EARTH'S CRYOSPHERE
SCIENTIFIC JOURNAL

Earth's Cryosphere, 2022, vol. XXVI, No. 4, pp. 16–31

REGIONAL AND HISTORICAL GEOCRYOLOGY

ORIGIN AND ISOTOPIC COMPOSITION OF PRECIPITATION AT EXTREMELY LOW TEMPERATURES IN YAKUTSK (EASTERN SIBERIA)

A.A. Galanin, M.R. Pavlova*, A.N. Vasil'eva, G.I. Shaposhnikov, N.V. Torgovkin**

Melnikov Permafrost Institute, Siberian Branch of the Russian Academy of Sciences,
ul. Merzlotnaya 36, Yakutsk, 677010 Russia

**Corresponding author; e-mail: nigaer@yandex.ru*

***Corresponding author; e-mail: nick1805torg@gmail.com*

Isotopic (^{18}O, D) and chemical composition of atmospheric precipitation (1–2-cm snow layer on the surface of the snow cover and crystalline hoar) that fell in December 2020–January 2021 under anticyclonic weather, extremely low temperatures (–47 to –52°C) and dense ice fogs has been studied at six sites along a 25-km profile from Yakutsk. Samples from the surface of the snow cover are characterized by the lightest compositions (δ^{18} = –41.04 ± 5.11‰, δD = –326.43 ± 34.16‰, d_{exc} = 1.91 ± 7.72‰) and are noticeably depleted of deuterium. From the suburbs to the center of Yakutsk, a significant weighting of the isotopic compositions (by 10‰ for $\delta^{18}O$ and 80‰ for δD), a decrease in d_{exc} (from +10 to –6‰), and a fourfold increase in mineralization due to impurities of calcium carbonate have been found. The isotopic compositions of the samples of crystalline rime ($\delta^{18}O$ = –30.89 ± 5.62‰, δD = –285.88 ± 12.82‰, d_{exc} = –28.79 ± 32.53‰) notably differ from the isotopic compositions of other forms of atmospheric precipitation, water, and ice in the studied region. These samples display the greatest variations in $\delta^{18}O$ (from –24‰ in Yakutsk to –37‰ at a distance of 25 km from its center), δD (from –255.4 to –285.9‰), and d_{exc} (from –80 to +11.5‰). The isotopic and chemical compositions of the investigated precipitation indicate a significant proportion of technogenic water vapor entering the atmosphere during the combustion of hydrocarbon fuel. Based on the model of the Gaussian mixture and deuterium excess of the studied samples, it has been found that the maximum share of technogenic moisture in crystalline hoar reaches 26–32% near heat-generating stations; it decreases to 13–18% in the central part of the city and to 6.5–8.8% in the suburbs. In the surface layer of the snow cover, it reaches 5–6% in the central part of Yakutsk and decreases to 1% or less in the suburbs.

Keywords: *stable isotopes of water, atmospheric precipitation, snow, crystalline hoar, ice fog, low temperatures, technogenic sources of precipitation, fractionation, Yakutsk, Eastern Siberia.*

Recommended citation: Galanin A.A., Pavlova M.R., Vasil'eva A.N., Shaposhnikov G.I., Torgovkin N.V., 2022. Origin and isotopic composition of precipitation at extremely low temperatures in Yakutsk (Eastern Siberia). *Earth's Cryosphere*, XXVI (4), 16–31.

INTRODUCTION

In cold regions with a sharply continental climate, a decrease in temperature below –35...–40°C is often accompanied by specific atmospheric precipitation: arctic haze, ice (frosty) fogs, and crystalline hoar. These types of precipitation are formed during clear anticyclonic weather by the condensation of water vapor from an extremely dehydrated and supercooled atmosphere.

Ice fogs and crystalline hoar are constantly observed in Antarctica [*Ekajkin, 2016*], the continental regions of Alaska and Canada [*Bowling et al., 1968*], northern Europe [*Gallagher, 2020*], Siberia [*Shver, Izyumenko, 1982*], northern China [*Xing et al., 2020*], and other regions (Fig. 1). They have a strong negative impact on all types of ground and air transport, obstruct visibility, lead to icing of aircraft and power transmission lines.

It is generally accepted that the main causes of ice fog are the advection of cold air masses and associated vertical temperature inversions, which contribute to the deep cooling of the lower troposphere [*Bowling et al., 1968; Gallagher, 2020*]. However, the densest ice fog and severe frost occur more often within large settlements and are the result of burning of various types of fuel [*Bowling et al., 1968; Shver, Izyumenko, 1982; Xing et al., 2020*]. Emissions of dust, soot, and combustion aerosols further contribute to the formation of ice fogs, causing the condensation of supercooled atmospheric water even at low relative humidity values [*Gallagher, 2020; Xing et al., 2020*].

In Salt Lake City (USA), during the coldest periods of the year, the proportion of atmospheric water vapor derived from combustion of hydrocarbon fuels (combustion-derived water, CDW) reaches 10–13% [*Gorski et al., 2015; Fiorella et al., 2018*]. In the metropolis of Xi'an (Northeastern China), the average share of CDW in the formation of winter precipitation is 6.2%, reaching 16.2% in some periods [*Xing et al., 2020*]. In absolute terms, about 10 million tons of CDW are emitted into the atmosphere of Xi'an annually, of which 52.5% is derived from combustion of natural gas; 45.8%, from coal; and 1.7%, from other types of hydrocarbons. The emitted CDW has the following isotopic characteristics [*Xing et al., 2020*]: natural gas – $\delta^{18}O = +13.2 \pm 0.7‰$, $\delta D = -160.8 \pm 2.8‰$, $d_{exc} = -266.5 \pm 3.8‰$; black coal – $\delta^{18}O = +4.2 \pm 1.3‰$, $\delta D = -102.2 \pm 16.3‰$, $d_{exc} = -135.5 \pm 26.4‰$. Combustion of various grades of gasoline and diesel fuel results in the formation of the most deuterium-depleted compositions ($-270‰ > d_{exc} > -330‰$). Close values ($-308‰ < d_{exc} < -125‰$) were obtained for CDW in the Salt Lake City area [*Gorski et al., 2015; Fiorella et al., 2018*].

The exotic isotopic composition of the CDW is determined both by the initial isotopic composition of hydrocarbon fuels and by the peculiarities of its oxidation during combustion. Water vapor is formed during the reaction of atmospheric oxygen enriched in ^{18}O atoms ($\delta^{18}O = +23.9‰$) relative to seawater [*Fiorella et al., 2018*] and fuel hydrogen significantly depleted in deuterium due to biochemical reactions during methane synthesis [*Sessions et al., 1999; Whiticar, 1999*]. Therefore, the water vapor formed during combustion is characterized by an unusually low deuterium excess [*Gorski et al., 2015; Fiorella et al., 2018; Xing et al., 2020*] compared to natural atmospheric moisture.

The unnatural, extremely deuterium-depleted isotopic composition of CDW differs sharply from the natural composition of the surface layer of the troposphere, in which the average value of d_{exc} near the dew point is about +10‰ [*Dansgaard, 1964*]. In the upper layers of the troposphere, it reaches +200‰, while in the most evaporatively fractionated surface waters it decreases to –60‰ [*Fiorella et al., 2018*]. The isotopic characteristics of CDW and atmospheric precipitation formed from it make it possible not only to identify the source of their origin but also to approximately estimate the volumes of combusted hydrocarbon fuels for specific areas [*Xing et al., 2020*].

In Yakutsk, a fall in temperature below –40°C is annually accompanied by stagnant phenomena in the atmosphere with the appearance of specific ice fog and crystalline hoar (Fig. 1). Fog density and hoar growth rate increase with decreasing temperature. So, in the central part of Yakutsk at –45°C, visibility does not exceed 1 km; at –50°C, it is no more than 100 m. The period of continuous ice fogs in Yakutsk, as a rule, lasts about 2 months from the beginning of December to the end of January, except for short periods of temperature rise to –40...–35°C. During winter fogs, small ice crystals of about 1 mm in size or less, in the form of needles, plates and six-ray snowflakes, almost continuously settle on the surface of the snow cover, roofs of houses, and branches of trees and shrubs. During this period, tree branches, electrical wires and other thin objects are encrusted with fine crystalline 4- to 5-cm-thick hoarfrost. At the end of winter period, when air temperature rises above –35°C, winter fogs are not formed, and hoarfrost on the trees and other objects gradually disappears as a result of sublimation and shedding.

Fig. 1. Ice fog and crystalline hoarfrost on tree branches regularly observed in Yakutsk and its environs from December to February at temperatures of –35°C and below.

To date, data on the isotopic composition (^{18}O and D) of CDW have been obtained and its significant role in the dynamics of the atmosphere over large megacities has been established [*Beesley, Moritz, 1999; Gorski et al., 2015; Fiorella et al., 2018; Xing et al., 2020*]. At the same time, data on the isotopic composition of atmospheric precipitation formed under conditions of extremely low temperatures are virtually absent.

Data on the isotopic composition of atmospheric precipitation during the coldest season in Yakutsk will be useful for the reconstruction of paleotemperatures based on the analysis of the isotopic composition of polygonal wedge ice.

The purpose of this article is to characterize the features of the formation of the isotopic compositions (^{18}O and D) of atmospheric precipitation falling in Yakutsk at extremely low temperatures. The factual material is the composition of snow cover and crystalline hoarfrost at six sites along a 25-km-long profile from the center of Yakutsk towards its outskirts studied in December 2020–January 2021 (Fig. 2).

