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CRYOGENIC MINERAL FORMATIONS IN THE CAVES OF PRIOLKHONIE REGION (WESTERN PRIBAIKALIE)

E.P. Bazarova[1], O.I. Kadebskaya[2]

[1] *Institute of the Earth Crust, SB RAS, 128, Lermontova str., Irkutsk, 664033, Russia; bazarova@crust.irk.ru*
[2] *Mining Institute, UB RAS, 78a, Sibirskaya str., Perm, 614007, Russia; icecave@bk.ru*

The paper provides insights about cryogenic mineral formations in four caves with perennial and seasonal aufeis occurrences studied in the Western Pribaikalie (Fore-Baikal) region. The study revealed that calcite and ikaite, its metastable phase, predominate in the cryogenic material, while gypsum and chalcedony are present in minor amounts. The differences in morphology of the cryogenic mineral formations were described with regard to the internal facial conditions controlling mineral formation. The $\delta^{13}C$ and $\delta^{18}O$ isotope composition of calcite cryogenic powder and calcite pseudomorphs after ikaite was determined. Their analysis revealed that the isotopic composition of pseudomorphs may be either similar to calcite powder, or differ significantly from it (the pseudomorphs are characterized by lighter isotopic composition of oxygen and carbon). Such difference established in the composition of ikaite from Malaya Baidinskaya cave is explained by the mineral formation under slow-freezing conditions.

Caves, cryogenesis, Western Pribaikalie, calcite, ikaite, coarse-grained cryogenic cave carbonates

INTRODUCTION

The Priolkhonie area (Fore-Olkhon zone) encompasses the southwestern shores of Lake Baikal contiguous to Olkhon island. The complexity of its geologic structure is explicated by synmetamorphic collisional collage associated with the early synorogenic collapse of the Olkhon collisional system and stems primarily from the diversity of combinations of rocks that differ in composition [*Fedorovsky et al., 1995*]. A concise description of the karst process (specifically, its morphology, history and geodynamics) as a major exogenous control in this area was provided by O.S. Gutareva [*2009*].

There are four caves with multiyear ice (Aya-Ryadovaya, Mechta, Bolshaya Baidinskaya and Malaya Baidinskaya) arranged into a system within the Priolkhonie area (Fig. 1). Their ice formations have been degrading since their discovery, which may be associated with these speleo-objects being well-visited, as well as with variations in airflow as a result of the excavation of new entrances (e.g. Aya-Ryadovaya cave), thereby aggravating an increasing trend in the mean winter and annual temperatures in the caves.

Presently, most of the research into cryogenic mineral formations in caves (or cryogenic cave minerals, CCMs) corresponds to a stage involving the data collection and accumulation, and the results are therefore generally interpreted as descriptive. Thus, numerous recent publications have provided ample descriptions of fine-to coarse-grained cryogenic formations from Russian and foreign caves [*Alekseeva, 1965; Dorofeev, 1966; Savenko, 1976; Andreychouk and Galuskin, 2001, 2008; Andreychouk et al., 2004, 2009; Žák et al., 2004, 2008, 2009, 2010, 2011; An-*

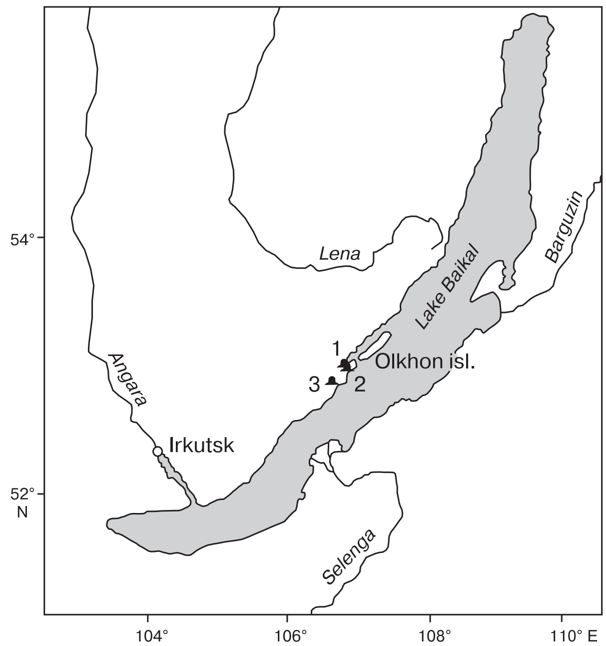

Fig. 1. Caves location scheme:

1 – Bolshaya and Malaya Baidinskaya caves, 2 – Mechta, 3 – Aya-Ryadovaya.

dreychouk, 2009; Lacelle et al., 2009; Richter et al., 2018; Teechara et al., 2018]. Cryogenic formations with crystals (crystals' aggregates) are ranked as fine (<1 mm), the so-called cryogenic powder, to coarse (from 1 mm to several centimeters) [*Žák et al., 2011*]. In Irkutsk region, where most caves are subjected to seasonal or perennial glaciation, cryogenic formations are an integral part of secondary mineral formations.

