SCIENTIFIC JOURNAL
EARTH'S CRYOSPHERE

Earth`s Cryosphere, 2014, vol. XVIII, No. 3, pp. 62–71 **http://earthcryosphere.ru/**

CRYOGENIC PROCESSES AND FORMATIONS

SPECIFIC CHARACTERISTICS OF CRYOGENIC MINERAL FORMATIONS OF OKHOTNICHYA CAVE IN PRE-BAIKAL AREA (IRKUTSK REGION)

E.P. Bazarova, A.M. Kononov, O.S. Gutareva, N.V. Nartova

Institute of the Earth Crust, Siberian Branch of the Russian Academy of Sciences, 128 Lermontov str., Irkutsk, 664033, Russia; bazarova@crust.irk.ru

Cryogenic minerals of two types (coarse-grained and fine-grained) have been discovered in the Okhotnichya cave, located in the western Pre-Baikal area. These formations are composed of rare metastable mineral ikaite ($CaCO_3 \cdot 6H_2O$), for the time being documented only in two caves in the world. Considering the abundance of coarse-grained cryogenic mineral formations, we could infer that cave ice may have covered the area of about 400 m^2 in Okhotnichya cave, with frost penetration into rocks to depths greater than 25 m within its area.

Caves, cryogenic mineral formations, ikaite, coarse-grained cryogenic cave carbonates

INTRODUCTION

In caves studies, geologist-karstologists have always paid much attention to the specific minerals of cryogenic origin. Many karst systems containing cryogenic minerals are now outside the permafrost zone development, which may be indicative of the paleogeocryologic processes in the past.

G.A. Maksimovich [*1947*] was, probably, among the first to mention of cryogenic formations of caves, and the one who brought into limelight earthy gypsum and scattered gypsum crystals formed on the ice cover in Kungur ice cave during its summer ablation. For the time being, however, a number of papers have addressed cryogenic minerals of caves [*Alekseeva, 1965; Dorofeev, 1966; Maksimovich and Panarina, 1966; Savenko, 1976; Andreychouk, 1989; Andreychouk and Galuskin, 2001, 2008; Moloshtanova et al., 2001; Andreychouk et al., 2004, 2005, 2007, 2009; Žãk et al., 2004, 2008, 2009, 2010, 2011; Potapov et al., 2008a,b, 2009; Andreychouk, 2009; Lacelle et al., 2009*] which generally describe cave formations of the Urals and, in particular, Kungur ice cave, Pinega and other world caves. As a rule, the material on the surfaces of ice formations or in place of their disappearance attests to the cryogenic origin of mineral formations. These mineral formations can be used in palaeoglaciological and paleoclimatic reconstructions, and besides their investigations has proven of great importance in sedimentology and mineralogy [*Andreychouk and Galuskin, 2008*].

More than a half of known caves in Irkutsk region are known for either seasonal or old ice (MY ice). Such abundance of cave ice was conditioned by a harsh winter climate and the development of perennially frozen rocks of various types (continuous, discontinuous, insular) in the area, as well as by their relatively high elevation above mean sea level, from 500 m (Central Siberian Plateau) to 2,500 m (Baikal-Sayan mountain region) [*Filippov, 1997*].

Cryogenic minerals found in the underground cavities in Irkutsk region were described for Bolshaya Baidinskaya [*Filippov, 1989*], Talovskaya, Bolshaya Onotskaya and Zagadai [*Filippov, 1997*], as well as Kholodnaya, Aya-Ryadovaya, Botovskaya and Khrustalnaya [*Bazarova, 2011b*] caves.

Okhotnichya cave, being unique in mineral sense among the caves both in Irkutsk region and entire Russian area, is discussed in detail in this paper, particularly, its mineral composition, occurrence conditions in the underground cavity and possible formation mechanisms of cryogenic minerals of two types.

METHODS OF STUDY

This paper presents the results of the analyses of cryomineral formations sampled in cooperation with speleologists from Irkutsk "Arabika" Speleological Club. The mineral composition was determined in the Analytical Center at the Institute of the Earth Crust, SB RAS (Irkutsk). The thermoanalysis was carried out by N.V. Nartova using Q-1500D Derivatograph, with the following survey parameters: sensitiveness (DTA – 250, TDG – 500, TG – 100), heating rate (10 °C/min), quantity weighed for analysis (100, 200, 500 mg), inert matter (Al_2O_3), atmosphere (air), heated (up to 1,000 °C), platinic crucibles; X-ray phase analysis was performed by Z.F. Ushapovskaya with Diffractometer DRON-3 in CuKα-radiation, with the X-ray diffraction patterns recorded using a copper-anode X-ray tube. L.A. Durban, the analyst, determined the chemical composition of underground water and cave ice by titrimetry, gravimetry and atomic absorption spectrometry, and other analysts, G.V. Bondareva and M.M. Samoilenko, gauged the chemical composition of host rocks through a silicate analysis. The underground water composition as well as the air temperature at the day surface and in the cave has been monitored the year round since 2010 in the cryomineral formations concentrations in Okhotnichya cave. The air temperature was measured with HOBO Pendant Temperature Data Logger #UA-001-64K (measurement accuracy: (±0.47 °C), measurement interval (every 3 hours)) and Tinytag Plus2 TGP-4500 (measurement accuracy: (±0.01 °C)).