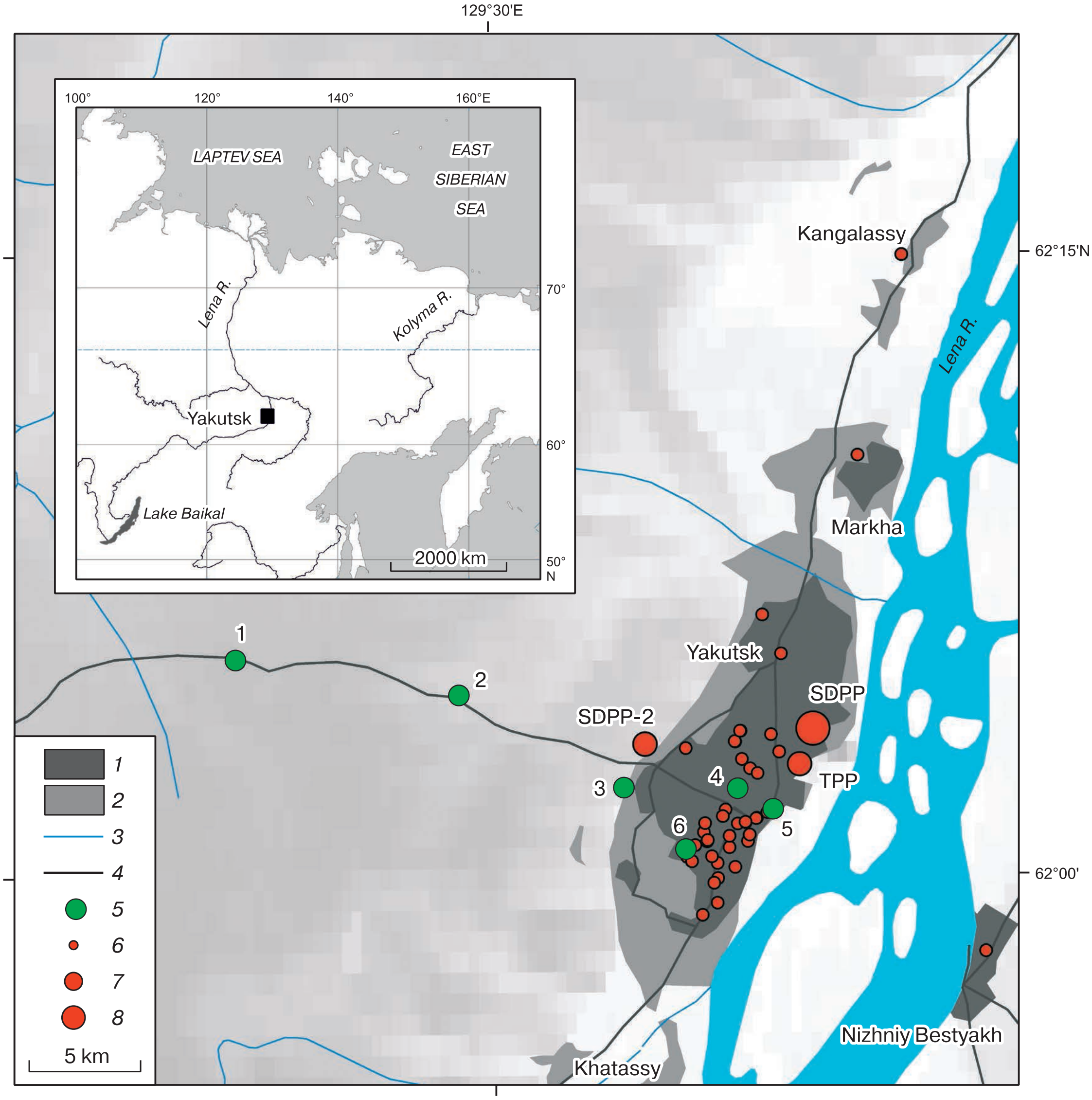

Fig. 2. Scheme of observation points (1–6) for snow cover and hoarfrost in the area of Yakutsk on December 14, 2020 and January 19, 2021.

1 – dense urban development with multistory buildings; *2* – one-story buildings; *3* – rivers; *4* – highways; *5* – observation points and their numbers; *6*–*8* – the largest sources of technogenic atmospheric emissions in Yakutsk (*6* – small heat generating stations (10–50 Gcal/h); *7* – powerful heat sources (469 and 497 Gcal/h); *8* – the largest heat source (661 Gcal/h)).

RESEARCH METHODS

The analysis of weather conditions for the period of sampling was carried out on the basis of data from the Yakutsk weather station [*Weather and Climate, 2004–2021*]. For the analysis, such indicators as the mean daily temperature (*T*), wind speed, atmospheric pressure, daily precipitation, visibility, and recordings of the thickness of crystalline frost on an ice machine were used. Figure 3 shows the time series of the dynamics of the main meteorological indicators from December 1, 2020 to February 28, 2021 with indication of sampling dates.

Atmospheric precipitation sampling was carried out at six observation points (o.p.) with natural vegetation along the transect stretching from the 25-th kilometer of the Vilyui tract to the center of Yakutsk (Fig. 2). The sampling was performed on December 14, 2020 (o.p. 6) and January 19, 2021 (o.p. 1–5) during peak air temperature drops to –48.0 and –50.9°C (Fig. 3). At each observation point, at least four precipitation samples were taken, including two hoarfrost samples from tree branches at a height of 1.0–2.0 m from the earth's surface, one precipitation sample from the snow cover surface (0–2 cm), one

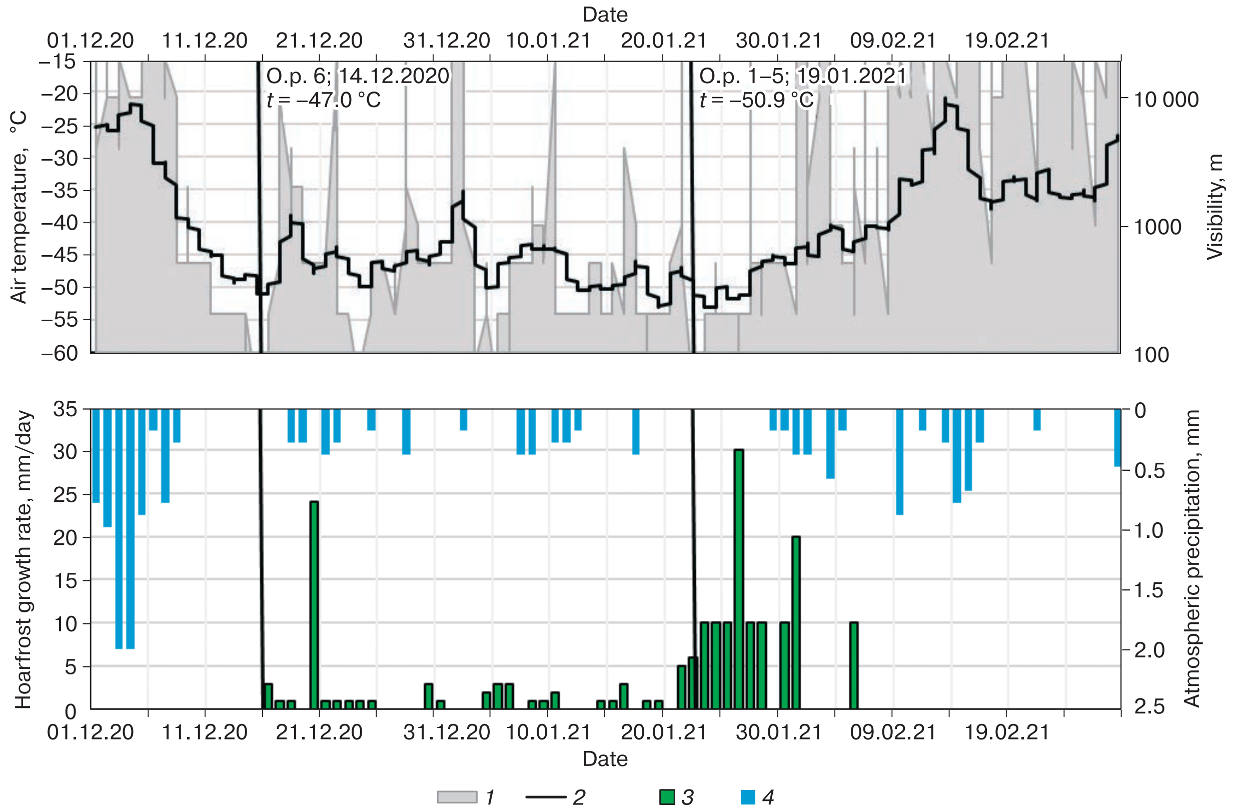

Fig. 3. Weather conditions in Yakutsk from December 1, 2020 to February 28, 2021 according to [*Weather and Climate, 2004–2021*].

1 – visibility; *2* – air temperature; *3* – growth rate of crystalline hoar; *4* – snow; o.p. – observation point.

averaged snow sample from the depth of 2–20 cm. The average thickness of the snow cover at the time of sampling was approximately the same at all sites (25–30 cm).

Observation point 1 (62°05′ N, 129°16′ E; 254 m a.s.l.) is located on the 25th kilometer of the Vilyui tract at a distance of 250 m from the highway, on the edge of a birch grove and a meadow. Weather conditions at the time of sampling: T = –52°C, calm, fog, maximum visibility 250–300 m.

Observation point 2 (62°04′ N, 129°28′ E; 219 m a.s.l.) is located on the 10th kilometer of the Vilyui tract at a distance of 200 m from the road, within a sparse birch grove. Weather conditions at the time of sampling: T = –52°C, calm, fog, maximum visibility 150–200 m.

Observation point 3 (62°02′ N, 129°36′ E; 158 m a.s.l.) is located on the suburbs of Yakutsk under the slope of Mount Chochur Muran at a distance of 200 m from the road, on the edge of a birch grove and meadow steppe. Weather conditions are similar to those at o.p. 1.

Observation point 4 (62°02′ N, 129°42′ E; 120 m a.s.l.) is located near the center of Yakutsk within a birch grove. Weather conditions at the time of sampling: T = –52°C, calm, fog, maximum visibility 100–150 m.

Observation point 5 (62°01′ N, 129°44′ E; 98 m a.s.l.) is located in the center of Yakutsk on the territory of a front garden with birch trees. Weather conditions at the time of sampling are similar to those at o.p. 4.

Observation point 6 (62°01′ N, 129°40′ E; 98 m a.s.l.) is located 20 m from the building of the Melnikov Permafrost Institute, Siberian Branch, Russian Academy of Sciences (MPI SB RAS), 100 m from the boiler house of the MPI SB RAS. Sampling was carried out within a birch grove. Weather conditions at the time of sampling: T = –48°C, calm, fog, maximum visibility 150–200 m.

The collected samples were packed in 10-mL airtight plastic bags and delivered to the laboratory of the MPI SB RAS. Next, the samples were melted at room temperature, poured into plastic cuvettes, and stored in a refrigerator at +5°C. Samples were analyzed within 1–2 weeks after sampling.

For the chemical analysis of snow and frost, samples were taken into plastic bags, melted at room temperature, and packed into 0.5-L plastic bottles prepared according to [*GOST 31861-2012, 2013*].

Taking into account the possibility of the influence of technogenic sources of water vapor on the formation of the isotopic compositions of the samples, the authors carried out mapping of the main heat generating stations of Yakutsk (Fig. 2). Among them, the largest are the Yakutsk Thermal Power Plant (SPP) (497 Gcal/h), State District Power Plant (SDPP) (661 Gcal/h), and SDPP-2 (469 Gcal/h). In addition, there are 45 more boiler houses with a capacity of 10 to 50 Gcal/h. All heat generating stations in Yakutsk operate on gaseous or liquid fuels and reach full capacity during the period of the lowest winter temperatures.

