensely mixed in a test-tube, water and kerosene form an emulsion, which breaks down very fast, so that the mixture does not have time to get frozen even at the outdoor temperature of  $-30\text{...}-25^\circ\text{C}$ . As clathrate hydrate was added, the emulsion would become more stable: the breakdown date slowed down sharply, and the mixture got crystallized, forming the material resembling the white cores lifted from the borehole.

To conduct more detailed studies of the unusual formations discovered in the borehole at Vostok Station, a piece of core 40 cm long was taken from the depth of 3703 m. The sample was first delivered to the Arctic and Antarctic Research Institute Arctic and Antarctic Research Institute (St. Petersburg), then it

was transported to the Limnological Institute (Irkutsk) and then to the Nikolaev Institute of Inorganic Chemistry (Novosibirsk). During the sample's transportation and storage, the temperature was maintained in the range between  $-20$  and  $-10^\circ\text{C}$ .

## THE METHODOLOGY OF THE LABORATORY STUDIES

In the study, five core fragments were used: those were parallelepipeds with the sides 10, 3 and 3 cm), packed in plastic film and externally in aluminum foil. Each of the core fragments was broken into pieces about 1 cm long, which were kept in liquid nitrogen. To prepare samples to be later used in X-ray diffraction studies from a set of pieces obtained from one core fragment, three were randomly selected. Then they were ground in a mortar cooled to the temperature of liquid nitrogen, and part of the powder obtained was loaded into a previously cooled sample holder. The procedure was repeated 8 times; with two samples prepared from each of the three core fragments, and one sample prepared from each of the two core fragments. The methodology of preparing samples was repeatedly checked on natural and artificial samples of methane hydrate. The powder diffraction patterns of the samples were investigated with a Bruker D8 Advance diffractometer ( $\text{CuK}\alpha$ ,  $\theta$ - $2\theta$  scanning mode, radiation  $\lambda = 1.5418 \text{ \AA}$ ), equipped with an Anton Paar installation for working at temperatures differing from room temperatures. The powder patterns were obtained at the temperature of  $-100^\circ\text{C}$ . In one case, finely ground crystalline silicon was added to the sample as an internal standard. The powder patterns of this sample were obtained at the temperatures  $-100$ ,  $-70$ ,  $-40$  and  $-10^\circ\text{C}$ .

The Raman spectra (RS) were recorded with the Triplemate SPEX spectrometer, equipped with a multi-channel detector LN-1340PB, Princeton Instruments, in the reverse scattering geometry. The spectral resolution was  $2 \text{ cm}^{-1}$ . To excite the spectrum, a line of 514 nm of a 50-milliwatt argon-ion laser was used. The procedure of registering the RS-spectrum was as follows: the sample was embedded into a cell covered with a thin window, which was washed with liquid nitrogen and had an opening for a light beam. To prevent icing of the window, dry gas was blown onto it. The spectrum was recorded at the liquid nitrogen temperature and at atmospheric pressure.

To determine the percentage of kerosene in the samples, one piece of the sample was placed into a sealed box with the known mass. The test-tube containing the sample was weighed and left to stay for 24 hours at room temperature. Excessive pressure was regularly bled down. After complete breakdown, the test-tube was weighed again, and the organic (upper) phase was carefully removed from

there, after which the test-tube with the remaining aqueous phase was weighed again. The content of kerosene in the sample was calculated as the difference between two last weighed values.