GENERAL INFORMATION ON THE CAVE AND MICROCLIMATIC CONDITIONS IN THE AREA OF CONCENTRATIONS OF CRYOGENIC MINERAL FORMATIONS

Okhotnichya cave is located in the western Pre-Baikal area. The climate is classified as distinctly continental with long harsh winters and short hot summers. The mean annual atmospheric temperatures range from –1.1 °C in Irkutsk to –2.7 °C in Bayanday. The amount of solar energy falling upon the day surface being not sufficient, this largely shapes the area's climate. The summations of annual radiation vary from 105 to 160 W/m^2. Given the atmospheric temperature inversions are caused by anticyclonic climate regime in winter, the temperature in the valleys tends to be 5–6 °C lower than that in the watershed areas with absolute elevations from 800 to 1,000 m. The amount of annual precipitations is distributed non-uniformly and totals 324 mm/year in the Tazheran steppes within the Pre-Olkhon area, and 468 mm/year in the Angara valley; the snow cover depth varies from 33 to 58 cm, respectively [*Geocryology..., 1989*].

The climatic conditions of the area have proven to be one of the main factors affecting the formation of perennially frozen rocks (PFR). The Pre-Baikal areas are subsumed into the southern geocryological zone of the development of insular permafrost [*Geocryological map..., 1991*].

The PFR thicknesses confined to the river valley sides of northern exposure, boggy parts of intermontane valleys, and northward slopes do not exceed 30 m. The permafrost temperature varies from –0.2 to –0.5 °C there. On the watershed slopes of the Primorsky Range, the permafrost occurs in all the terrain elements, and its thickness tends to grow up to 80 m there [*Engineering geology..., 1968*]. PFR thickness varies from 40 to 60 m in the vicinities of Bayanday village, with the in situ temperatures from –0.5 to –1.0 °C. The depth of active layer reaches 1.7–2.5 m. The temperature of seasonally frozen soils averages at 1.6 °C. The depth of annual temperature variations* constitutes 8–10 m [*Leshchikov, 1978*].

In terms of hydrogeology, Okhotnichya cave is related to fissure-vein cavern waters of the Primorsky Range. The underground water regime is largely determined by the precipitation depth and characterized by the availability of stable winter low water. The aquifers of the Baikalian rock weathering zone are, basically, drained by a large amount of springs with flow rate from tenths to 1–2 l/s. The springs aligned to the outcrops and carstified massifs have greater flow rates of 0.3–1.0 to 4.5–8.0 l/s. The underground water composition includes hydrocarbonate magnesium-calcium and sulphate-hydrocarbonate calcium-sodium, with mineralization not greater than 0.2–0.3 g/dm^3 [*Pinneker et al., 1968*].

The entrance to the cave opens up in the northern slope of the Primorsky Range outskirts separating the Uglovaya and Elovka rivers basins. Its absolute elevations reach 800–1,000 m. The cave was formed within the oncolite and stromatolite limestones and dolomites of the Upper-Proterozoic Uluntui Formation. A big grotto 15–20 m wide and 5–10 m high begins just at the entrance, and it goes deep down into the cave, as a steeply inclined block talus. Okhotnichya cave is ranked third in length in the Baikal region. It measures up to 5,700 m in lenght at 77 m amplitude (according to the Arabika Speleoclub data). The cave system is laid along a series of subparallel faults of north-northeast strike (Fig. 1). The galleries exhibit both spacious and narrow passages, as high as 25 m, with characteristic slit-like section.

The cave largely represents secondary formations of different origin: residual, avalanchine, water mechanical, water chemogenic, cave snow and ice (seasonal formations) and organogenic. Cryogenic minerals were found in places of old and seasonal ice extent in close vicinity to the cave's entrance.

The underground waters of Okhotnichya cave discharge into the cave's galleries through a system of fractures and accumulate, forming lakes and small puddles. Two hydrogeochemical zones, conditioned by the involvement of the underground water in leaching of host rocks of various compositions, are clearly discriminated in the cave. The underground water of one zone confined to sulphate-carbonate rocks (limestones and dolomites with small gypsum interbeddings) is characterized by sulphate-hydrocarbonate calcium composition and mineralization value of 56–339 mg/dm^3:

$$M\,290;\ \frac{HCO_3\,63\,SO_4\,36\,Cl\,0.8}{Ca\,85\,Mg\,13\,Na\,1.7\,K\,0.3};\ \text{pH}\,7.5;\ t = 1.6\ ^\circ\text{C}.$$

* The depth of the lower boundary of gas thermal circulations layer with zero amplitudes.