For all the wide recognition of the Priolkhonie caves, only few research works have addressed their geology and secondary mineralogy. Besides, there is still a lack of information on cryogenic mineral formations from these caves, despite the detailed characterization of their ice types available from earlier research conducted by E.V. Trofimova [*2006*].

This paper sets out to provide insights into the existing conditions of cryogenic formations in Aya Ryadovaya, Mechta and Bolshaya and Malaya (here and elsewhere B. and M.) Baydinskaya caves, and to analyze their mineral, chemical and isotopic compositions.

RESEARCH METHODS

The research methodology included sampling, general reconnaissance and photographic documentation of ice collected from caves, along with temperature measurements in the underground cavities. The temperature was measured with the FLUKE 971 thermohydrometer (measurement resolution: 0.1 °C). In Aya cave, two samples of cryogenic formations were collected from the aufeis surface. In Mechta cave, residual cryogenic powder was sampled from a large ice stalagmite relic at the entrance of a cave. In B. Baydinskaya cave, cryogenic formations were sampled from the surface of perennial ice in the upper grotto, along with sampling fine-grained mineral formation of probably cryogenic origin in the lower grotto, at the foot of perennial ice body. Cryogenic formations were sampled in the lower part of M. Baydinskaya cave, putatively from the place of melted out aufeis. The samples were transported in air-tight containers and kept in a thermos with ice, to preserve metastable minerals. The host rocks and ices were sampled as well.

The morphology and chemical composition of cryogenic formations were studied using VEGA 3 LMH Scanning Electron Microscope (SEM) with the INCA Energy 350/X-max 20 Energy Dispersive X-Ray Spectroscopy (EDXS) application at the Mining Institute, Ural Branch of RAS, Perm (analyst: O.V. Korotchenkova). The samples were dried at room temperature prior to their spray-coating with carbon and then placed in a high vacuum chamber.

Carbon and oxygen isotope analyses were performed at the University of Innsbruck by the Innsbruck Quaternary Research Group (headed by professor Christoph Spötl, the Full member of the Austrian Academy of Sciences) involving GasBench II with the Carbonate-Option autosampler assisted sample preparation and loop injection interface coupled to the Thermo Fisher Scientific isotope ratio mass spectrometers DELTA V, in line with the methodology provided in [*Spötl and Vennemann, 2003*] and using the international standard isotopic reference materials NBS 19 and LSVEC.

Determinations of the amounts of petrogenic elements for the host rocks were performed at the Shared Resources Center of the Institute of the Earth's Crust of Siberian Branch of the Russian Academy of Sciences (SB RAS), Irkutsk, using the silicate analysis method (analysts: M.M. Samoilenko and G.V. Bondareva). The chemical composition of the cave ice melts were determined by the titration, gravimetric and atomic absorption spectrometry methods (analyst: L.A. Durban from the Institute of the Earth's Crust SB RAS).

The X-ray phase analysis of the B. Baidinskaya cave sample was performed at the Perm State University (analyst: G.A. Isayeva) using the D2 Phaser (Bruker, Germany), an amorphous and crystalline phase analysis tool designed for X-ray powder diffraction applications. The samples X-raying (temperature: 21 °C; humidity: 64 %) required no cooling system. The device characteristics are: X-ray tube with copper anode (radiation: CuK_α, λ = 1.540 60 Å), 30 kV generator with output current of 10 mA; linear detector – LYNXEYE; Ni-filter. A diffractogram was obtained with the powder sample placed in a cuvette (X-raying situation: divergent gap 1.0 mm, primary Soller slit 2.5°, secondary 2.5°; angular range: from 5 to 80° 2θ; pulse gaining speed at each point: 1.0 s; step: 0.02°). The resultant curve processing (smoothing, searching for peak), along with the qualitative and semi-quantitative analysis was performed using the Diffrac.Eva software. The PDF-2 powder diffraction database (2010) was used to search for mineral phases.

DESCRIPTION OF THE CAVES

Aya cave was discovered by a team of the Irkutsk Geological Administration during their exploration of carbonate deposits in the Aya and Ust'-Anga bays back in 1946–1953. The pioneering description of the cave was provided in the monograph authored by G.P. Vologodsky [*1975*]. In 1993, Aya cave was connected to Ryadovaya cave, and is presently an integrated part of the Aya-Ryadovaya karst system. The cave is located in the northeastern portion of the Aya massif on the south-western shore of Lake Baikal. The length of the karst system is 1350 m with an amplitude (measured between the altitudes of the extreme upper and lower points) of 70 m [*Osintsev, 2010*]. The multiyear aufeis detected in the cave's extremity (Ledyanoy grotto) has now completely melted and succeeded by thin-layered seasonal ice formations. The sampling site temperature was –0.3 °C.