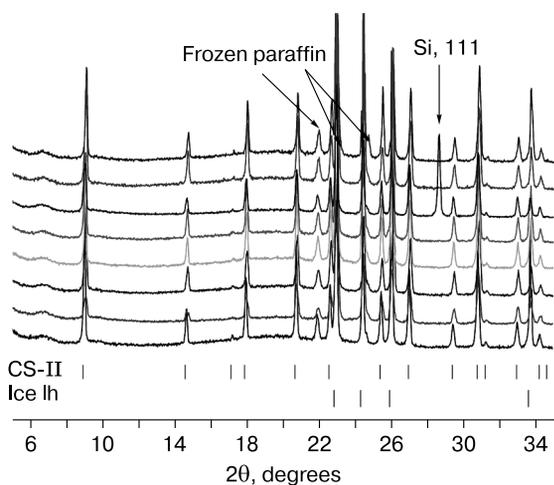
To determine the content of Freon in the sample, the volumetric method was used. A turned-over measuring cylinder filled with saline solution was put into a chiller with saline solution. The entire assembly was put into a dessicator at 40 °C and was kept there until the temperature got stabilized, with the temperature sensor of the dessicator immersed into the saline solution. A piece of the sample extracted from the liquid nitrogen was kept in air for 5 seconds to let liquid nitrogen evaporate, after which it was placed onto the bottom of a stainless steel box with the known mass, the box with the sample was weighed again in a tightly closed insulating foam container. To avoid breakdown of the sample when moving it in the saline solution, the weighed sample was isolated from the environment by the frozen ice 'cap'. Then the box with the sample covered with the ice cap was quickly placed under the overturned measuring cylinder and was kept at 40 °C for 30 minutes to ensure complete breakdown of the sample and temperature stabilization. The volume of the gas yielded during gas hydrate decomposition was recorded by the level of gas in the measuring cylinder, and the measured volume of gas was reduced to normal conditions.

Quantitative X-ray diffraction phase analysis was performed by the method of admixing the analyzed phase [Rusakov, 1977]. First the frozen original hydrate was weighed in the insulating foam container (1.4409 g), after which ice was added to it, and the mixture obtained was weighed again (1.6959 g of ice was added). The samples of the original hydrate and

of the mixture of hydrate and ice were carefully ground, after which their powder diffractograms were recorded. The hydrate share was calculated by the ratio of the total intensities of 11 strong reflexes of the hydrate and 4 ice reflexes, which were in the  $2\theta$  range from 7 to 35°.

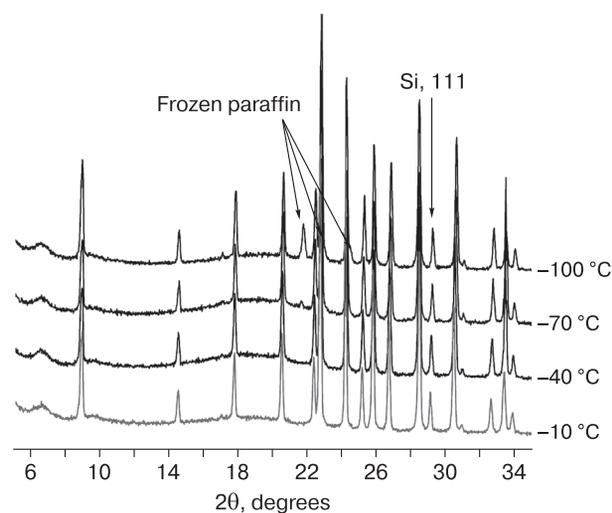
## RESULTS AND DISCUSSION

The X-ray powder diffraction of different sample fragments provided eight powder diffraction patterns, which proved to be nearly identical (Fig. 3). The majority of the reflexes on the powder diffraction patterns may be indexed in supposition of the presence of two phases in the samples – the gas hydrate of a cubic structure II (hereinafter to be referred to as CS-II) and ice Ih (common ice). Shown in Fig. 3 are the positions of reflexes expected for the hydrate CS-II and ice [Rottger *et al.*, 1994; Murshed *et al.*, 2007]. It is to be noted that it is the structural type CS-II that should be expected to be for clathrate hydrate of HCFC-141b (1,1-dichloro-1-fluoroethane), the hydrate composition corresponding to HCFC-141b·17H<sub>2</sub>O [Brouwer *et al.*, 1997; Ohmura *et al.*, 1999]. Crystalline silicon was added to one of the samples, and its reflex (111) is indicated in Fig. 3. For this sample, dependence of the parameter of the unit cell on temperature was investigated (see below). Finally, all the powder diffraction patterns demonstrate one clear reflex at  $2\theta = 21.9^\circ$  and shoulders of large reflexes at  $2\theta = 23.2, 24.7^\circ$ , which were interpreted as referring to solidified kerosene. According to the data provided by [Heyding *et al.*, 1990], in the temperature range of 21–24° for  $2\theta$  there are strong reflexes of solid mixtures of paraffin, the emergence of which could be expected in kerosene freezing. It is shown in



**Fig. 3. Powder diffraction patterns of the samples obtained at the temperature of –100 °C.**

The reflexes of hydrate CS-II and ice are shown by dashed lines; the reflexes not referring to these substances are marked.