Analysis of the composition of stable isotopes (^{18}O and D) was carried out in the Russian–German Isotope Laboratory of the MPI SB RAS (Yakutsk) by laser absorption IR spectrometry on an automated complex PICARRO L2140-i with the technology of resonator ring spectroscopy CRDS (Cavity Ring Down Spectroscopy). The adopted internal water standards (MilliQ A-45, HDW-1, MXW, HGL-1, SEZ-2) and the AWIPotsdam protocol of the Stable Isotope Laboratory of the Alfred Wegener Institute (Potsdam, Germany) were applied. The reproducibility of δ^{18}O and δD measurements was ±0.04 and ±0.1‰, respectively (standard deviation 1σ, n = 6, measurement time 100 s).

Calibration was performed at least three times per standard run of a cassette of 33 liquid samples. At the end of the analysis, the 1σ values for δ^{18}O and δD were corrected for the combined standard deviation based on the method [*van Geldern, Barth, 2012*], which makes it possible to achieve a reproducibility of more than 0.01‰. A total of 26 samples were analyzed (Table 1).

Analysis of the ionic composition and other chemical properties of crystalline hoarfrost and snow samples was carried out by routine methods

Table 1. **Isotopic compositions of samples of fine crystalline hoarfrost and snow cover in the vicinity of Yakutsk in December 2020 – January 2021**

Observ. Point-Sample	δ^{18}O,‰	1σ,‰	δD,‰	1σ,‰	d_{exc}	Sample nature
			Site 1			
1-1	–36.60	0.02	–285.89	0.04	6.90	Hoarfrost on birch branches at a height of 1–2 m
1-2	–35.85	0.02	–286.55	0.04	0.21	Hoarfrost on birch branches at a height of 1–2 m
1-3	–45.04	0.01	–349.92	0.08	10.36	Snow cover surface (0–2 cm)
1-4	–30.31	0.02	–224.22	0.03	18.26	Average snow stock (2–20 cm)
			Site 2			
2-1	–37.42	0.02	–289.46	0.01	9.93	Hoarfrost on birch branches at a height of 1–2 m
2-2	–37.99	0.02	–292.34	0.06	11.57	Hoarfrost on birch branches at a height of 1–2 m
2-3	–46.45	0.02	–361.72	0.10	9.86	Snow cover surface (0–2 cm)
2-4	–31.05	0.02	–230.51	0.04	17.88	Average snow stock (2–20 cm)
			Site 3			
3-1	–35.35	0.01	–290.04	0.01	–7.27	Hoarfrost on willow branches at a height of 1–2 m
3-2	–33.72	0.02	–284.13	0.05	–14.36	Hoarfrost on willow branches at a height of 1–2 m
3-3	–45.01	0.01	–354.02	0.01	6.06	Snow cover surface (0–2 cm)
3-4	–29.36	0.01	–222.16	0.04	12.75	Average snow stock (2–20 cm)
			Site 4			
4-1	–30.77	0.01	–273.97	0.07	–27.84	Hoarfrost on birch branches at a height of 1–2 m
4-2	–30.18	0.01	–271.73	0.02	–30.27	Hoarfrost on birch branches at a height of 1–2 m
4-3	–38.37	0.01	–313.55	0.01	–6.55	Snow cover surface (0–2 cm)
4-4	–28.03	0.01	–213.66	0.02	10.61	Average snow stock (2–20 cm)
			Site 5			
5-1	–31.71	0.01	–279.85	0.03	–26.20	Hoarfrost on birch branches at a height of 1–2 m
5-2	–29.30	0.01	–271.83	0.02	–37.44	Hoarfrost on birch branches at a height of 1–2 m
5-3	–37.37	0.01	–304.05	0.05	–5.06	Snow cover surface (0–2 cm)
5-4	–28.65	0.01	–219.13	0.05	10.06	Average snow stock (2–20 cm)
			Site 6			
6-1	–22.95	0.01	–261.52	0.11	–77.93	Hoarfrost on a metal fence at a height of 1.5 m
6-2	–24.22	0.04	–260.74	0.10	–66.94	Hoarfrost on birch branches at a height of 1–2 m
6-3	–22.13	0.01	–258.78	0.10	–81.70	Hoarfrost on birch branches at a height of 1–2 m
6-4	–24.21	0.01	–255.41	0.05	–61.73	Hoarfrost on the roof of a car at a height of 1.5 m
6-5	–34.02	0.01	–275.36	0.10	–3.21	Snow cover surface (0–2 cm)
6-6	–29.30	0.01	–221.26	0.02	13.14	Average snow stock (2–20 cm)

Table 2. **Chemical composition of crystalline hoar and snow cover in Yakutsk in January 2021**

Observ. Point-Sample	pH	Eh	Concentrations of main cations and anions, mg/L										Hard-ness, meq/L	Mineral-ization, g/L	Chemical type (according to A.V. Shchukarev)	Concentrations of micro-components, mg/L				
			Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_2^-	NO_3^-				Sr^{2+}	Li^+	Ba^{2+}	HPO_4^-	F^-
1-2	7.28	556	4.08	2.11	0.4	0.10	1.90	24.95	2.30	0.69	0.03	4.00	0.380	0.0417	HCO_3 76/Ca 38 Mg 32	0.659	0.000	0.000	0.235	0.249
1-4	7.70	543	0.76	0.46	0.1	0.0	0.1	4.49	0.40	0.17	0.01	0.70	0.075	0.0073	HCO_3 74/Ca 43 Mg 43	0.000	0.016	0.000	0.049	0.040
2-2	7.17	545	4.53	0.46	0.2	0.05	0.5	13.97	1.8	0.52	0.01	1.00	0.264	0.0233	HCO_3 76/Ca 73	0.000	0.094	0.000	0.025	0.120
2-4	7.38	544	1.53	0.64	0.1	0.1	0.2	6.99	0.4	0.21	0.01	0.70	0.128	0.0109	HCO_3 74/Ca 50 Mg 35	0.000	0.025	0.000	0.026	0.017
3-2	6.64	517	18.12	3.67	0.4	2.00	5.00	79.85	8.00	3.46	0.10	8.00	1.206	0.1294	HCO_3 75/Ca 55	0.731	0.000	0.061	0.022	0.022
3-4	7.33	485	5.13	1.01	0.4	0.2	0.9	19.96	0.70	0.35	0.01	1.30	0.339	0.0306	HCO_3 88/Ca 60	0.283	0.000	0.000	0.015	0.297
4-2	7.20	443	18.12	1.83	0.5	1.5	5.7	74.86	9.0	1.73	0.15	5.00	1.055	0.1202	HCO_3 79/Ca 59	1.399	0.000	0.059	0.271	0.049
4-4	7.63	433	12.08	0.92	0.4	0.65	2.80	45.91	2.50	1.21	0.20	2.10	0.678	0.0699	HCO_3 85/Ca 65	0.450	0.000	0.000	0.042	0.655
5-2	7.81	393	27.18	0.92	1.3	4.6	7.5	105.3	13.40	2.25	0.20	8.00	1.432	0.1725	HCO_3 78/Ca 63	0.567	0.000	0.072	0.042	1.200
5-4	7.73	403	12.84	1.01	2.2	1.80	3.40	48.91	3.30	2.94	0.20	2.50	0.723	0.0804	HCO_3 80/Ca 57	0.532	0.000	0.033	0.435	0.435

in the certified laboratory of the Melnikov Permafrost Institute, Siberian Branch of the Russian Academy of Sciences. In total, ten samples were analyzed (Table 2).

Isotopic and chemical compositions of sediments at extremely low temperatures

The isotopic composition (δD and δ^{18}O) of the entire set of samples (26 samples) is characterized by great variability both within one observation point depending on the type of sample (Table 1) and along the studied profile. On Fig. 4*a*, the entire sample is clearly divided into two linearly elongated sets of points. The first one is formed by samples of averaged snow cover (from a depth of 2–20 cm) and is described by the equation $\delta D = 8.38 \cdot \delta^{18}O + 24.98$ ($R^2 = 0.99$, $n = 12$), the coefficients of which are close to the equation $\delta D = 8.17 \cdot \delta^{18}O + 21.9$ ($R^2 = 0.99$, $n = 8$) obtained by T.S. Papina et al. [*2017*] for winter precipitation in 2014 in Yakutsk. On the whole, these equations point to the location of these compositions near the main meteoric water line (MMWL), which indicates their natural (atmospheric) origin under the conditions of kinetic (Rayleigh) fractionation. The second linear set is formed by samples of crystalline hoarfrost and surface snow (from a depth of 0–2 cm) and is extrapolated by the equation $\delta D = 2.22 \cdot \delta^{18}O - 206.9$ ($R^2 = 0.96$, $n = 14$), the coefficients of which indicate an unnatural source of atmospheric moisture, extremely depleted of deuterium. On Fig. 4*b*, all the studied compositions and the regressions approximating them are shown separately depending on the type of samples, which makes it possible to assess their role in the isotopic structure of the entire sample.

The samples of the average snow stock (2–20 cm) are characterized by the heaviest composition compared to the other samples ($\delta^{18}O = -29.45 \pm 1.1‰$, $\delta D = -221.8 \pm 5.57‰$, $d_{exc} = 13.78 \pm 3.52‰$). Their position near the local meteoric water line (LMWL) (Fig. 4*b*) and positive deuterium kurtosis (close to 10) indicate condensation under conditions of an equilibrium (Rayleigh) process [*Dansgaard, 1964*]. At the same time, the linear regression equation itself $\delta D = 4.98 \cdot \delta^{18}O - 75.3$ ($R^2 = 0.92$, $n = 6$) of these compositions differs significantly from the MMWL and LMWL equations for Yakutsk by a significantly lower slope, which is usually associated with the processes of evaporation fractionation [*Dansgaard, 1964; Papina et al., 2017; Galanin et al., 2019*].

According to the dependence [*Dansgaard, 1964*]

$$\delta^{18}O = 0.68\,t° - 13.6, \quad -30°C < t° < 0°C, \qquad (1)$$

the precipitation of this composition fell at temperatures from –21 to –25°C.

According to the dependence [*Papina et al., 2017*]

$$\delta^{18}O = 0.59\,t^\circ - 19.7\ (R^2 = 0.88), \quad (2)$$

precipitation of the studied composition fell out at temperatures from −14 to −19°C.

In general, Eqs. (1) and (2) give convergent results and indicate that the studied precipitation fell at the very beginning of winter (in October–November 2020). Indeed, the main amount of snowfall in Yakutsk fell in October and November at temperatures of −12... −25°C (Fig. 3), while in December 2020 and January 2021, when the temperature dropped to −45...−50°C, the amount of precipitation was extremely low [*Weather and Climate, 2004–2021*]. Instead of snowfall during December–January, under conditions of anticyclonic calm weather, dense ice fogs and active growth of crystalline frost were observed (Fig. 3). The sum of observed atmospheric precipitation for the coldest month and a half did not exceed 7–10 mm.