The study of Mechta cave (other names previously used by investigators were: Instituta Geografii cave, Srednyaya (Middle) Baidinskaya cave, or Khariktinskaya cave) was commenced in the 1960s [*Belyak, 1966; Vologodsky, 1975*]. The cave is located 10 km south of the Olkhonskie Vorota strait, its elevation is about 250 m above Lake Baikal's water level. The length passages total 830 m, with an amplitude of 52 m. When discovered, Mechta cave had a 16 m long perennial ice body, behind which patches of firn ice and ice stalagmites up to 3 m in height were observed [*Belyak, 1966*]. Presently, ice formations in the cave have severely degraded, and the area of perennial ice has considerably shrunk. The sampling site temperature was +0.1 °C.

Bolshaya and Malaya Baidinskaya caves (elevation: ca. 300 m above Lake Baikal), discovered by B.E. Petrie in 1913 are located at a distance of 300 m from Mechta cave, on a treeless plateau between two small rivers' (Bag-Orso and Nugda) valleys. A detailed description of the cavities, supplemented by sketches and dimensions is given in [*Khoroshikh, 1955*]. Later, these caves named as "Ozernaya" and "Ledyanaya", were described by G.P. Vologodsky [*1975*]. Numerous archeological finds in both the caves included: arrowheads, knives, bone awls, pot-

Table 1. **Chemical composition of karstified host rocks with cut-in caves (mas.%)**

Component	Aya	Mechta	Bolshaya Baidinskaya	Malaya Baidinskaya
SiO_2	1.27	0.70	3.04	1.17
TiO_2	< blod	< blod	< blod	< blod
Al_2O_3	< blod	< blod	< blod	< blod
Fe_2O_3	< blod	< blod	< blod	< blod
FeO	< blod	0.13	0.18	0.10
MnO	0.01	0.01	0.07	0.01
MgO	0.70	1.46	20.12	0.94
CaO	55.02	52.70	33.36	55.25
Na_2O	0.02	0.08	0.08	0.08
K_2O	< blod	0.01	0.04	< blod
P_2O_5	0.06	0.08	0.26	0.03
H_2O^-	0.21	0.22	< blod	< blod
Cl-lod	0.95	29.81	0.65	1.49
CO_2	41.14	14.71	42.35	40.78
Sum	100.33	99.91	100.15	100.29

Note. Limit of detection (lod) of petrogenic oxides (mas.%): TiO_2 – 0.02, Al_2O_3 – 0.25, MnO – 0.01, K_2O – 0.01, Fe_2O_3 – 0.2, FeO – 0.02, P_2O_5 – 0.03, H_2O^- – 0.01. < blod – components content below limit of detection; cl – calcination loss (i.e. during sample calcination) (cl-lod – 0.02).

Concentrations of petrogenic elements for host rocks were determined by the silicate analysis method (analysts: M.M. Samoilenko and G.V. Bondareva) at the Shared Resources Center of the Institute of the Earth's Crust SB RAS.

Table 2. **Chemical composition and mineralization (TDS) of cryogenic formations from Mechta, Bolshaya and Malaya Baidinskaya caves**

Sample No.	TDS, mg/L	pH	Measurement unit	Components concentrations										
				NH_4^+	K^+	Na^{2+}	Mg^{2+}	Ca^{2+}	HCO_3^-	CO_3^{2-}	SO_4^{2-}	Cl^-	NO^{2-}	NO^{3-}
Mechta cave														
1	464.49		mg/L	<0.1	0.63	1.03	72.96	3.01	378.22	–	4.0	3.55	<0.01	<0.44
		6.65	mg-eqv./L		0.02	0.04	6.0	0.15	6.2		0.08	0.1		
			%-eqv.		0.26	0.72	96.6	2.42	97.13		1.3	1.57		
2	97.65		mg/L	<0.1	0.47	0.17	0.61	21.04	65.9	–	3.0	2.13	<0.01	1.33
		7.65	mg-eqv./L		0.01	0.01	0.05	1.05	1.08		0.06	0.06		0.02
			%-eqv.		1.07	0.66	4.47	93.8	88.24		5.1	4.9		1.75
Bolshaya Baidinskaya cave														
3	156.24		mg/L	0.15	0.22	0.56	1.82	35.07	89.09	10.8	3.0	3.55	0.1	0.88
		9.35	mg-eqv./L	0.01	0.01	0.02	0.15	1.75	1.46	0.36	0.06	0.1	0	0.01
			%-eqv.	0.43	0.29	1.26	7.74	90.29	73.04	18.01	3.12	5.0	0.11	0.71
Malaya Baidinskaya cave														
4	40.76		mg/L	0.1	0.43	0.29	0.36	7.01	23.19	–	4.0	1.42	0.08	0.88
		7.25	mg-eqv./L	0.01	0.01	0.01	0.03	0.35	0.38		0.08	0.04	0	0.01
			%-eqv.	1.35	2.69	3.08	7.33	85.54	73.19		16.04	7.7	0.33	2.73
5	90.69		mg/L	0.1	0.75	0.23	1.46	16.63	57.97	0.3	6.0	1.06	1.75	0.44
		8.05	mg-eqv./L	0.01	0.02	0.01	0.12	0.83	0.95	0.01	0.12	0.03	0.04	0.01
			%-eqv.	0.56	1.95	1.02	12.19	84.29	81.89	0.86	10.77	2.59	3.28	0.61