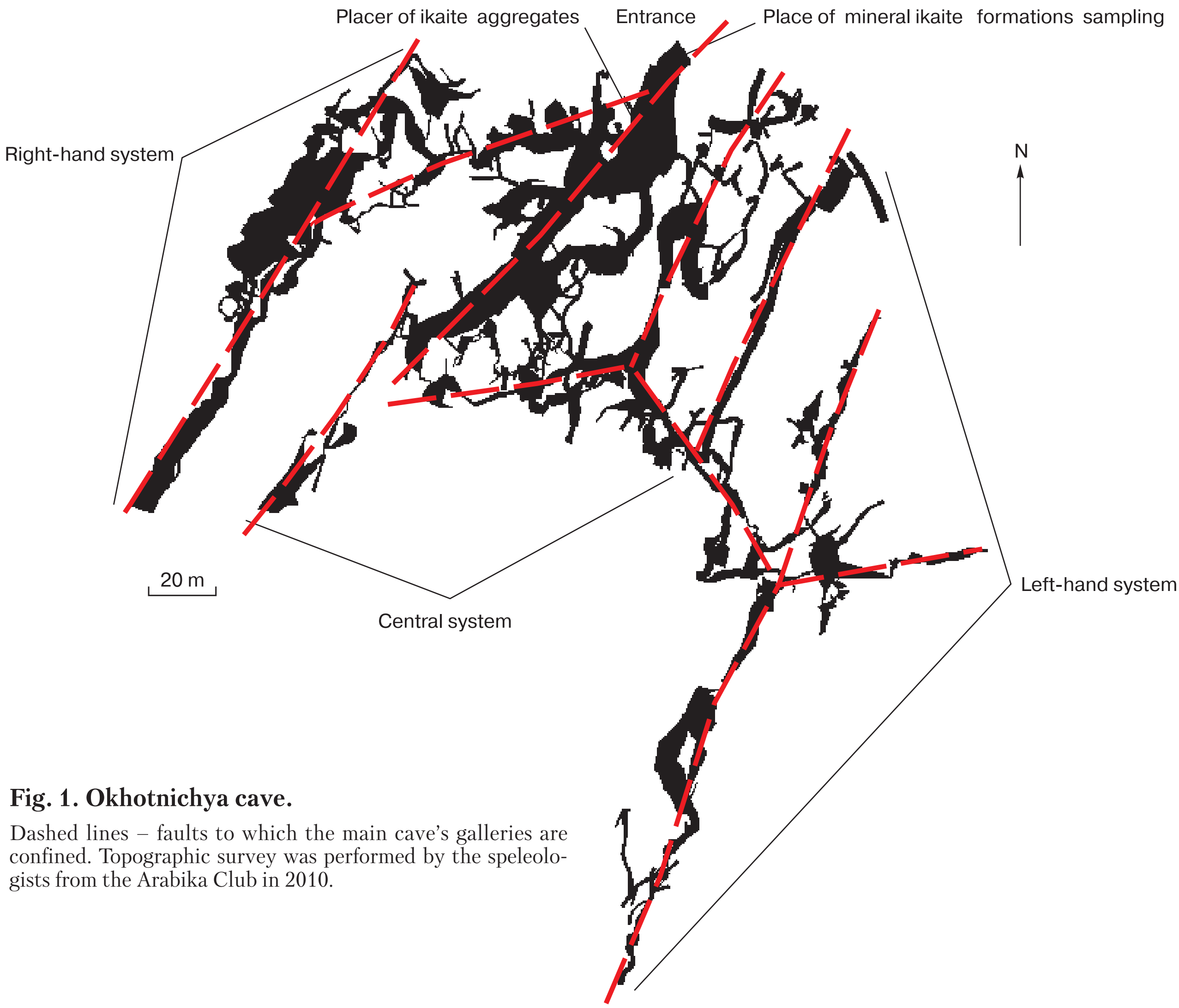

Fig. 1. Okhotnichya cave.

Dashed lines – faults to which the main cave's galleries are confined. Topographic survey was performed by the speleologists from the Arabika Club in 2010.

Within this zone, the secondary gypsum formations are abundant, among them antholites (the so-called "gypsum flowers" [*Hill and Forti, 1997*]) and crystallictites. The water of another zone was formed in carbonate rocks (limestone, dolomite) and is characterized by hydrocarbonate magnesium-calcium composition with mineralization of 258 to 300 mg/dm^3:

$$M\,277;\ \frac{HCO_3\,91\,SO_4\,7.2\,Cl\,1}{Ca\,63\,Mg\,35\,Na\,0.8\,K\,0.5};\ pH\,7.6;\ t = 1.2\ ^\circ C.$$

The zone is characterized by predominantly calcite secondary formations and the absence of gypsum ones.

The seasonal air temperature variations were derived from the March 2010 through November 2011 temperature monitoring in places of cryogenic mineral formations concentrations. Temperatures below freezing become stable late in November and reach their minimum of –1.34 °C mid-December. In March–April, air temperature rises to values close to above zero. Maximum temperature of +0.34 °C recorded from the end of summer to late autumn and then in November sharply drops down to values below freezing, which bears the evidence of the summer atmospheric circulation pattern changing to that of winter. The reported mean annual temperature was 1.26 °C. On the day surface, near the cave's entrance the air temperature varies within wider limits, though. Over the time of observations, the temperature was documented as: 29.95 °C maximum, –35.23 °C minimum, and 0.48 °C on average.

Inside the cave, where temperature is subject to the least variations, the measurement were done with a higher precision logger, according to which the air temperature: 1.23 °C minimum, 1.32 °C maximum, 1.26 °C annual average.

The temperature measurements showed that most of the year the air temperature is close to 0 °C in places of ikaite occurrence, whereas in deeper parts of the cave the temperature tends to rise, with its values changing very little.

The low (down to −1.34 °C) air temperatures lead to the formation of different ice forms in Okhotnichya cave. At the time the cave was found it had cave ice measured about 4 m^2 in area in the near-entrance grotto. In present day, the ice has gone, with only seasonal ice stalagmites as high as 0.5 m observable in its place (Fig. 2).

The ice in Okhotnichya cave is distinguished by its formation mechanism, subsumed either into congelation or ablimation types. Ablimation ice formation is evidenced at the cave's entrance, when ice is crystallized from warm and humid air of the cave in the form of tabular and acicular crystals (Fig. 3, *a*). In deeper parts of the cave, congelation or mixed ice formation predominates, with ice being formed either from water solutions or in the course of water condensation. Aggregates of massive ice build up in the cave's lows and at the foot of large blocks, whereas ice stalactites tend to form on the gently sloping domes, and stalagmites beneath them (Fig. 3, *b*). Comb-shaped ice forms can be seen on the steep walls of the cave gallery (Fig. 3, *e*). In some cases, ice buildups on the cave's walls are represented by aggregates of fanciful acicular crystals (Fig. 3, *d*).