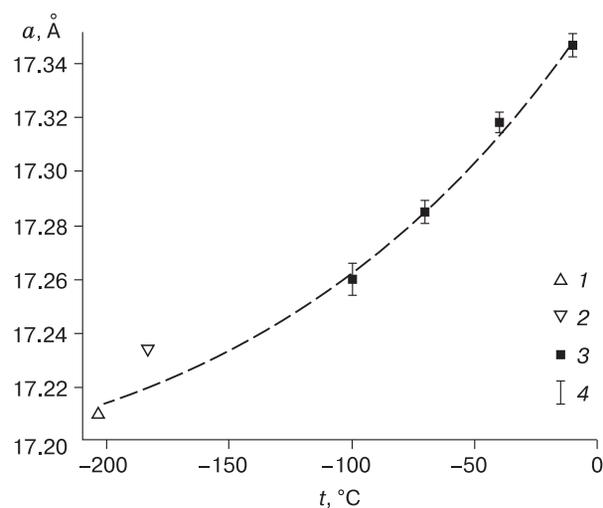


**Fig. 4. Powder diffraction patterns of one of the samples obtained at different temperatures.**

The reflexes not referring to hydrate CS-II and ice Ih are marked.

the studies described below that these reflexes disappear at the temperatures higher than  $-70$  °C (Fig. 4). This corroborates assignment of the reflexes done by the authors. It follows from the data obtained that the remaining components of frozen kerosene form an amorphous solid phase.

For one of the samples, powder diffraction patterns were obtained at four temperature values (Fig. 4; at temperatures higher than  $0$  °C, the sample intensely decomposed). The only change that occurred with the rise of temperature was the disappearance of reflexes referring to frozen kerosene, i.e., the paraffins which precipitated from the kerosene got melted. Due to the presence of the internal standard (crystalline silicon), corrections could be made in these diffraction patterns, related to the imperfect geometry of the sample and to the error of adjusting the goniometer. To specify the parameters of the unit cell, reflexes were used in the range of  $20$ – $35^\circ$  at  $2\theta$  with intensities not less than  $5\%$  of the maximum values in this range. Specified by the positions of eight reflexes, the parameters of the unit cell of hydrate CS-II proved to be equal to  $17.347(2)$ ,  $17.318(2)$ ,  $17.285(2)$  and  $17.260(3)$  Å at  $-10$ ,  $-40$ ,  $-70$  and  $-100$  °C. (Shown hereinafter in brackets are the mean-square deviations of the respective values in the units of the last character). The data obtained on the parameters of the hydrate's unit cell (Fig. 5) are in satisfactory agreement with the literature data regarding the parameter of the unit cell of the hydrate HCFC-141b [Brouwer *et al.*, 1997; Murshed *et al.*, 2007]. Calculated by the positions of four reflexes, the parameters of the unit cell for ice corresponded with the data of [Rottger *et al.*, 1994] within  $\pm 0.005$  Å, ensuring independent control of correctness of deter-



**Fig. 5. Dependence of the parameter of the unit cell  $a$  of hydrate HCFC-141b on temperature  $t$  versus the literature data.**

1 – the data provided by [Murshed *et al.*, 2007]; 2 – [Brouwer *et al.*, 1997]; 3 – this study; 4 – the measurement error.

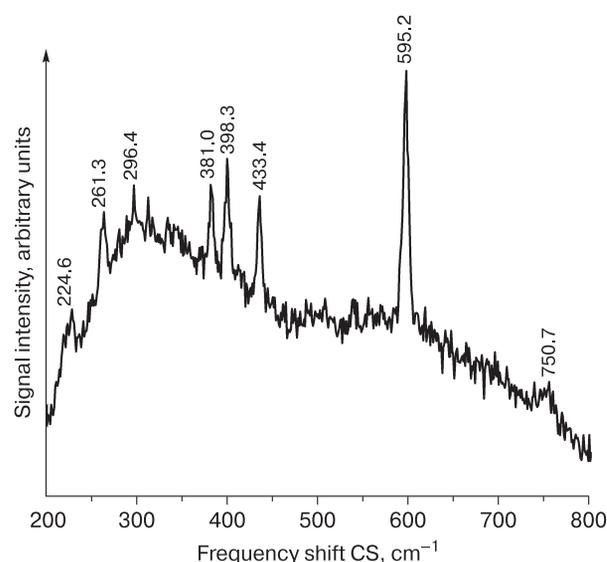
mining the parameters of the unit cells. From the data shown in Fig. 5, density of hydrate HCFC-141b was obtained from the temperature range from  $0$  to  $-100$  °C. The composition of the hydrate was taken to be HCFC-141b· $17\text{H}_2\text{O}$ . It appeared that the hydrate density could be expressed with the equation