At the ratio $\delta^{18}O/d_{exc}$, snow samples are approximated by the equation $d_{exc} = -3.02 \cdot \delta^{18}O - 75.3$ ($R^2 = 0.88$, $n = 6$) (Fig. 5). An increase in the deuterium excess in precipitation during the coldest days is associated with a faster decrease in the rate of fractionation of $H_2{}^{18}O$ molecules compared to $HD^{16}O$ [*Dansgaard, 1964*].

Negative correlations of d_{exc} with $\delta^{18}O$ and D are also characteristic of precipitation formed under conditions of equilibrium cooling (freezing) of a limited volume of water vapor in semi-closed and closed systems, for example, in caves with difficult air exchange [*Lacelle et al., 2009; Galanin, 2020*]. Unfortunately, the issues of the correlation of the deuterium kurtosis with the values of δD and $\delta^{18}O$ remain poorly covered in the scientific literature.

Samples from the snow cover surface (0–2 cm) are characterized by the lightest composition ($\delta^{18}O = -41.04 \pm 5.11$‰, δ D = −326.43 ± 34.16‰, $d_{exc} = 1.91 \pm 7.72$‰), which naturally becomes heavier along the sampling profile towards the center of Yakutsk (Figs. 4 and 6; Table 1). If we take into account similar weather conditions and air temperature (−45...−53°C) in Yakutsk and its environs in December 2020–January 2021, then the heaviest composition ($\delta^{18}O$ = −35...−38‰, d_{exc} = −6...−3‰) was formed in the central part of the city (o.p. 4–6), while the lightest ($\delta^{18}O$ = −45...−46‰, d_{exc} = 6–10‰) was formed in the outskirts of the city (o.p. 1–3). In terms of temperatures according to Eqs. (1) and (2), in Yakutsk (o.p. 4–6), precipitation of the upper (0–2 cm) snow layer condensed at the temperature range of −29...−34°C; beyond Yakutsk (o.p. 1–3), temperatures were lower (−45...−56°C). In fact, as observations at the Yakutsk weather l station (Fig. 3) and air temperature measurements at the time of sampling indicate, the weather conditions for all sampling points were approximately the same.

Samples taken from the surface of the snow cover 15–20 km from Yakutsk lie near the LMWL and are determined by positive values of $d_{exc} \approx +10$‰, which are characteristic of the equilibrium (Rayleigh) condensation of atmospheric vapor at low tem-

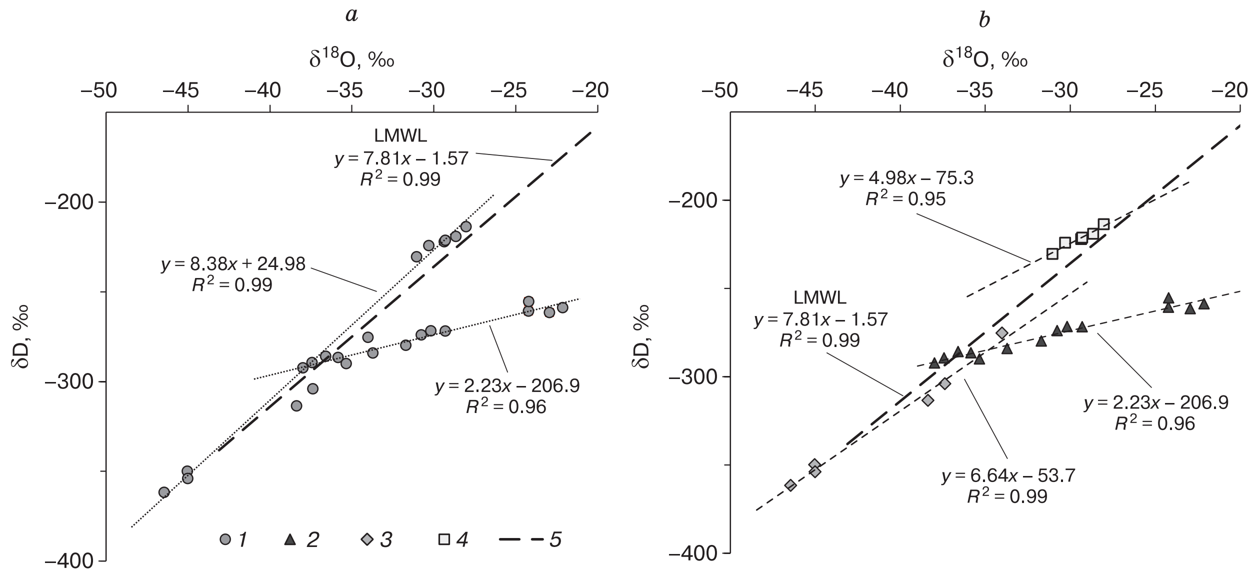

Fig. 4. The $\delta^{18}O/\delta D$ ratio in samples of snow cover and crystalline hoarfrost during the period of extreme subzero temperatures in the winter of 2020/21 in Yakutsk and its suburbs.

a – the entire sample; *b* – different groups of samples; *1* – crystalline hoarfrost; *2* – snow cover (including samples from the surface); *3* – snow cover surface (0–2 cm); *4* – annual precipitation in Yakutsk according to GNIP data [*Kurita et al., 2004*]; *5* – water vapor emitted into the atmosphere during the combustion of hydrocarbon fuels [*Xing et al., 2020*]. LMWL is a local line of meteoric waters.

peratures (Fig. 5). On the contrary, the samples taken in Yakutsk (o.p. 4–6) are characterized by negative d_{exc} values from –3 to –6‰, which is very uncharacteristic of fresh natural winter precipitation and indicates a different source of their origin.

The influence of an anthropogenic source on the composition of precipitation in Yakutsk in December 2020–January 2021 is emphasized by the nature of the variation in the isotopic composition along the studied profile (Fig. 4), which cannot be explained by the processes of equilibrium kinetic (Rayleigh) fractionation or by partial sublimation of snow from the surface. In the latter case, the similarity of weather conditions along the observation profile would lead to the same manifestation of sublimation and related fractionation effects at all sampling points.

The deuterium kurtosis of the surface snow samples also shows a significant negative correlation with the values of δD and $\delta^{18}O$ (Fig. 5). The regression looks like $d_{ex} = -1.36 \cdot \delta^{18}O - 53.7$ ($R^2 = 0.81$, $n = 6$).

Crystalline hoarfrost samples are characterized by the most exotic composition ($\delta^{18}O = -30.89 \pm 5.62$‰, $\delta D = -285.88 \pm 12.82$‰, $d_{exc} = -28.79 \pm 32.53$‰), which was not previously observed by the authors in natural atmospheric precipitation, as well as in all known types of terrestrial and ground ice in the region [*Galanin et al., 2019*]. Along the profile (Fig. 6), this composition experiences the strongest variation in $\delta^{18}O$, more than 1.5 times from –24‰ at o.p. 6 to –37‰ at o.p. 1. In the same interval, the δD values show less significant variations (by a factor of 1.12), decreasing from –255.4‰ (o.p. 6) to –285.9‰ (o.p. 1). The disproportionate decrease in $\delta^{18}O$ and δD values along the profile is clearly reflected in the d_{exc} value. Its lowest values from –66.9 to –81.8‰ (o.p. 6) and from –26.2 to –37.4‰ (o.p. 5) are typical for the territory of Yakutsk. As the distance from the city center increases, d_{exc} naturally increases and reaches positive values of 6.9–11.5‰ in hoarfrost samples taken at a distance of 15 and 25 km from the city center.

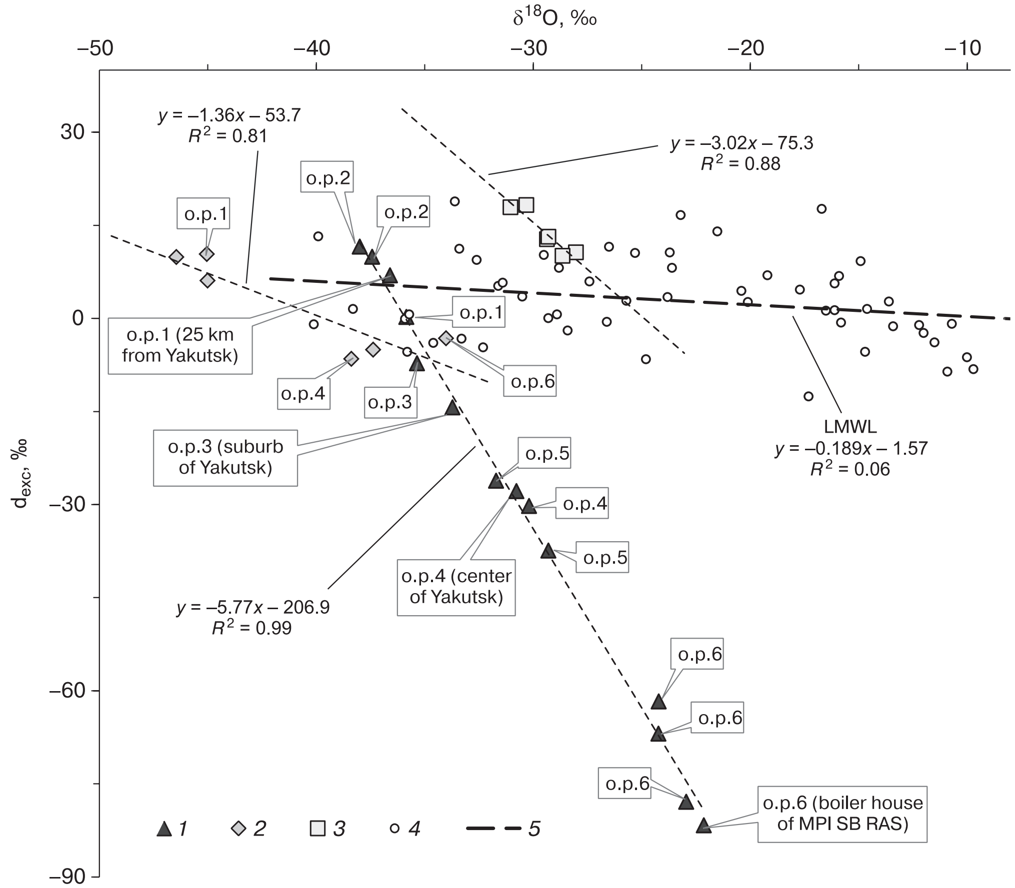

Fig. 5. The relationship between $\delta^{18}O$ and d_{exc} values in atmospheric precipitation during the period of extreme subzero temperatures in the winter of 2020/21 in Yakutsk and its suburbs.