Note. 1 – ice stalagmite, 2 – aufeis (ice coating), 3 – aufeis (ice coating), 4 –upper portion of aufeis, 5 – lower portion of aufeis. Dash indicates the absence of component.

The chemical composition of the cave ice melts was determined using the titration, gravimetric, and atomic absorption spectrometry (AAS) methods (analysts: L.A. Durban) hydrogeology laboratory of the Institute of the Earth's Crust SB RAS.

tery, pieces of birch bark, along with human remains found in Malaya Baidinskaya cave. As P. Khoroshikh points out, the caves served as a temporary home and burial place for the Kurykans, a Siberian tribe who inhabited the area in the vicinity of Lake Baikal in the VI–X centuries.

Bolshaya Baydinskaya cave consists of two grottoes subdivided on two levels and separated by a multiyear ice body, through which an entrance was made in 1984, to form a passage to the lower grotto. The ice body sized 9.5 m (thickness) by 14 m (length) is, according to A.G. Filippov, composed by aufeis and lake ice [*Filippov and Shevelev, 2011*]. The cave, which totals 69 m in length, descends to a depth of 10.6 m. In addition to the multiyear ice body, seasonal ice occurring as atmogenic crystals was also found near the entrance. The sampling sites' temperature varied from −0.1 to +0.1 °C.

Malaya Baydinskaya cave begins with a small sump, which passes into a grotto (20 m in length and from 1 to 4 m in width), having several branches and niches. The total length of the cave is 52 m, its depth is 5.4 m. The observed chemogenic calcite formations are corallites and crystallictites with their dendritic habits described as needle-like crystals and fused spherulites, respectively. Ice formations on the floor occur as perennial ice, probably of infiltration origin. The sampling site temperature was 0 °C.

All these caves are cut in Upper Archean – Lower Proterozoic marbles grouped into the Olkhon series. The chemical composition of host rocks is shown in Table 1.

Given that groundwaters from the zone of aeration is largely responsible for the chemical composition of ice formations in the caves, ice melts of this type host rocks are characterized as: ultra-fresh to fresh (TDS: 40.76–464.49 mg/L), slightly acidic to slightly alkaline (pH: 6.65–9.35), and calcium-bicarbonate in composition (Table 2).

MINERAL COMPOSITION AND MORPHOLOGY OF CRYOGENIC FORMATIONS

Cryogenic formations sampled from the coating aufeis in Aya cave appear under the microscope mainly as flattened crusts composed of calcite with minor impurities of sulfur (1.14 mas.%) and magnesium (0.32 mas.%). Calcite crusts are dominantly of two types, consisting of: (1) single aggregates of calcite crystals, as a combination of sharp and obtuse rhombohedral structure (Fig. 2, *a*); (2) spherulite aggregates of laminar structure (Fig. 2, *b*), sometimes overgrown with smaller calcite crystals (Fig. 2, *c*). Practically all crusts have a flat base (partly having shell-like texture (Fig. 2, *d, e*)) accentuating their prominently expressed laminar structure (Fig. 2, *f*) produced by repeated crystallization stages, which is additionally evidenced by small calcite crystals formed on spherulite surfaces (Fig. 2, *c*). The reported sporadic impurities of Na, Al and Si on the crust surfaces were prompted by the presence of clay particles in the feed solution.

The samples of cryogenic formations collected from the ice stalagmite in Mechta cave are white, powdery, have no crystals that are visible to the naked eye. In respect to their mineral composition, cryogenic formations are represented by calcite (Fig. 3, *a*). These are generally crusts with a flat base covered with a brush of crystals (Fig. 3, *b*, *c*). The zoning articulated in the flat base suggests periodicity in the mineral precipitation (Fig. 3, *c*). There are both non-split (Fig. 3, *d*) and split aggregates (Fig. 3, *e*), sometimes to single spherulites (Fig. 3, *f*).