Ice on vertical walls of the cave and on the surface of clays produces forms consisting of individual elongated and curved crystals of cylindrical section (Fig. 3, *c*). Antholites ("gypsum flowers") also have the form of this kind. In clayey deposits, ice forms fine- schlieren cryogenic textures.

Melts of ice stalagmites from Okhotnichya near-entrance grotto have low mineralization (45 mg/dm^3 on average). In terms of their composition, ice melts contain hydrocarbonate-calcium with low content of magnesium and relatively high content of chlorine and CO_3^{2-} :

$$M\,45;\ \frac{HCO_3\,94\,Cl\,4.3\,CO_3\,1.7}{Ca\,96.5\,Mg\,2\,K\,1.3\,Na\,0.3};\ \ pH\,8.3.$$

The Ca:Mg ratio in the ice melt reaches 85.7, which appears to be much higher than the mean value for the cave's underground water that equals 4.4. The low magnesium content in the ice melts and their inconspicuous mineralization attest to the fact that condensation waters are involved in the formation of ice.

OCCURRENCE CONDITIONS AND COMPOSITION OF CRYOGENIC FORMATIONS

At present only two types of cryogenic cave formations have been identified in carbonate caves [*Žãk et al., 2011*]: fine-grained cryogenic carbonates ("powder" or residual flour, as was termed by *B.R. Mavlyudov* [*2008*]) actually is found in all caves with underground ice, and much rarer type of coarse-grained cryogenic carbonates (known only in 20 caves in the world), built up of crystals or crystalline aggregates measuring a few centimeters in size. Cryogenic formations of both types were found in Okhotnichya cave.

Fig. 2. Seasonal ice stalagmites in the near-entrance grotto of Okhotnichya cave.

Fine-grained cryogenic formations of the first type are ubiquitous at the foot of ice stalagmites in the near-entrance grotto of the cave, as well as on ice blocks up to 2.0 × 1.5 m in size observable at the beginning of the left-hand cave system (Fig. 1). Coarse-grained cryogenic formations as individual crystals and crystalline aggregates measuring up to 2 cm, form a placer in the distal part of the nearby-entrance grotto, 25 m beneath the level of the entrance into the cave.

A sample of fine-grained cryogenic minerals taken in the near-entrance grotto at the foot of ice stalagmite appeared to be farinaceous light-yellow mass 1 mm thick. The thermoanalysis identified ikaite in its composition, however, the X-ray phase analysis showed the presence of both calcite and ikaite. The calcite admixture was most likely to have introduced by quick decay of ikaite at room temperature. The detailed examination of the total fine-grained mass under the binocular microscope revealed individual distinctly coarse amber-colored crystals measuring to 2 mm (their amount accounts for 10 % of the total sample mass) and fine black disseminations of what could be organic matter. Once the mineral grains have lost crystallization water, within a few minutes' time they changed their color to white and fell to pieces, when touched.

The placers of coarse-grained cryogenic minerals are visible on the surface of host rock blocks (Fig. 4). The total area of crystals distribution is about 3 m^2. There can be observed both fine (to 1 mm) crystals and their aggregates localized in the upper portion of the placer, and coarse (to 2 cm) crystalline aggregates

Fig. 3. Morphology of ice formations in Okhotnichya cave.

a – ablimation acicular and scale crystals in the near-entrance part of the cave; *b* – congelation ice (ice stalactites and stalagmites); *c* – ice crusts consisting of individual crystals like "gypsum flowers"; *d* – aggregates of acicular ice crystals; *e* – congelation ice crust with incrustive comb-shaped formations.

occurring essentially on the blocks in the lower portion of the placer.

The coarse-grained carbonates of the placer are made up of ikaite, as also are the fine-grained cryogenic carbonates described above. A sample of coarse-grained cryogenic carbonate from the Okhotnichya placer was surveyed with a diffractometer DRON-3 in CuKα-radiation. Prior to taking the analysis the sample was placed in the freezing chamber. The sample consists of ikaite $CaCO_3 \cdot 6H_2O$ with the following unit cell parameters: a = 8.85(1) Å, b = 8.25(1) Å, c = 11.01(1) Å, β = 110.5(1)°; V = 754 Å^3, indexed by ikaite from ASTM PDF*; slight traces of what may have been gypsum (7.69; 3.07).

The sequence of the formation of various morphologic types of coarse-grained cryogenic carbonates during ice formation [*Žãk et al., 2011*] has been established. Finer ikaite crystals of the Okhotnichya placer can be assigned to the first type of harpoon- and fan-like aggregates; aggregates of irregular spherical shape vaguely resembling standard cave corallites belong to another type. These shapes are characterized as “cauliflower” and “mushrooms” (see [*Žãk et al., 2011*]). Cryogenic carbonates appearing at the final stage of ice formation can be subsumed into the third type, which includes the rounded concave saucer-shaped ikaite aggregates abundant everywhere in Okhotnichya cave (both in the above described placer and in place of once-existing aufeis near the cave’s entrance) (Fig. 4). Acicular crystals radially growing from the single foundation form such “saucers”.

Apart from the mentioned shapes related to the coarse-grained cryogenic carbonates forms from the world caves, the Okhotnichya placer contains unique, not documented in any other caves, ikaite crystalline aggregates in the shape of flat plates covered with druses measuring up to 1 mm. Such aggregates are distinguished by their greatest sizes (up to 2 cm). Given the crystals of this type are poorly developed on their lower surface, this appears to be a typical feature of all the complanate formations (patelloid and tabular aggregates).