1 – crystalline hoarfrost on trees at a height of 1.0–1.5 m above the snow cover; *2* – the surface of the snow cover (0–2 cm); *3* – averaged snow cover from a depth of 2–20 cm; *4* – atmospheric precipitation in Yakutsk according to GNIP data [*Kurita et al., 2004*]; *5* – local line of meteoric waters (all seasons) for the city of Yakutsk based on GNIP data. 1–6 – numbers of observation points (o.p.).

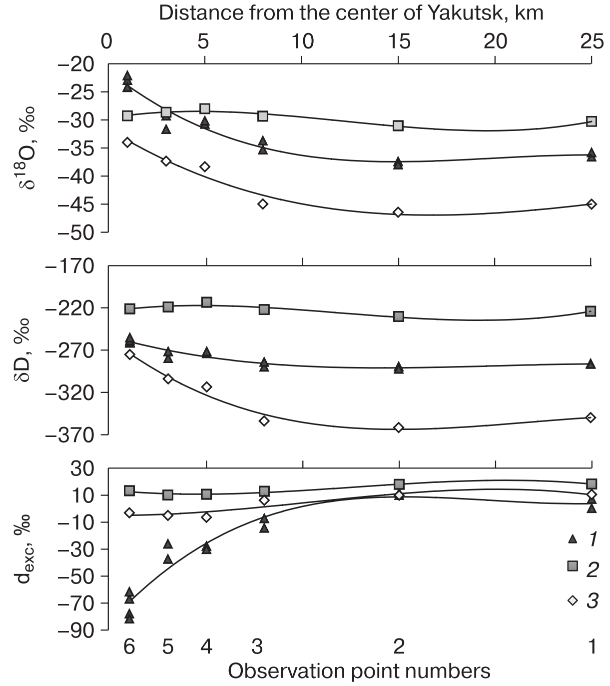

Fig. 6. Variation of the isotopic composition of the crystalline hoarfrost and snow cover along the profile of observation points.

1 – crystalline hoarfrost; *2* – the surface of the snow cover (0–2 cm); *3* – averaged snow cover (2–20 cm) at the end of January 2021.

The regression equation for the composition of crystalline hoar $\delta D = 2.23 \cdot \delta^{18}O - 206.9$ ($R^2 = 0.96$, $n = 14$) is characterized by an extremely low slope, indicating intensive evaporative fractionation of the moisture source. Among natural ices, the closest slope coefficient (2.7) was found for the composition of sinter ice in cold caves of Canada [*Lacelle et al., 2009*].

The exotic isotopic composition of crystalline hoar and the position of the observation points relative to the heat generating stations of Yakutsk (Fig. 2) allow us to conclude that the latter are the main source of moisture. Thus, the most contrasting isotope anomaly in crystalline hoar was established at o.p. 6 on the territory of the MPI SB RAS, 100 m from the nearest boiler house. The hoarfrost sample taken here on December 14, 2020 had the heaviest ($\delta^{18}O = -22.1$‰, $\delta D = -258.8$‰) and extremely fractionated composition with extreme values of $d_{exc} = -81.7$‰. Such a composition is not typical of the Earth's atmosphere and is probably formed during the combustion of hydrocarbon fuels at temperatures well above 100°C.

In terms of Eq. (1), the deposition of crystalline hoarfrost in different parts of the profile occurred at significantly different temperatures. Thus, the heaviest composition was formed in the center of Yakutsk and especially near the boiler house of the MPI SB RAS (o.p. 6) at a temperature of –15...–18°C. With distance from the city center, the condensation temperature naturally decreased, and the lightest composition was formed at a distance of 15–25 km from Yakutsk (o.p. 1) at a temperature of –35...–42°C.

Compared to snow cover samples, the composition of crystalline frost from tree branches is characterized by a high negative correlation between the deuterium excess and $\delta^{18}O$, described by the equation $d_{exc} = -5.77 \cdot \delta^{18}O - 206.9$ ($R^2 = 0.99$, $n = 14$) (Fig. 5).

Chemical composition of samples. According to the classification of S.L. Shvartsev [*1996*], in terms of total mineralization, all the samples of hoarfrost and snow are classified as ultra-fresh (0.0073–0.1725 g/L); in terms of total hardness, they are soft (0.075–1.432 meq/L). The samples taken in the suburban area (o.p. 1 and 2) are characterized by a bicarbonate magnesium-calcium composition, while urban samples (o.p. 3–5) are characterized by a bicarbonate calcium composition according to the classification of A.V. Shchukarev [*Shvartsev, 1996*].

Hoarfrost and snow cover samples are predominantly characterized by a neutral and slightly alkaline reaction (6.64 < pH < 7.81). The latter is typical for samples from the city center, which is due to pollution with ash from city boilers and vehicle emissions. The redox potential (400 < Eh < 550) in general indicates oxidizing conditions; its values are minimal within the city, and gradually increase in the suburbs both in hoarfrost and in the snow cover.

Within all observation points, the mineralization of crystalline hoarfrost is always two–four times higher than that of snow cover, which also indicates a strong genetic relationship of the former with an anthropogenic (technogenic) source. With distance from the city center, the concentrations of most cations and anions decrease in frost and snow cover by 4–20 times (Table 2, Fig. 7). This also indicates the technogenic origin of mineral pollutants, the content of which in Yakutsk exceeds the sanitary standards by 1.8 times on the average [*Makarov, Torgovkin, 2020*].

Among all cations, the maximum concentrations are characteristic of Ca^{2+} and reach 27.18 mg/L in the melt of crystalline hoarfrost from Yakutsk. Among the anions, HCO_3^- prevails, which indicates an increased emission of carbon dioxide within the city as a result of fuel combustion. The increase in the concentration of chloride ion in the city is also probably due to the anthropogenic factor, as sodium chloride is used to clear snow and ice from roads. The concentrations of all nitrogen compounds increase towards the center of Yakutsk by 3–4 times in snow cover and by 8–10 times in hoarfrost. Their sources are mainly the products of atmospheric nitrogen oxidation during the combustion of hydrocarbon fuel by heat-generating stations.

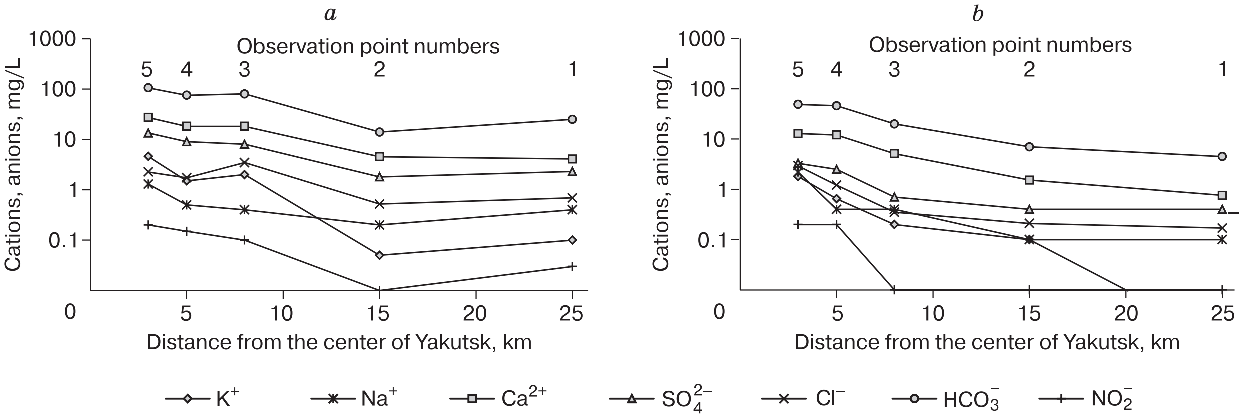

Fig. 7. Variation of the main cations and anions in (*a*) crystalline hoarfrost and (*b*) snow cover with distance from the center of Yakutsk along the sampling profile.

Among trace components in samples of hoarfrost and snow outside Yakutsk, there are small amounts of lithium (0.016–0.094 mg/L), fluorine (0.017–0.249 mg/L), and phosphorus (0.026–0.049 mg/L). In urban samples of snow cover, the contents of phosphorus (0.297–0.655 mg/L) and strontium (0.283–0.532 mg/L) increase significantly, while barium (0.059–0.072 mg/L) appears in hoarfrost samples, and the contents of strontium (0.567–1.399 mg/L) and phosphorus (1.200 mg/L) sharply increase.

In general, the chemical composition of crystalline hoarfrost and snow in Yakutsk shows significant similarity, which is due to the technogenic pollution of the city air by emissions from heat generating stations. Moreover, the maximum concentrations of pollutants are concentrated in crystalline frost, which is actively formed on trees and other objects in December and January. This is due to the fact that at the indicated time all heat generating stations in Yakutsk reach full capacity and emit maximum concentrations of pollutants – mainly water vapor and ash.

The calm weather prevailing during the period with the lowest temperatures does not contribute to the dispersion of emissions from heat generating stations, which form a continuous cloud of ice fog covering an area of about 100 km^2. The maximum fog density and the lowest visibility are typical for the central part of the city. The influence of anthropogenic sources of water vapor and chemical pollutants can be traced in the isotopic and chemical compositions of crystalline frost and snow cover to a distance of 10–15 km from the center of Yakutsk.

Thus, the isotopic and chemical compositions of atmospheric precipitation during the cold season is determined by the source of the CDW. The most exotic composition was found for precipitation in the center of the city and in the immediate vicinity of the thermal power station of the MPI SB RAS (o.p. 6). This composition is very similar to the composition of the CDW found earlier in other regions [*Gorski et al., 2015; Fiorella et al., 2018*] and is characterized by very low deuterium kurtosis values.

Influence of technogenic sources on the isotopic composition of atmospheric precipitation

Currently, Yakutsk is the largest and fastest growing city located in an extremely cold climate. In some years, extreme mean January temperatures down to –64.4°C (1891) and maximum summer temperatures of +38.4°C (2011) were recorded here [*Shver, Izyumenko, 1982*]. The mean annual precipitation varies from 147 mm (2001) to 330 mm (1971). The ratio of winter to summer precipitation is approximately 1:6 [*Gavrilova, 1962; Shver, Izyumenko, 1982*]. Snow cover usually appears in the first ten days of October and disappears at the end of April. The average thickness of the snow cover does not exceed 25–30 cm.

In recent decades, the growing pace of construction has led to an increase in the number and capacity of heat generating stations (Fig. 2), and the number of cars and other consumers of hydrocarbon fuel is growing.