Cryogenic formations from the upper grotto of Bolshaya Baidinskaya cave were sampled on the sloping surface of aufeis affected by thawing. These are composed predominantly of Ca (37.9 mas.%) with minor impurities of S (1.15 mas.%) and Mg (0.32 mas.%). Cryogenic formations are represented by crystals (1–2 mm), light-golden in color, while their aggregates (up to 5 mm) are of more intense honey color (Fig. 4, *a*). The X-ray diffraction analysis determined the mineral to be ikaite partly converted to calcite (Fig. 5). Under an electron microscope, the surface of crystals appears porous due to their dehydration (Fig. 4, *b*). Among the total mass of dehydrated elongated needle- and fiber-like crystals up to 5 μm in size, globular varieties (globules) measuring around 50 μm are observed (Fig. 4, *c*). The powder collected at the toe of perennial ice body in the lower grotto is composed of calcite (Fig. 4, *h*) admixed with clay, silica (Fig. 4, *g*) and particles of gypsum, which forms rounded aggregates of lamellar crystals (Fig. 4, *e*), and (judging from the crystal morphology and mineral composition) is considered to be not cryogenic.

The M. Baydinskaya cryogenic formations are aggregates of ikaite crystals up to 1 cm in size (Fig. 4, *d*), honey- and amber-colored, on a small-crystal substrate which is white and light gray in color. Upon dehydration, ikaite texture becomes spongy porous in aggregates (Fig. 4, *f*). The substrate is composed of calcite and clay minerals.

CARBON AND OXYGEN ISOTOPIC COMPOSITION

The O and C isotope composition of cryogenic powder, calcite pseudomorphosis after ikaite and corallites were compared with the isotopic composition of host rocks (Fig. 6). The analytical error at 1σ is 0.1 % for both isotopes.

The isotopic composition of the host rock equals: $\delta^{18}O$ −6.5 ‰ VPDB and $\delta^{13}C$ +0.2 ‰ VPDB (Aya cave); $\delta^{18}O$ −7.4 ‰ and $\delta^{13}C$ +0.2 ‰ (Mechta cave); $\delta^{18}O$ −7.3 ‰ and $\delta^{13}C$ −1.9 ‰ (B. and M. Baidins-

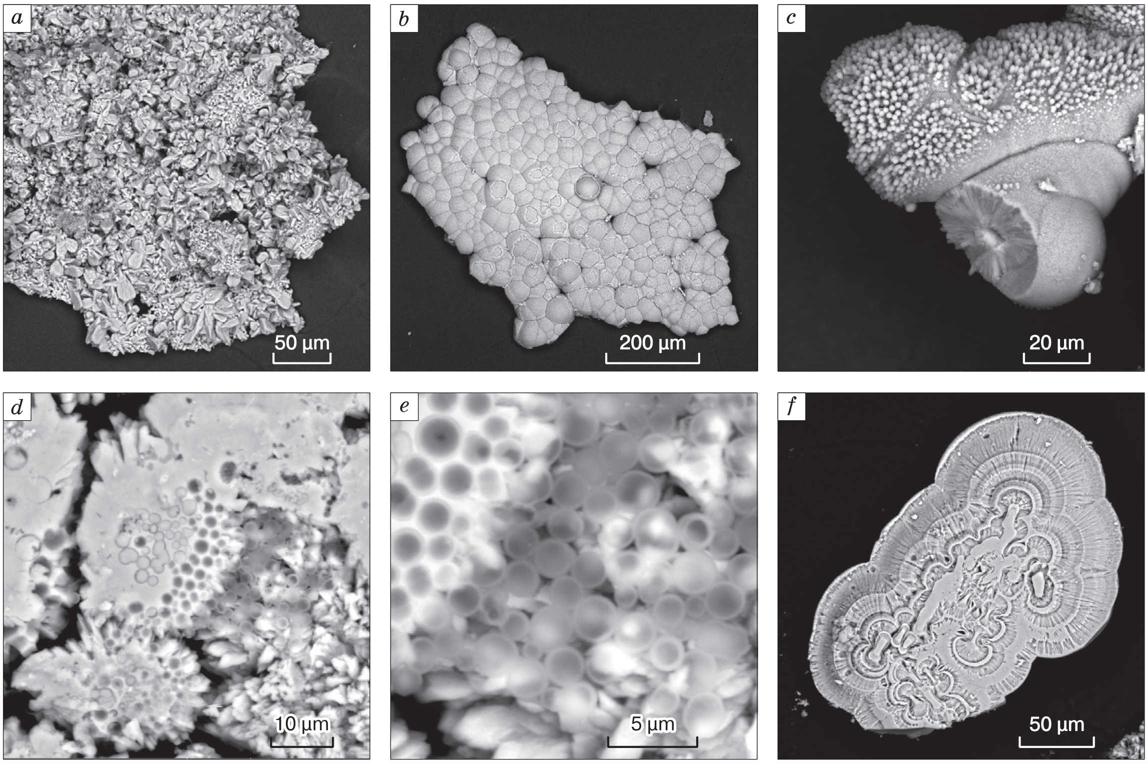

Fig. 2. Morphology of cryogenic powder collected from aufeis (ice coating) in Aya cave:

a – crusts consisting of individual aggregates of calcite crystals; *b* – crusts consisting of spherulite aggregates; *c* – internal structure of spherulite crusts with smaller calcite crystals on the surface; *d–f* – plane base of crusts formed on the ice surface.