$$\rho(t) = 1075.0(4) - 0.1844(64)t,$$

where  $\rho$  is the hydrate density,  $\text{kg/m}^3$ ;  $t$  is the temperature, °C.

The RC-spectrum, obtained from the sample under study looks as presented in Fig. 6. The general look of the spectrum corresponds to the literature data from the spectrum of the hydrate of HCFC-141b [Greathouse *et al.*, 2007; Murshed *et al.*, 2007]. In accordance with [Greathouse *et al.*, 2007], the only band in the CS-spectrum of HCFC-141b which gets significantly displaced when the hydrate is formed corresponds to the valence vibration C–Cl (an intense band in the range of  $585$ – $602$   $\text{cm}^{-1}$ ). At  $0$  °C, the position of this band in liquid HCFC-141b corresponds to  $586.6$   $\text{cm}^{-1}$ ; in hydrate –  $593.4$   $\text{cm}^{-1}$ . At the temperature of  $-160$  °C, this band was observed at  $602$   $\text{cm}^{-1}$  in the hydrate spectrum [Murshed *et al.*, 2007]. In the spectrum shown in Fig. 6, this band is at  $595.2$   $\text{cm}^{-1}$ . Thus, its position satisfactorily complies with that expected for the hydrate HCFC-141b· $17\text{H}_2\text{O}$ .

The fraction of kerosene in the sample we measured was on average  $37.7(1.7)$  mass.% by the results of four measurements. Recalculation of the measured volumes of gas which yielded from the sample as the hydrate decomposed showed the fraction of the hydrate HCFC-141b in the mixture to be  $7.5(0.5)$  mass.% (four measurements, when recalculated, the composition of the hydrate was taken to be



**Fig. 6. The combination scatter (CS) spectrum of a sample under study.**

HCFC-141b-17H<sub>2</sub>O). At the same time, according to the X-ray phase analysis data, the fraction of hydrate in the mixture was 23.8 mass.% (the proportions of total intensities of the reflexes of ice and hydrate were 0.989 and 0.399 for the original sample and of the mixture of the sample and ice). The fraction of kerosene in the sample corresponds, within error, to the results of the field measurements. At the same time, the data on the fractions of hydrate in the mixture obtained by different methods essentially differ. Considering the fact that the methods used had been repeatedly used before, a gross error in conducting the experiments should be hardly considered as probable.

The presence of kerosene is an important characteristic of the samples investigated in this study. It is quite probable that part of the hydrate HCFC-141b that yielded during decomposition could get dissolved in kerosene, which resulted in the low content of hydrate determined by this method. At the same time, in different fragments of the hydrate plug, the fraction of its components may vary due to somewhat differing conditions of hydrate formation; however, the data required for more detailed analysis are missing. In addition, the fragment of the sample investigated in this study was stored for more than six months at the temperatures from  $-20$  to  $-10$  °C, i.e., under conditions when the kerosene contained in it was in a liquid state. Some part of the hydrate could get decomposed during this period. Hence, we can assume that the most probable fraction of kerosene in the sample is 37–39 mass.%, while the fraction of hydrate is 20–40 mass.% (the remaining component is ice). It is to be noted that insignificant scatter in the relative ratios of hydrate and ice was also reported in [Murshed *et al.*, 2007].