Fig. 4. Placer of coarse-grained cryogenic mineral formations from the distal part of the near-entrance grotto.

DISCUSSIONS

Mineral ikaite (hexahydrate of calcium carbonate, $CaCO_3 \cdot 6H_2O$) was discovered in 1963 in Ikka-Fjord, Greenland, close to the town of Ivigtut [*Pauly, 1963*]. Ikaite is a metastable mineral stable at a temperature of −1.9 to 7 °C [*Hugget et al., 2005*] that was first discovered in 2008 in Scarisoara cave, in underground cavities conditions [*Onac, 2008*], and then in cryomineral formations of Koda cave [*Žãk et al., 2010*]. In this region, besides Okhotnichya cave, ikaite was found in the cryomineral formations of Khrustalnaya and Kholodnaya caves [*Bazarova, 2011a*]. It should be noted that Okhotnichya, Khrustalnaya and Kholodnaya caves are confined to the uniform Uluntui Formation rocks.

Given that until the present time ikait finds has been known only in Scarisoara and Koda caves, it may be concluded that the presence of this mineral is indicative of the specific conditions in the underground cavities where it actually forms. The composition of cryogenic minerals depends on the chemical composition of water, which in turn is aligned with the lithology of host rocks [*Andreychouk and Galuskin, 2008*]. Table 1 provides the data obtained from silicate analysis of limestones and dolomites, where Okhotnichya cave originated, and the results of analysis of ikaite from the crystalline placer. Considering the mineral metastability, a thorough examination was given to the exsiccated matter, i.e. ikaite changed to calcite.

It is known that ikaite precipitates instead of calcite or aragonite in sea water or in solutions containing magnesium, phosphates and organic matters [*Gurvich and Bystrova, 2009*]. *J. Bischoff et al.* [*1993*] provided the results of water analyses from springs and Mono Lake. At its lakeside ikaite precipitates as long as both lake and spring water blend together. The magnesium content in the spring water varies within wide limits of 23 to 83 mg/l, and 33 mg/l in lake water. This being the case, the authors suggest that water temperature close to the freezing point and high concentration of ortho-phosphates have proven to be the best conditions for ikaite deposition. *J. Rodriguez-Blanco et al.* [*2014*] indicate that a metastable mineral of monohydrocalcite, which is often deposited together with ikaite, including the best known

* American X-ray card-index ASTM PDF. Issue 37, No. 416.

Table 1. **Chemical composition of host rocks from Okhotnichya and Khrustalnaya caves and the Okhotnichya coarse-grained cryogenic carbonates (mas.%)**

Sample	Place of sampling	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	LIC	CO_2	SO_3	SrO	Total
1	Okhotnichya, host rocks	1.99	<0.02	0.96	0.30	0.32	0.01	8.90	43.28	0.06	0.20	0.09	0.38	2.40	41.17	<0.05	0.13	100.19
2		2.00	0.05	0.90	0.26	<0.2	<0.01	1.43	52.36	0.11	0.21	0.09	0.36	2.22	40.21	0.05	–	100.25
3		1.36	0.03	0.51	<0.2	<0.2	<0.01	6.09	47.22	0.07	0.09	0.26	0.47	2.00	41.66	0.13	–	99.89
4		0.57	0.02	0.39	0.36	<0.2	<0.01	0.46	54.95	0.02	0.07	0.03	0.58	0.77	42.27	<0.05	–	100.49
5		0.71	<0.02	0.30	0.32	<0.2	0.01	0.46	54.56	0.11	0.09	0.05	0.49	1.48	41.72	0.05	–	100.35
6		0.41	<0.02	<0.25	<0.2	<0.2	<0.01	1.61	54.02	0.01	0.03	0.10	0.47	0.89	42.60	<0.05	–	100.14
7		0.35	<0.02	<0.25	<0.2	<0.2	<0.01	16.83	36.22	0.15	0.02	0.03	0.38	0.47	45.32	<0.05	0.04	99.81
8	Khrustalnaya, host rocks	6.68	0.02	1.20	0.22	0.39	0.01	11.26	37.40	0.12	0.15	0.03	0.36	2.37	39.77	<0.05	0.05	100.03
9		2.79	0.03	1.36	0.36	0.38	0.01	9.00	41.91	0.11	0.31	0.04	0.42	3.97	39.27	0.05	0.06	100.06
10	Okhotnichya, coarse-grained cryogenic carbonates	0.72	<0.02	0.26	<0.2	<0.2	<0.01	0.08	52.46	0.02	0.05	0.11	1.26	3.75	41.14	<0.05	0.04	99.89

Note. A dash means a component was not determined. Limits of petrogenic oxides (mas.%): TiO_2 0.02, MnO 0.01, K_2O 0.01, Fe_2O_3 0.2, FeO 0.2, SO_3 0.05, P_2O_5 0.03, Al_2O_3 0.25, H_2O 0.01. Losses during calcinations (LIC) 0.02. The analyses were made by silicate method (G.V. Bondareva and M.M. Samoilenko).

ikaite manifestation in the Ikka-Fjord, is formed in solutions with a Mg:Ca ratio of 0.17 to 65.

Organic matter is most likely to have been supplied into Okhotnichya cave with infiltration water discharging through the soils and roof of the cave.