Sources and volumes of CDW in Yakutsk. Despite climate warming, in recent decades in Yakutsk, an increase in the intensity and duration of winter ice fogs, as well as in the thickness of crystalline frost on trees, wires, and other objects has been observed. In addition, fogs begin to appear at air temperatures higher than –35°C, at which stable clear weather was previously observed. These phenomena are directly related to the increase in the volume of combusted hydrocarbons and the complete transition to natural gas. Thus, a sharp increase in the density and duration of ice fogs, as well as the rise in the temperature of their appearance, occurred in Yakutsk after the launch of an additional large SDPP-2 unit in 2017 (Fig. 2).

In total, there are three large thermal power plants operating in Yakutsk and generating about half of the heat energy, and about 40 boiler houses with a capacity of 10–50 Gcal/h each. In addition, a certain amount of emissions is formed during the heating of private houses and the operation of vehicles. The total heat generation in Yakutsk during winter peak loads can be estimated at about 2000 Gcal/h.

Currently, all heat generating plants in Yakutsk have been switched to gas fuel, which consists mainly of methane and emits significantly more CDW than hard coal. The combustion of 1 kg of this gas releases about 13.3 Mcal of heat, as well as 2.21 kg of high-temperature water vapor [*Kuznetsov, 2010*]. With a capacity of 2000 Gcal/h, it is necessary to burn about 150 tons of natural gas every hour. At the same time, about $3.3 \cdot 10^5$ kg of CDW will be released into the atmosphere per hour, about $2.4 \cdot 10^8$ kg during the coldest month, and for the entire heating season this value can be $1.0 \cdot 10^9$ kg.

In Yakutsk, during the period of extremely low temperatures and calm weather, the CDW-released into the atmosphere quickly condenses, forming a scattering zone with a radius of about 10 km and an area of 314 km^2 ($3.14 \cdot 10^8$ m^2) in the center in Yakutsk. Assuming that during the two coldest months $2.4 \cdot 10^8$ kg of CDW is released into the atmosphere of Yakutsk, which is completely condensed within this zone, it is possible to approximately estimate the amount of technogenic precipitation ($2.4 \cdot 10^8$ kg/$3.14 \cdot 10^8$ m^2 = 1.53 kg/m^2 = 1.53 mm). Thus, during the two coldest months, 1.53 kg of technogenic precipitation falls on 1 m^2 of the 10-km zone around Yakutsk, which is equivalent to 1.53 mm. The share of CDW in the isotopic composition of precipitation varies significantly depending on the distance from the emission source. Therefore, 7–10 times more CDW (10–15 mm) should precipitate near the CDW sources, and its amount should decrease to 0.5–1.0 mm towards the suburbs of the city. This conclusion is well supported by visual observations of the thickness of crystalline hoar, which increases several times near heating plants and in the center of the city compared to the suburbs.

During the period of the lowest temperatures, the heat generating stations of Yakutsk reach their maximum capacity and emit the maximum amount of CDW. At the same time, a decrease in air temperature leads to an increase in the speed and narrowing of the condensation zone, which causes an increase in the share of CDW in precipitation near the sources of their release. The above estimates of CDW in Yakutsk are very approximate.

Estimation of the relative share of water vapor from the combustion of hydrocarbon fuels in Yakutsk based on the deuterium kurtosis and the Gaussian mixture model. The high proportion of CDW in the precipitation of the coldest period in Yakutsk is confirmed by calculations using the method based on a comparison of the deuterium excesses of in the samples and in the initial CDW [*Xing et al., 2020*]. This approach is based on the Gaussian mixture model, which makes it possible to calculate the proportion (X) of the anthropogenic source of water vapor in the sample based on the deuterium kurtosis using the formula

$$d_1 = d_2X + d_3(1 - X). \quad (3)$$

Here, the values d_1, d_2, d_3 are the deuterium excesses of the samples, the source of CDW, and the natural background. Assuming that the CDW had a minimum impact on the isotopic composition of precipitation at observation points 1 and 2 (15 and 25 km from Yakutsk), their averaged deuterium kurtosis was used as background values (d_3 = 10‰). Since almost all thermal power plants in Yakutsk use gaseous fuel, the deuterium excess of water vapor from natural gas combustion (d_2 = –266‰) was taken as the value of the deuterium surplus of the CDW [*Xing et al., 2020*]. Substituting the values of the deuterium excess of the studied samples (d_1) into equation (3) and solving it by the iteration method, we obtain the values of the share of CDW in the studied samples.

The performed estimates show that the highest values of the share of CDW (26–32%) are reached in the samples of crystalline hoarfrost taken at o.p. 6 on the territory of the MPI SB RAS, 100 m from the boiler house (–61.7‰ > d_{exc} > –80‰).

In the center of Yakutsk (o.p. 4 and 5), the composition of crystalline hoarfrost (–26.2‰ > d_{exc} > –37.4‰) testifies to the share of CDW of about 13–18%. In hoarfrost samples from the suburbs of Yakutsk (o.p. 3) with values of –7.3‰ > d_{exc} > –14.4‰, the proportion of CDW varies from 6.5 to 8.8%. In the surface layer of the snow cover, the share of CDW is 5–6% in the central part of Yakutsk and decreases towards the suburbs to 1% or less.

Discussion about the sources and mechanisms of formation of the isotopic composition of atmospheric precipitation in Yakutsk during the coldest season. The first systematic data on the isotopic composition of atmospheric precipitation in Yakutsk were obtained within the framework of the International Project for the Development of the Siberian Observation Network SNIP (Siberian Network of Isotopes in Precipitation) [*Kurita et al., 2004*]. Within the framework of this project, 43 samples were analyzed in Yakutsk, of which only a few characterize the isotopic composition of precipitation during the cold season.

Using the data from the SNIP database, the LMWL for North Asia was substantiated, which has the form $\delta D = 7.9 \cdot \delta^{18}O + 2.9$ and takes into account only mean monthly atmospheric precipitation with a volume of more than 10 mm [*Kurita et al., 2004*]. At the same time, the values given in the SNIP database for 43 precipitation samples from Yakutsk are approximated by the equation $\delta D = 7.81 \cdot \delta^{18}O - 1.57$ ($R^2 = 0.99$) [*Galanin et al., 2019*].

According to [*Kurita et al., 2004*], the normalized mean annual isotopic composition for Yakutsk is characterized by $\delta^{18}O = -19.31$‰, and $\delta D = -153.9$‰; for precipitation from December to February, $\delta^{18}O = -33.0$‰, and $\delta D = -265.8$‰. The latter data poorly correlate with the results obtained by us, because precipitation in December 2020 and January 2021 had a significantly lighter composition ($\delta^{18}O = -41.04 \pm 5.11$‰, $\delta D = -326.43 \pm 34.16$‰, $d_{exc} = 1.91 \pm 7.72$‰). Such a significant discrepancy may be due to higher (by 4–5°C) mean winter temperatures recorded for the period from 1996 to 2000 [*Weather and Climate, 2004–2021*].

Fractionation of the isotopic composition of the snow cover as a result of its recrystallization ("metamorphization of the isotopic composition"). A study of the isotopic composition of the snow cover along the transect from Yakutsk to Magadan was performed within the framework of the international TVSSE (Trans-Verkhoyansk Snow Survey Expedition) in March 2001 [*Kurita et al., 2004*]. A total of 16 vertical isotope profiles were studied. In all sections of the snow cover, regardless of its thickness, four main stratigraphic layers were identified, differing in the morphology of snow crystals: freshly fallen snow, granular crystals (firn), crystals of deep frost in the form of goblets, and columnar crystals of deep frost [*Kurita et al., 2005*].

In all sections, a significant vertical variation of the isotopic composition was established (Fig. 8). It was especially pronounced in the snow cover of the Central Yakut Plain, as well as in the intermontane depressions of the Verkhoyansk and Kolyma Highlands, where $\Delta\delta D$ and Δd_{exc} in the snow reached 100 and 20‰, respectively [*Kurita et al., 2005*]. However, only three layers were isotopically expressed in most sections (Fig. 8).

A characteristic feature of all isotope profiles is the heaviest composition in the lower layers of the snow cover, which make up from 50 to 70% of its thickness. The same layers are characterized by the highest positive values of deuterium excess (10...25‰) [*Kurita et al., 2005*]. The lightest compositions are characteristic of the upper parts of all profiles and do not show a significant connection with the crystalline types of snow. At the same time, they have the lowest deuterium kurtosis (0...10‰). The isotopic composition of fresh snow in the surface layer (1–2 cm) is significantly heavier in most of the profiles and has a low d_{exc} value.

Similar vertical variations in the values of δD and d_{exc} are characteristic of the snow cover sections at o.p. 1–6 in Yakutsk and its environs in January 2021 (Fig. 8). For comparison, the sections also show samples of crystalline hoarfrost taken from tree branches at a height of 1.0–1.5 m above the snow cover surface. All sections are characterized by a heavier composition of the lower layer (–250...–220‰), which has the highest deuterium kurtosis (10...20‰) decreasing towards Yakutsk. The upper layer of snow cover with distance from Yakutsk (o.p. 1–3) is characterized by a significant decrease in δD to –350...–360‰ and a simultaneous increase in deuterium excess to +6...+10‰. In Yakutsk, the δD value in the upper snow cover varies from –275 to –313‰ and increases towards the city center. While the deuterium kurtosis significantly decreases and takes on negative values (–3...–6‰). The layer of crystalline frost at all sampling points is characterized by a significant weighting of its isotopic composition. The maximum increase in the value of δD by 50–60‰ is observed outside the impact zone of Yakutsk at o.p. 1 and 2, while d_{exc} practically does not change. Within the territory of Yakutsk (o.p. 4–6) in the layer of crystalline hoarfrost, the values of δD increase by 10–30‰, while the deuterium kurtosis sharply decreases to extremely low negative values (–27...–80‰). The lowest d_{exc} values are found in the samples taken in the center of Yakutsk (–27...–32‰) and near the building of the MPI SB RAS (–80‰). The authors attribute the latter to the influence of technogenic steam from the burned fuel. With the exception of the top layer of snow cover and crystalline frost at o.p. 4–6, the remaining isotopic profiles are very similar to the snow cover of other ultracontinental regions of Yakutia (Fig. 8) [*Kurita et al., 2005*].

Experimental studies show that as a result of a significant temperature gradient between the surface and the base of the snow cover, the processes of sublimation and desublimation develop in it, which leads to recrystallization and the formation of a deep hoarfrost layer. These processes are accompanied by significant isotope fractionation affecting mainly the base and the surface of the snow cover. while the isotopic composition of the middle part of the snow cover does not change significantly. The essence of this process is as follows [*Sommerfeld et al., 1991; Hachikubo et al., 2000*]. In winter, sublimation of light H_2O molecules and their upward migration through the pores in the snow cover from a warmer base to its much colder top and crystallization (desublimation) of these molecules in the near-surface layer take place. Conversely, in spring, the top of the snow cover heats up stronger than the base, which leads to the reverse process of the transfer of light molecules to the lower layers of the snow cover.