In conclusion, it is worthwhile considering the issue of correspondence of the temperature and pressure in the location of the hydrate plug's formation to the equilibrium conditions of hydrate HCFC-141b. It follows from the available data on the phase diagram of the 'water–HCFC-141b' system [Liang *et al.*, 2001] that at temperatures lower than 0 °C, the CS-II hydrate should exist in it at all the pressures concerned. At the same time, in the borehole the hydrate is formed not from pure HCFC-141b but from its solution in kerosene. In this case, kerosene acts as inert diluent but reduces the chemical potential of the hydrate, which does not take part in the hydrate formation. In this case, kerosene acts as inert diluent, which does not take part in the hydrate formation as such but reduces the chemical potential of the hydrating agent. This may lead to reduction of the equilibrium temperature of the hydrate at the given pressure, as well as to complete termination of hydrate formation. Due to the absence of respective data (both experimental and modeling), it is hardly probable to make an a priori conclusion regarding the possibility of hydrate formation in the borehole drilled at Vostok

Station. The results of the study conducted clearly suggest that in the zone of mixing the subglacial water with the drilling fluid in the borehole at Vostok Station, the process of formation of anthropogenic Freon hydrates takes place.

The differences in the look of hydrate formations and in the degrees of their filling the borehole volume after the first and second unsealing procedures of Lake Vostok seem to be related to different conditions of their formation. In the first case, formation of the white material filling 30–40 % of the borehole volume in the range of the depths 3415–3427 m at the fluid pressure of about 30.5 MPa and the temperature of the ambient ice  $-9.5$  °C. In the second case, the solid plug, which filled the borehole without ruptures and pores within the range of depths 3697.57–3708.12 m, formed practically immediately at the pressure of 33.5 MPa and the temperature of  $-3.7$  °C, which was rather close to the melting point of ice at this depth ( $-2.6$  °C [Lipenkov and Istomin, 2001]). Completion of crystallization of pure water at such temperature takes much longer time than that which passed from the moment the lake was unsealed to the rise of the first hydrate core to the surface, – the presence of liquid water in the borehole above and under the hydrate plug indicates that. It is likely that in the zone of mixing the subglacial water with the drilling fluid emulsion is formed (similar to that formed when these liquids were shaken in the test-tube at atmospheric pressure), which accelerates both hydrate formation and crystallization of water drops in the disperse system 'the mixture of kerosene with Freon–water'. In addition, closeness of the emulsion temperature to the melting point of ice may contribute to fast formation of the hydrate [Stern *et al.*, 1996; Murshed *et al.*, 2007].

In general, the observations made after the first and second unsealing procedures indicate that, the closer to the lake surface water is mixed with the drilling fluid in the borehole, the more intense and large-scale its formation of the solid hydrate plug blocking the borehole. This rules out the possibility of using the existing borehole at Vostok Station for direct studies of the water mass of the subglacial lake without changing the composition of the drilling fluid (for example, elimination of Freon from the bottom-hole zone) or without replacing, fully or partially, (only in the bottom-hole zone) with the new drilling fluid, environmentally neutral and not reacting with water. As such fluid, hydrophobic silicon oils, for example, can be used. From the viewpoint of physical properties, low-molecular dimethylsiloxanes can be used, as they have low viscosity, low chilling points, and densities close to that of [Talalay, 2007]. However, the final decision regarding suitability of these fluids to be used under conditions of the deep borehole at Vostok Station may be taken only after conducting their field tests.

## CONCLUSIONS

As a result of the drilling works conducted at the Russian Antarctic Vostok Station, the largest subglacial Lake Vostok was unsealed twice – in 2012, borehole 5G-2 reached the lake surface, and in 2015, the lake was unsealed with borehole 5G-3. Further drilling of these boreholes showed that solid white substance was formed in the zone of mixing of the drilling fluid and of the lake water, which fully or partly filled the borehole volume and thus blocked the access to the subglacial lake, excluding the possibility of casting sampling and measuring instruments into it.

The conducted studies of the samples of this material have allowed us reliably to determine that it contained 20–40 mass.% of clathrate hydrate of Freon HCFC-141b, 37–39 mass.% kerosene and ice Ih. This type of Freon in its mixture with kerosene was used as a drilling fluid in the borehole. Considering the high content of the hydrate in the sample, we can suppose that, as the lake water penetrated into the borehole, emulsion of the drilling mixture got formed in water or that of water in the drilling mixture, while formation of the hydrate occurred already from the disperse system.

The data obtained are of great importance for developing the technology of direct studies of the subglacial Lake Vostok using the existing deep borehole. It suggests the necessity of replacing the used drilling fluid, at least in the lower part of the borehole, with another fluid that does not react with subglacial water. As a preliminary solution, silicon oil having low viscosity and a low chilling point may be recommended as such a fluid.

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