The ikaite accumulations found in the cave belong to the second hydrochemical zone of hydrocarbonate magnesium-calcium waters. A higher content of magnesium ions in the water within this zone (up to 35 % equ.) suggests their input contributed by the host rock leaching. The host rocks composing the arch of the near-entrance grotto are characterized by the highest content of magnesium oxide (MgO – 16.83 mas.%) (Table 1, sample No. 7). At the same time, the content of oxide of phosphorus in the host rock samples is very low, as is the content of phosphorus ions in the cave's water. Magnesium and phosphorus in the exsiccated matter from the crystalline placer testify that a part of these components precipitates from the solution as an isomorphic admixture (the content of magnesium oxide, MgO, is 0.08 mas.%, phosphorus oxide, P_2O_5, 0.11 mas.%). The change in the chemical composition of the underground water in winter times, the presence of underground ice and specific minerals, along with low air temperature in the near-entrance grotto of the cave testify that the environment is notably favorable for cryogenesis.

Cryogenic mineral formation takes place during water-to-ice phase transitions. Crystallization of ice from ultrafresh and fresh solutions causes their cryogenic concentration and salt saturation, which leads to the equilibrium displacement and prompts the formation of cryogenic minerals [*Ivanov, 1998*]. Precipitated carbonate and sulphate salts solve slightly in the course of ice melting, which enables chlorines to pass into a liquid phase. Some specific features of cryogenic metamorphization of natural water were discussed in detail in a number of publications [*Gitterman, 1937; Nelson and Thompson, 1954; Anisimova, 1971; Kononova, 1974; Fotiev, 1996, 2002; Ivanov, 1998; Alekseev, 2000*]. V. Andreychouk and K. Žãk addressed the cryogenic mineral formation in gypsum and carbonate caves in their papers [*Žãk et al., 2004, 2008, 2009, 2010, 2011; Andreychouk and Galuskin, 2008; Andreychouk et al., 2009*].

The two revealed types of cave carbonates in Okhotnichya cave have different mechanisms of formation. Fine-grained cryogenic carbonates formed at quick freezing of a thin water layer at the ice surface (for example, in wintertime on seasonal ice formations in the near-entrance part of the cave). Stages of such minerogenesis with the formation of fine-grained cryogenic carbonates were directly observed in the caves and described by K. Žãk et al. According to their observations, the particles buried in the ice mass are released during vigorous ice evaporation in warm seasons and accumulate at the foot of ice bodies or on their surfaces. Apart from evaporation, ice melting may take place as well, leaving pits on the aufeis surfaces and allowing for cryogenic formations aggregate in them.

The formation mechanism of coarse-grained cryogenic carbonates has never been directly observed, though. The aggregates of complanate patelloid and tabular forms with crystals less developed in their lower part have been identified in Okhotnichya cave. This suggests that cryogenic formations developed during the slow freezing of relatively large volumes of water (puddles, small lakes or hydrogenic ice massifs) at the cave bottoms and precipitated on the surface of stony blocks, following the ice melting out. This formation mechanism was inferred in relation to caves in Slovakia [*Žãk et al., 2009, 2011*]. Along with the Cold Wind Cave [*Žãk et al., 2009*], similar calcite aggregates of various forms termed "cave grapes" were discovered in Geologov and some other caves in the Ural Mts [*Mavlyudov, 2008*].

In the distal and lower-most part of the near-entrance grotto of Okhotnichya cave there are most coarse-grained cryogenic carbonates. Their formation is assisted by convective overturn of cold air inside the grotto, providing conditions for cryogenic concentration of solutions that form ice. Ice showing a high concentration of dissolved salts in the lower part of the cave is formed due to more mineralized residual solutions flowing from ice in the upper part of the grotto. In the course of further melting of more mineralized ice, big crystal-jams and aggregates began to form. This mechanism typifies, on the whole, ice formation of river aufeis, with ice getting more mineralized as it moves away from the outflows of aufeis-forming water [*Ivanov, 1998*]. The same effects are observable during the formation of ice in the caves [*Mavlyudov, 2008*].

During 2006, cave ice remains underwent complete degradation in the near-entrance part, which is indicative of the microclimatic changes in the cave. Given the large spread area of cryogenic minerals at blocks of host rocks, there may have occurred a thick ice layer in the past. As individual crystalline aggregates were disclosed in the near-entrance grotto within tens of meters from the placer and also at the bottom of a well leading from the near-entrance grotto to the left system of the cave (a single finding), it is believed that in the past the underground ice filled the whole near-entrance grotto.

The placer described nere has been known since the cave's discovery (2006). These mineral formations were regularly sampled in different seasons over the past two years and as their mineral composition remained unchanged, it signifies the possibility of long-term ikaite conservation in the cave conditions.

CONCLUSIONS

Two varieties of cryogenic cave minerals were found in Okhotnichya cave, in particular: fine-grained and coarse-grained carbonates. The mineral composition of the carbonates is represented by a rare metastable mineral of ikaite. That said, earlier finds of coarse-grained cryogenic carbonates either consisted of calcite or represented calcite phantom crystals (pseudomorphs) in ikaite (glendonite) [*Onac, 2008*], but not pure ikaite.

The formation of different types of cave ice as well as specific cryogenic minerals was dictated by the climate specificity in the area, permafrost-hydrogeological conditions and cave microclimate.

The formation of ikaite instead of calcite in Okhotnichya cave appears to have been prompted by geochemical features of host rocks and underground water that formed, first, cave ice and then ikaite formations. The cave's constant microclimatic conditions with near-zero temperatures are favorable for long-term conservation of this metastable mineral.