In other words, as a result of the so-called process of metamorphization of the isotopic composition of the snow cover, the composition of the latter becomes heavier within the subliming layer and, conversely, under the influence of desublimation, the composition of the layer becomes isotopically lighter [*Sommerfeld et al., 1991; Hachikubo et al., 2000; Ku-*

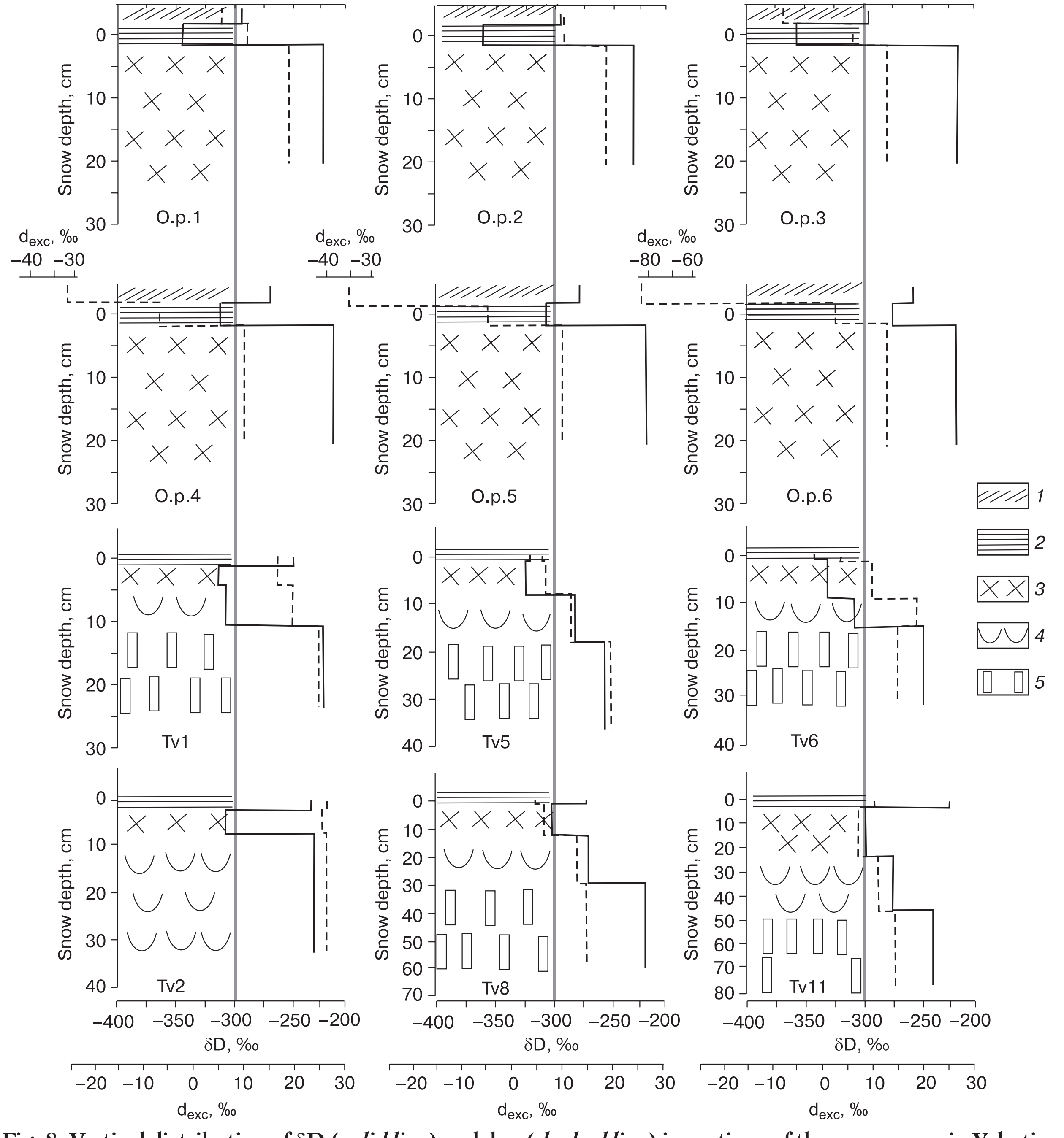

Fig. 8. Vertical distribution of δD (*solid line*) and d_{exc} (*dashed line*) in sections of the snow cover in Yakutia.

Observation points: o.p. 1–6 – Yakutsk and environs in December 2020–January 2021 (data from this article); Tv1–Tv11 – snow cover sections in March 2001 along the Trans-Verkhoyansk TVSSE profile according to [*Kurita et al., 2005*] (authors' designations). Precipitation type: *1* – hoarfrost on tree branches at a height of 1.0–1.5 m from the surface; *2* – loose fresh snow; *3* – fine-grained snow; *4* – large crystals of deep hoarfrost in the form of goblets; *5* – large columnar crystals of deep hoarfrost.

rita et al., 2005]. At the same time, despite the presence of signs of significant recrystallization in the studied sections of the spring snow cover along the TVSSE profile, it is not possible to explain both the heavy composition and the high kurtosis of the lower snow layers as a result of "metamorphization" [*Kurita et al., 2005*]. Indeed, kinetic fractionation and weighting of the isotopic composition of the lower layers of snow, their deuterium kurtosis should decrease. Conversely, if the light isotopic composition of the upper layers of the snow cover is associated with post-sedimentary enrichment in light isotopes as a result of desublimation, then their deuterium kurtosis should increase.

Thus, vertical variations in the isotopic composition of the snow cover in spring along the TVSSE profile are due to differences in the initial composition of snow precipitation at the beginning, middle, and end of the winter period rather than to the snow cover metamorphism [*Kurita et al., 2005*]. The most isotopically heavy snow with a high deuterium kurtosis fell at the beginning of the winter period at relatively high air temperatures from undepleted moisture-bearing masses. The lightest snow is associated with the coldest period of winter, while its low deuterium excess is due to the large depletion of the air mass. Finally, a more isotopically heavier thin surface layer was formed in spring as a result of blizzard transport and new portions of snowfall that fell at higher temperatures at the end of the winter period [*Kurita et al., 2005*]. These conclusions are fully consistent with our results.

Isotopic composition of atmospheric precipitation in the winter period 2013–2014. A new series of observations over the isotopic composition of atmospheric precipitation in Yakutsk was carried out from October 2013 to September 2014 [*Malygina et al., 2015; Papina et al., 2017*]. A different sampling strategy was used than in previous studies [*Kurita et al., 2004, 2005*]. The sampling site was equipped on the roof of the building of the MPI SB RAN, located in the suburbs of Yakutsk (103 m a.s.l.). Snow was collected as it fell, melted, and immediately packed into sealed cuvettes with a volume of 10–20 mL. The analysis was performed at the Chemical Analytical Center of the Institute for Water and Environmental Problems of the Siberian Branch of the Russian Academy of Sciences (IWEP SB RAS), where the samples were sent in batches 2–3 times a year.

Selected cold season precipitation in 2013–2014 in Yakutsk (8 samples) are approximated by the equation $\delta D = 8.17{\cdot}\delta^{18}O + 21.9$ ($R^2 = 0.99$, $n = 8$) and are characterized by weighted average values $\delta^{18}O = -31.65‰$ and $\delta D = -237.1‰$. Except for single outliers, the authors note a high value of $d_{exc} > +10‰$ for all samples [*Papina et al., 2017*]. Moreover, during the cold season, a continuous lightening of the isotopic composition and an increase in the deuterium surplus were observed, the highest value of which (+21.4‰) is typical for precipitation in February–March.

In addition to atmospheric precipitation, in January 2014, the vertical variation of the isotopic composition in the snow cover was studied at the Tuymada weather station, located 500 m from the building of the MPI SB RAS [*Malygina et al., 2015*]. Here, on a site of a natural pine–birch forest, a snow cover with a thickness of 21 cm was opened with a pit, in which three layers were visually distinguished. The lower layer (6 cm) was mainly composed of deep hoarfrost; the middle layer (12 cm) consisted of medium-grained white snow, and the upper layer (3 cm) consisted of freshly fallen slightly compacted blizzard snow.

Seven samples were taken every 3 cm, the analysis of which showed a large variation in the isotopic composition along the section. The composition of the lower layer was the heaviest ($\delta^{18}O = -17.1‰$, $\delta D = -160.6‰$), and the composition of the upper layer was the lightest ($\delta^{18}O = -45.0‰$, $\delta D = -350.6‰$). Even more unusual were the values of the deuterium kurtosis and its regular increase from −17.1‰ at the base of the lower layer to +25.3‰ in the middle layer and again decreasing to +10‰ in the upper layer.

The heavy composition of the lower snow layers and the low negative kurtosis are explained by the authors by the process of "metamorphization of the isotopic composition" [*Malygina et al., 2015*] as a result of the enrichment of the lower snow layers with isotopically heavier water vapor crystallization products (hoarfrost) coming from the underlying soil. This definition is completely different from the understanding of the process of "metamorphization of the isotopic composition" of the snow cover, considered in [*Sommerfeld et al., 1991; Hachikubo et al., 2000; Kurita et al., 2005*]. According to the results of these experiments, the isotopic composition of the lower layers of snow, which is heavier and depleted in deuterium, is associated only with isotope exchange within the snow cover profile, and not with the addition of moisture from outside.

The extremely high positive (+25.3‰) values of the deuterium kurtosis established by N.S. Malygina et al. [*2015*] in the middle snow layer of Yakutsk.

Thus, the data of N.S. Malygina et al. [*2015*] and T.S. Papina et al. [*2017*] strongly contradict the results of TVSSE [*Kurita et al., 2005*], according to which, in all 16 studied profiles of spring snow cover, the lower snow layer has the heaviest isotopic composition and the highest deuterium kurtosis. At the same time, the upper lightest layers are characterized by a low deuterium kurtosis reaching negative values in some samples.

The regression equation $\delta D = 7.01{\cdot}\delta^{18}O - 19.7$ ($R^2 = 0.97$, $n = 8$), which characterizes the entire set of samples in the snow cover section, also calls into question [*Malygina et al., 2015*]. Its coefficients, according to the authors, indicate a significant "metamorphization" of the isotopic composition of the initial snow precipitation. In addition, this equation is almost identical to the regression equation $\delta D = 7.22{\cdot}\delta^{18}O - 18.9$ ($R^2 = 0.95$, $n = 23$) obtained for Yakutsk atmospheric precipitation that fell during the warm period of 2014 [*Papina et al., 2017*]. The great similarity of these equations, which characterize fundamentally different atmospheric precipitation in different seasons of the year in the same area, raises questions about the reliability of the initial data.