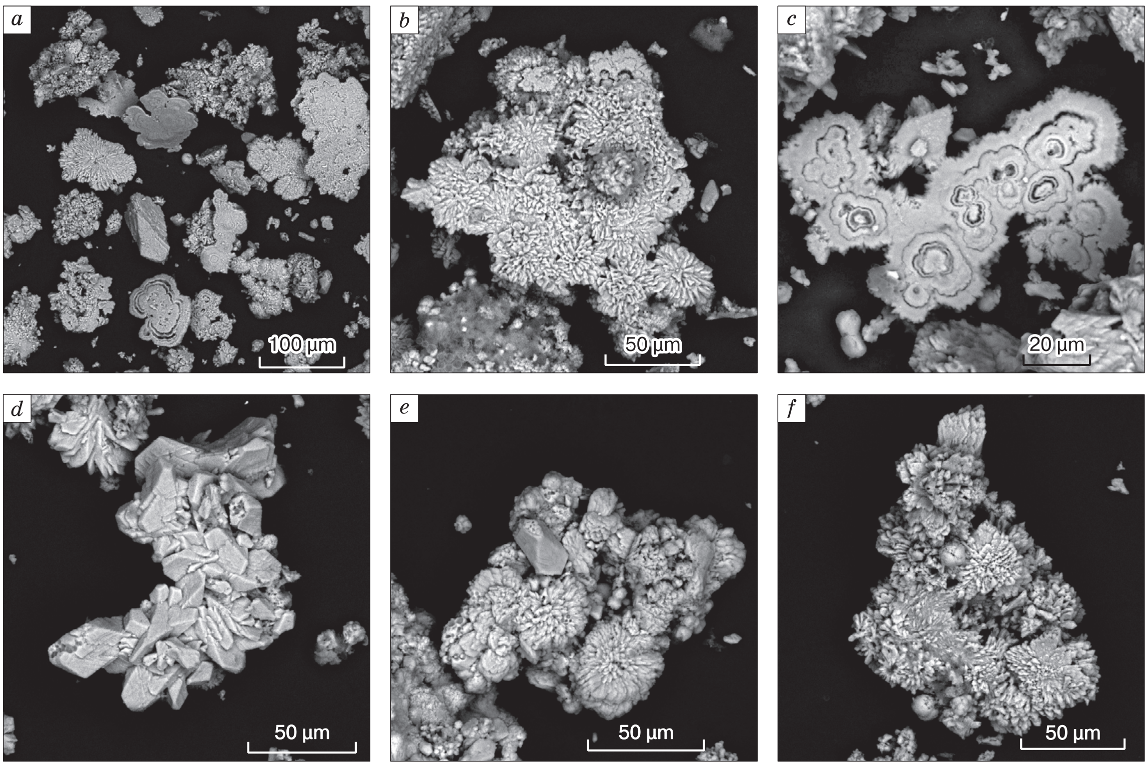

Fig. 3. Morphology of cryogenic powder collected from Mechta cave:

a – general view of mineral aggregates in the sample; *b* – calcite crusts with plane base and crystal brush in the upper part; *c* – growth zones in mineral aggregates; *d–f* – crystal aggregates with varying degree of splitting (from smooth-edged to spherulites).