The form of cryogenic mineral aggregates has prompted some insights into their formation mechanisms and provided indications of ice distribution scales in the past. On the basis of the colected data on the areal extent of coarse-grained ikaite formations, it can be suggested that the once-occurring ancient ice body and covering actually all the area of the near-entrance grotto was comparable to its size, with its length and width measuring up to 20 m total area of about 400 m^2.

In future, the dating of coarse-grained crystalline aggregates is supposed to be done in order to obtain evidence of the time span of their origination, which may have coincided with the formation of a thick strata of ground ice.

The authors express their gratitude to the speleologists of the Arabika Club for their help in collecting the samples, for providing the available data on and some photographs of the cave, and for carrying out topographic survey. Much credit goes personally to Z.F. Ushchapovskaya, G.V. Bondareva, M.M. Samoilenko and L.A. Durban, the analysts of the Institute of the Earth Crust, SB RAS, for the preformed analyses.

References

Alekseev, S.V., 2000. Cryogenesis of underground water and rocks by the example of the Daldyn-Alakit region of Western Yakutia (in Russian). SB RAS, Novosibirsk, 119 pp.

Alekseeva, E.V., 1965. Ice formations of the Divya cave. Caves. (in Russian) Perm, Issue 5 (6), pp. 28–29.

Andreychouk, V.N., 1989. Some original deposits in the Kungur ice cave connected with its glaciation. Mineraly i otlozheniya peshcher i ih prakticheskoe znachenie (in Russian). Perm dom nauki i tekhniki, Perm, pp. 22–23.

Andreychouk, V., 2009. Cryomineral formations from Koungour Ice Cave (Russia). Proc. of the 15th Intern. Congress of Speleology (Kerrvilley, July 19–26, 2009). Kerrvilley, Texas, USA, vol. 1, p. 277–282.

Andreychouk, V.N., Galuskin, E.V., 2001. Cryogenic mineral formations of the Kungur icecave. Caves (in Russian). Perm, Issue 27–28, pp. 108–116.

Andreychouk, V.N., Galuskin, E.V., 2008. Cryomineral formations of caves: introduction in problematics (in Russian). Speliologia i karstologia, No. 1, pp. 67–80.

Andreychouk, V., Galuskin, E., Persoiu, A., 2005. Cryomineral formations of Scarisoara Cave (Romania). Glacier cave and Glacial Karst in High Mountains and Polar Regions. Inst. of Geography, RAS, Moscow, p. 85–86.

Andreychouk, V., Galuskin, E., Ridush, B., 2004. Cryomineral formations from North Bukovinian Caves. 1st Intern. Workshop on Ice Caves: Abstracts. Milano, Italy, Univ. Milano, p. 36–37.

Andreychouk, V.N., Galuskin, E.V., Ridush, B.T., 2007. Cryogenic mineral formations from gypsum caves of Bukovina (in Russian). Severny Speleoalmanakh, Issue 7, pp. 40–52.

Andreychouk, V.N., Ridush, B.T., Galuskin, E.V., 2009. Pionerka Cave: conditions and specific character of cryogenic minerogenesis (in Russian). Speleologia i karstologia, No. 2, p. 54–69.

Anisimova, N.P., 1971. Formation of chemical composition of underground water of subgelisols (by the example of central Yakutia) (in Russian). Nauka, M., 195 pp.

Bazarova, E.P., 2011a. Cryomineral formations of some caves in the Irkutsk region. Karstovye sistemy Severa v menyayushcheisya srede: collection of theses Intern. conf., devoted to 300th anniversary of M.V. Lomonosov (in Russian). MGU, M., pp. 23–26.

Bazarova, E.P., 2011b. Cryomineral formations of the Khrustalnaya cave Pre-Baikal areas (Irkutsk region). Speleologia i spelestologia: (in Russian), Naberezhnye Chelny, NISPTR, pp. 49–52.

Bischoff, J.L., Stine, S., Rosenbauer, R.J., Fitzpatrick, J.A., Stafford, T.W., 1993. Ikaite precipitation by mixing of shoreline springs and lake water, Mono Lake, California, USA. Geochimica et Cosmochimica Acta, vol. 57, p. 3855–3866.

Dorofeev, E.P., 1966. Calcite films and gypsum crystals in the Kungur cave. Caves (in Russian). Perm, Issue 6 (7), pp. 39–46.

Engineering geology of Pre-Baikal, 1968 / G.B. Palshin (ed.) (in Russian). Nauka, M., 189 pp.

Filippov, A.G., 1989. Cave Geology on the Baikal side. Proceedings of 10th Intern. congress on speleology (Budapest, 13–20 Aug., 1989). Budapest, Hungary, vol. 2, pp. 583–585.

Filippov, A.G., 1997. Cave ices of Irkutsk region (in Russian). Svet. Vestn. Kiev. karst.-spel. tsentra Kiev, No. 2 (17), pp. 13–16.

Fotiev, S.M., 1996. Regularities in cryogenic metamorphization of chemical composition of marine water (in Russian). Kriolitozona i podzemnye vody Sibiri. IMZ SB RAS, Yakutsk, p. II, pp. 16–26.

Fotiev, S.M., 2002. Cryometamorphic cycle of underground water formation in mineral wealth of geological structures of Russia in Quaternary period (in Russian). Geoekologia, No. 1, pp. 5–17.

Geocryological map of the USSR, 1991. Scale 1:2.5 mln (in Russian). E.D. Ershov (ed.). Min-vo Geologii SSSR; MGU, M.

Geocryology of the USSR, 1989. Middle Siberia (in Russian) / E.D. Ershov (ed.). Nedra, M., 414 pp.