According to the authors of this article, the problematic interpretation of the results obtained by N.S. Malygina et al. [*2015*] and T.S. Papina et al. [*2017*] for winter precipitation is due to the significant influence of CDW. Indeed, the sampling site – institute's roof – is located less than 100 m from the boiler house chimney. The boiler house, as shown by the data of this article, is a powerful source of CDW in winter. The same applies to the Tuymada station, where the snow cover section was studied. It is located at a distance of about 700 m from the boiler house.

CONCLUSIONS

The isotopic (^{18}O, D) and chemical compositions of atmospheric precipitation (crystalline hoar, snow cover surface, average snow stock) that fell in Yakutsk and its environs in December 2020–January 2021 was studied during the period of extremely low temperatures (from –47 to –52°C).

It was found that atmospheric precipitation of that period differed in its isotopic composition in on the type of precipitation (snow, hoarfrost) and on the distance from the center of Yakutsk. The main thickness (2–20 cm from the surface) of the snow cover on all plots is composed of precipitation at the beginning of winter, which fell at relatively high temperatures from –12 to –25°C in October–November 2020. In all observation points, this snow had the same isotopic composition ($\delta^{18}O$ = –29.45 ± 1.1‰, δD = = –221.8 ± 5.57‰, d_{exc} = 13.78 ± 3.52‰) attesting to its formation under the conditions of equilibrium kinetic fractionation and an insignificant fraction of CDW.

In the subsequent period, from mid-December 2020 to January 2021, precipitation in Yakutsk formed under conditions of anticyclonic calm weather and extremely low temperatures from –45 to –53°C. The total amount of precipitation in this period was about 6 mm and formed a thin surface layer of snow (0–2 cm) and hoarfrost of up to 10 cm in thickness on tree branches and other objects.

Samples from the surface of the snow cover (0–2 cm) had the lightest isotopic composition ($\delta^{18}O$ = –41.04 ± 5.11‰, δD = –326.43 ± 34.16‰, d_{exc} = 1.91 ± 7.72‰) and were noticeably impoverished in deuterium. Along the studied 25-km-long profile towards the center of Yakutsk, the composition became heavier by 10‰ in $\delta^{18}O$ and by 80‰ in δD with a decrease in d_{exc} from +10 to –6‰, and a fourfold increase in mineralization due to calcium carbonate impurities.

The most exotic isotopic composition ($\delta^{18}O$ = = –30.89 ± 5.62‰, δD = –285.88 ± 12.82‰, d_{exc} = –28.79 ± 32.53‰), which is not characteristic of any natural atmospheric precipitation, surface and ground waters, and ice in the region, was found for samples of crystalline hoarfrost, with the greatest changes in $\delta^{18}O$ from –24‰ in Yakutsk to –37‰ at a distance of 25 km from its center. In the same interval, δD changed from –255.4 to –285.9‰, and d_{exc} increased from –80 to +11.5‰.

In crystalline hoarfrost, the maximum proportion of CDW (26–32%) was obtained near the sources of the CDW (the building of the MPI SB RAS); in the central part of the city, it reached 13–18%; in the suburbs, it varied from 6.5 to 8.8%. In the surface layer of the snow cover, the share of CDW was 5–6% in the central part of Yakutsk and decreased towards the suburbs to 1% or less.

The exotic composition and the nature of the spatial variation of the isotopic composition indicate the decisive role of the anthropogenic source of water vapor in precipitation in Yakutsk at temperatures below –45°C. The influence of the isotopic composition of the anthropogenic source of water vapor is clearly manifested within a radius of up to 10 km from the center of Yakutsk. On the whole, this conclusion agrees well with the conclusions of predecessors about the presence of unknown sources of atmospheric moisture in Yakutsk in winter [*Kurita et al., 2005*].

The increase in recent years in the duration and frequency of ice fogs, as well as in the thickness of crystalline hoarfrost in Yakutsk, according to the authors, may be associated with the operation of a new state district power station and the transfer of most heat generating stations to gaseous fuel, which is characterized by a large specific emission of anthropogenic water vapor derived from fuel combustion.

Funding. *This work was supported by the Russian Science Foundation (grant No. 21-17-00054, https://rscf.ru/project/21-17-00054/).*

References

Beesley J.A., Moritz R.E., 1999. Toward an explanation of the annual cycle of cloudiness over the Arctic Ocean. *J. Climate*, No. 12, 395–415. DOI: 10.1175/1520-0442(1999)012<0395:TAEOTA>2.0.CO;2.

Bowling S.N., Ohtake T., Benson C.S., 1968. Winter pressure systems and ice fog in Fairbanks, Alaska. *J. Applied Meteorol.* **7** (6), 961–968. DOI: 10.1175/1520-0450(1968)007<0961:WPSAIF>2.0.CO;2.

Dansgaard W., 1964. Stable isotope in precipitation. *Tellus*, XVI (4), 436–468.

Ekajkin A.A., 2016. Stable Isotopes of Water in Glaciology and Paleogeography. Methodological Guidelines. St. Petersburg, SSC RF AANII, 68 p. – https://www.researchgate.net/publication/311419330_Stabilnye_izotopy_vody_v_

Fiorella R., Bares R., Lin J. et al., 2018. Detection and variability of combustion-derived vapor in an urban basin. *Atmos. Chem. Phys.* **18**, 8529–8547. DOI: 10.5194/acp-18-8529-2018.

Galanin A.A., 2020. Stable isotopes ^{18}O and D in cave ice of the Lena Pillars National Nature Reserve (Eastern Siberia). *Earth's Cryosphere* XXIV (1), 3–19.

Galanin A.A., Pavlova M.R., Papina T.S. et al., 2019. Stable isotopes ^{18}O and D in main sources of water runoff and permafrost of Central Yakutia (Eastern Siberia). *Ice and Snow* **59** (3), 333–354. DOI: 10.15356/2076-6734- 2019-3-414.

Gallagher M., 2020. Ice fog: the current state of knowledge and future challenges. *Meteorol. Monographs* **58**, 4.1–4.24. DOI: 10.1175/AMSMONOGRAPHS-D-17-0002.1.

Gavrilova M.K., 1962. The Climate of Central Yakutia. Yakutsk, 63 p. (in Russian).

Gorski G., Strong C., Good S. et al., 2015. Vapor hydrogen and oxygen isotopes reflect water of combustion in the urban atmosphere. *PNAS*, **112** (11), 3247–3252.

GOST 31861-2012, 2013. Water. General Requirements for Sampling. Moscow, Standardinform, 35 p. (in Russian).

Hachikubo A., Hashimoto S., Nakawo M., Nishimura K., 2000. Isotopic mass fractionation of snow due to depth hoar formation. *Polar Meteorol. Glaciol.*, No. 14, 1–7. – https://www.pnas.org/content/pnas/112/11/3247.full.pdf

Kurita N., Sugimoto A., Fujii Y. et al., 2005. Isotopic composition and origin of snow over Siberia. *J. Geophys. Res.* **110**, p. D13102. DOI: 10.1029/2004JD005053.

Kurita N., Yoshida N., Inoue G., Chayanova E.A., 2004. Modern isotope climatology of Russia: A first assessment. *J. Geophys. Res.* **109**, p. D03102. DOI:10.1029/2003JD003404.

Kuznetsov A.M., 2010. Specific fuel consumption for heat generation at CHPPs. *Novosti Teplosnabzheniya,* No. 4 (116), 22–23. – http://www.ntsn.ru/ (in Russian).

Lacelle D., Lauriol B., Clark I.D., 2009. Formation of seasonal ice bodies and associated cryogenic carbonates in Caverne de l'Ours, Que'bec, Canada: Kinetic isotope effects and pseudo-biogenic crystal structures. *J. Cave Karst Studies* **71** (1), 48–62.

Makarov V.N., Torgovkin N.V., 2020. Pollution of the atmosphere of the city of Yakutsk by suspended substances. *Prirodn. Res. Arkt. Subarkt.* **25** (1), 43–50. DOI: 10.31242/2618- 9712-2020-25-1-4.

Malygina N.S., Papina T.S., Eirikh A.N. et al., 2015. Isotopic composition of atmospheric precipitation and snow cover in Yakutsk. *Nauka Obrazovan.* **79** (3), 10–15 (in Russian).

Papina T.S., Malygina N.S., Eirikh A.N. et al., 2017. Isotopic composition and sources of atmospheric precipitation in Central Yakutia. *Earth's Cryosphere* XXI (2), 52–61.

Sessions A.L., Burgoyne T.W., Schimmelmann A., Hayes J.M., 1999. Fractionation of hydrogen isotopes in lipid biosynthesis. *Organic Geochem.* **30** (9), 1193–1200. DOI: 10.1016/S0146-6380(99)00094-7.

Shvartsev S.L., 1996. General Hydrogeology. Moscow, Nedra, 423 p. (in Russian).

Shver Ts.A., Izyumenko S.A. (Eds.), 1982. Climate of Yakutsk. Leningrad, Gidrometeoizdat, 246 p. (in Russian).

Sommerfeld R.A., Judy C., Friedman I., 1991. Isotopic changes during the formation of depth hoar in experimental snowpacks. In: *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*, Spec. Publ. H.P. Taylor, J.R. O'Neil, I.R. Kaplan (Eds.). St. Louis, Geochem. Soc., No. 3, 159–168. – https://www.geochemsoc.org/files/1714/1269/7652/SP-3_205-210_Sommerfeld.pdf

van Geldern R., Barth J., 2012. Optimization of instrument setup and post-run corrections for oxygen and hydrogen stable isotope measurements of water by isotope ratio infrared spectroscopy (IRIS). *Limnol. Oceanogr. Methods* **10**, 1024–1036. DOI: 10.4319/lom.2012.10.1024.

Weather and Climate. Data Base Catalog, 2004–2021. – http://www. pogodaiklimat.ru (accessed: February 26, 2021).

Whiticar M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chemical Geol.* **161** (1–3), 291–314. DOI: 10.1016/S0009-2541(99)00092-3.

Xing M., Liu W., Li X. et al., 2020. Vapor isotopic evidence for the worsening of winter air quality by anthropogenic combustion-derived water. *PNAS*, **117** (52), 33005–33010. DOI: 10.1073/pnas.1922840117.

Received July 13, 2021
Revised June 10, 2022
Accepted July 17, 2022

Translated by A.V. Muravyov