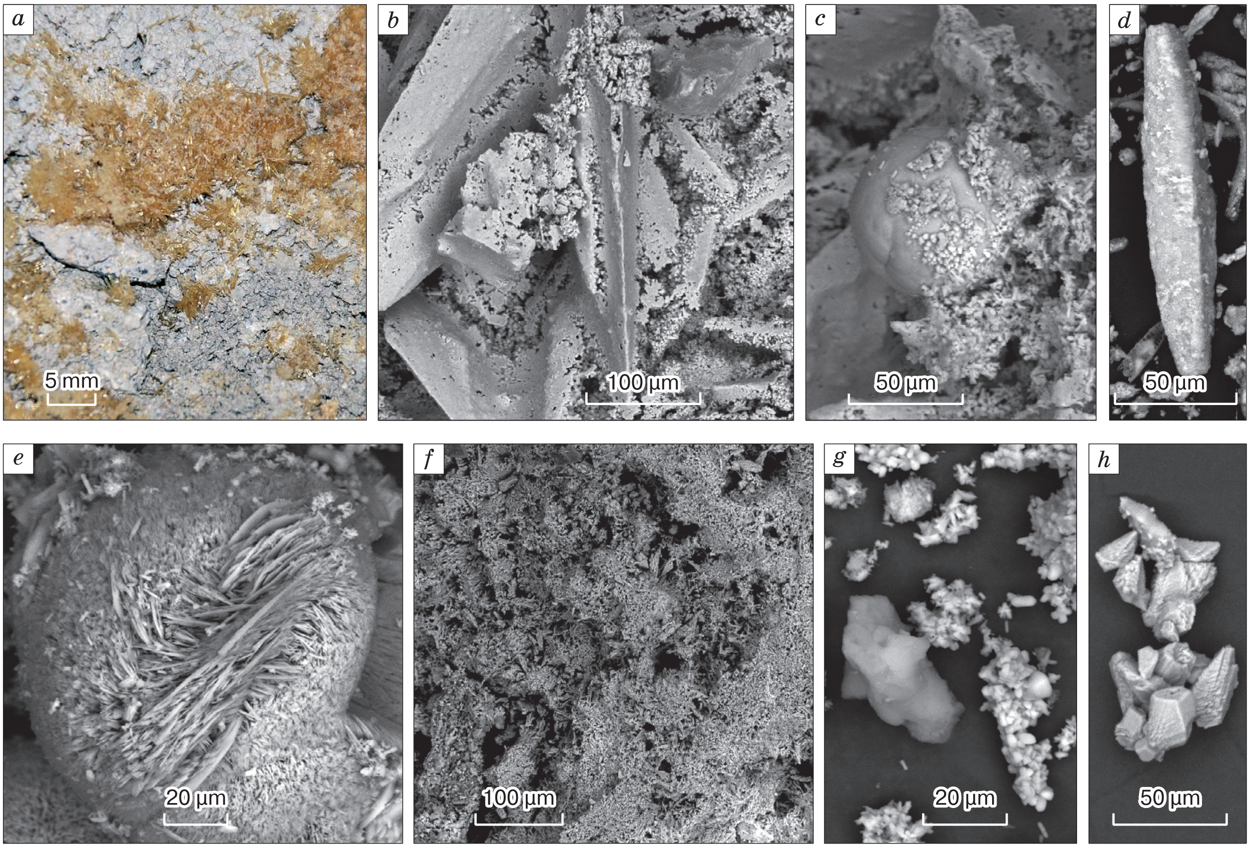

Fig. 4. Morphology of cryogenic minerals collected from Bolshaya and Malaya Baidinskaya caves:

a – ikaite crystals on the aufeis surface in the upper grotto of Bolshaya Baidinskaya cave; *b* – dehydrated porous surface of ikaite crystals; *c* – globules in the total mass of dehydrated ikaite crystals; *d* – single ikaite crystal from Malaya Baidinskaya cave; *e* – spherulite aggregate of laminar gypsum crystals; *f* – internal structure of ikaite crystals from Malaya Baidinskaya cave; *g* – cotton wool-like silica from the lower grotto of B. Baidinskaya cave; *h* – calcite crystals from the lower grotto of B. Baidinskaya cave.