Gitterman, K.E., 1937. Thermoanalysis of sea water. Concentration of sodium chloride brines by natural freezing out (in Russian). Solyanaya laboratoria, Issue 5, part 1, pp. 5–23.

Gurvich, E.M., Bystrova, O., 2009. White Sea flyers (in Russian). Khimia i Zhizn, No. 3, pp. 32–35.

Hill, C., Forti, P., 1997. Cave Minerals of the World. Huntsville, USA, Natl. Speleol. Soc., 463 pp.

Hugget, J.M., Schultz, B.R., Shearman, D.J., Smith, A.J., 2005. The petrology of ikaite pseudomorphs and their diagenesis. Proc. of the Geologistsr Association, vol. 116, p. 207–220.

Ivanov, A.V., 1998. Cryogenic metamorphization of chemical composition of natural ice, freezing and melt waters (in Russian). Dalnauka, Khabarovsk, 163 pp.

Kononova, R.S., 1974. Cryogenic metamorphization of subpermafrost water of Eastern-Siberian artesian area (in Russian). Sov. Geologia, No. 3, pp. 106–115.

Lacelle, D., Laurioland, B., Clarc, I.D., 2009. Formation of seasonal ice bodies and associated cryogenic carbonates in Caverne de l,Ours, Quebec, Canada: Kinetic isotope effects and pseudogenic crystal structures. J. Cave and Karst Studies, vol. 71, No. 1, p. 48–62.

Leshchikov, F.N., 1978. Frozen rocks of Pre-Angara and Pre-Baikal (in Russian). Nauka, Novosibirsk, 140 pp.

Maksimovich, G.A., 1947. Cave ice (in Russian). Izv. Vsesoyuz. geogr. o-va, No. 5, pp. 537–549.

Maksimovich, G.A., Panarina, G.N., 1966. Chemical composition of ice in caves in Perm region. Caves (in Russian). Perm, Issue 6 (7), pp. 33–38.

Mavlyudov, B.R., 2008. Glaciation of caves (in Russian). Inst. of Geography RAS, M., 290 pp.

Moloshtanova, N.E., Maksimovich, N.G., Nazarova, U.V., 2001. Mineral composition deposits of Kungur ice cave. Caves (in Russian). Perm, Issue 27 (28), pp. 116–128.

Nelson, K.H., Thompson, T.G., 1954. Deposition of salts from seawater by frigid concentration. J. Marine Research, vol. 13, No. 2, p. 166–182.

Onac, B.P., 2008. Ikaite in the Scarisoara ice deposit: precipitation and significance. 3rd Intern. Workshop on Ice Caves (IWIC–III) – Kungur Ice Cave (Perm, May 12–17, 2008). Perm Region, Russia, p. 28.

Pauly, H., 1963. Ikaite. A new mineral from Greenland. Arctic, vol. 16, p. 263–264.

Pinneker, E. V., Pisarsky, B.I., Lomonosov, I.S., et al., 1968. Hydrogeology of Pre-Baikal (in Russian). Nauka, M., 170 pp.

Potapov, S.S., Parshina, N.V., Kadebskaya, O.I., 2009. Ice formations and connected with them crystallization of cryogenic gypsum in Oktyabrskiye caves (Perm Territory). Cave (in Russian). Perm, Issue 32, pp. 60–67.

Potapov, S., Parshina, N., Shavrina, E., Maksimovich, N., Kadebskaia, O., 2008a. Mountain flour on ice stalagmites on Pinega caves. 3rd Intern. Workshop on Ice Caves: Abstracts (Perm, May 12–17, 2008). Kungur ice Cave, Perm Region, Russia, p. 34.

Potapov, S.S., Parshina, N.V., Titov, A.T., et al., 2008b. Cryomineral formations of Pinega caves. Mineralogia tehnogeneza (in Russian). IMUrO RAS, Miass, pp. 18–43.

Rodriguez-Blanco, J.D., Shaw, S., Bots, P., Ronsal-Herrero, T., Benning, L.G., 2014. The role of Mg in the crystallization of monohydrocalcite. Geochimica et Cosmochimica Acta, vol. 127, p. 204–220.

Savenko, E.V., 1976. Mineral films on ice formations of caves. Caves (in Russian). Perm, Issue 16, pp. 21–24.

Žãk, K., Hercman, H., Orvošovã, M., Jačkovã, I., 2009. Cryogenic cave carbonates from the Cold Wind Cave, Niìzke Tatry Mountains, Slovakia: Extending the age range of cryogenic cave carbonate formation to the Saalian. Intern. J. Speleol., vol. 38 (2), p. 139–152.

Žãk, K., Onac, B., Persoiu, A., 2008. Cryogenic carbonates in cave environments: A review. Quatern. Intern., vol. 187, iss. 1, p. 84–96.

Žãk, K., Skála, R., Filippi, M., Plášil, J., 2010. Ikait – málo známy minerál zaledněnich jeskyni: vyskyt v občasném sezónnim zaledněni jeskyně Koda (Cesky kras). Bull. Miner.-Petrol. Odd. Nar. Muz. (Praha), vol. 18/1, p. 109–115.

Žãk, K., Smida, B., Filippi, M., Zivor, R., Komasko, A., Vybiral, S., 2011. New locality of cryogenic cave carbonates in the Czech Republic and Slovakia. Speleoforum, vol. 30, p. 103–110.

Žãk, K., Urban, J., Cilek, V., Hercman, H., 2004. Cryogenic cave calcite from several Central European caves: age, carbon and oxygen isotopes and a genetic model. Chem. Geol., vol. 206, p. 119–136.

Received December 11, 2012