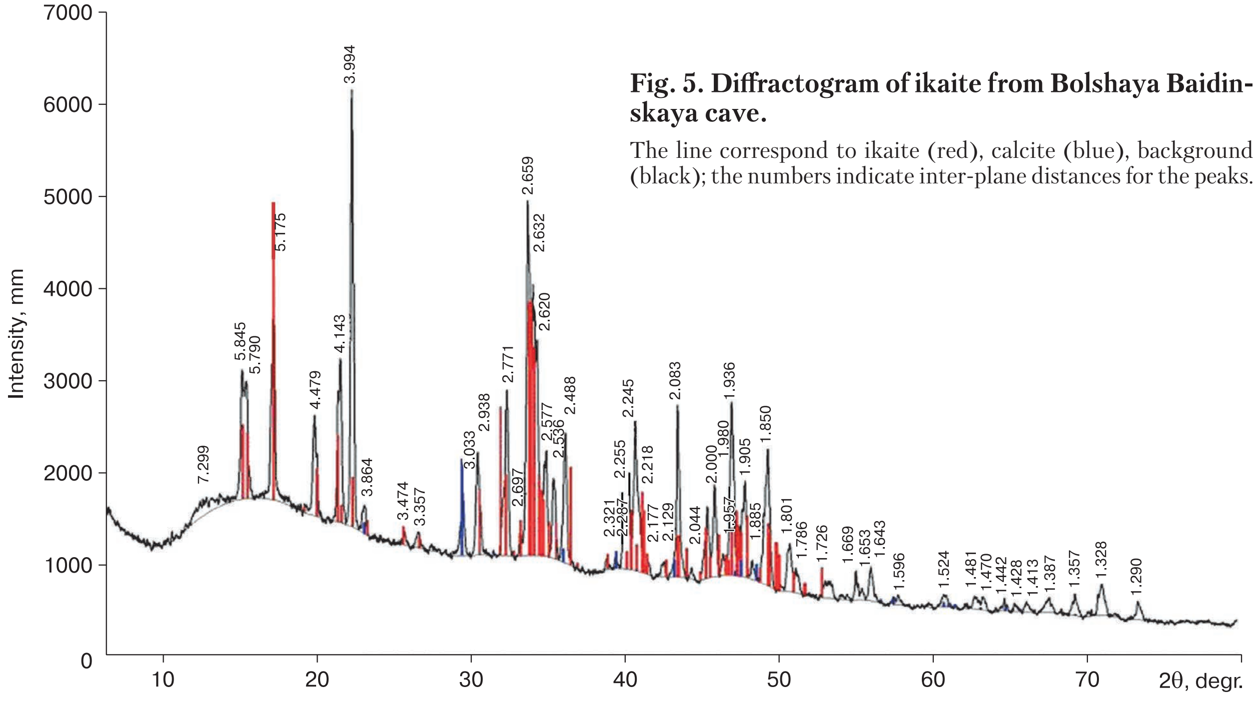

Fig. 5. Diffractogram of ikaite from Bolshaya Baidinskaya cave.

The line correspond to ikaite (red), calcite (blue), background (black); the numbers indicate inter-plane distances for the peaks.

kaya caves). These values generally correspond to the composition of typical marine sedimentary carbonates.

The O and C isotopic composition of cryogenic powder equaled $\delta^{18}O$ –7.0 ‰ and $\delta^{13}C$ +7.9 ‰ (Aya cave), and $\delta^{18}O$ –5.3 ‰ and $\delta^{13}C$ +13.2 ‰ (Mechta cave).

The $\delta^{18}O$ and $\delta^{13}C$ isotope composition of cryogenic powder from Aya and Mechta caves correlates with the isotopic composition of calcite formed under conditions of rapid (shock) crystallization. The formation of such crystals was controlled by the kinetic effect associated with rapid removal of CO_2 and the non-equilibrium water evaporation process [*Killawee et al., 1998*], which is accentuated by the increasing $\delta^{13}C$, while the $\delta^{18}O$ value is almost constant. The freezing occurs so rapidly that the oxygen isotope fractionation between water and ice does not take place, whereas mobile isotope ^{12}C passes into carbon dioxide [*Žák et al., 2018*].

The isotopic composition of ikaite from Bolshaya Baidinskaya cave is similar to that of cryogenic powder ($\delta^{18}O$ –6.5 ‰ and $\delta^{13}C$ +7.3 ‰) suggesting a close mechanism of their formation, with its crystallization occurring during the solutions freezing in the open system conditions.

Lighter compositions of both oxygen carbon, recorded in ikaite from M. Baidinskaya cave ($\delta^{18}O$ –22.3 ‰ and $\delta^{13}C$ –3.3 ‰) allows to attribute it to CCMs that were formed under conditions of slow freezing of ice, with the mechanism of formation dominated by the heavy oxygen isotope ^{18}O in the crystalline structure of ice. Lighter ^{16}O molecules have more kinetic energy and are more mobile, as compared to heavy ones, inasmuch as ice, while freezing, becomes enriched (against water) with heavy isotopes.

The values for the O and C isotope compositions of corallites (secondary calcite structures), sampled in Aya ($\delta^{18}O$ –9.4 ‰ and $\delta^{13}C$ –6.2 ‰), Mechta ($\delta^{18}O$ –10.3 ‰ and $\delta^{13}C$ –7.8 ‰) and M. Baidinskaya ($\delta^{18}O$ –10.3 ‰ and $\delta^{13}C$ –6.7 ‰) caves, are similar to drapery formations (flowstone) from caves located in the Urals and Siberia [*Kadebskaya and Chaikovskiy, 2013*].

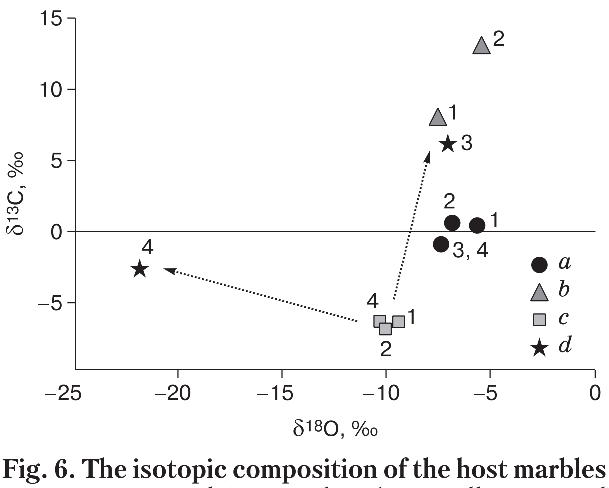

Fig. 6. The isotopic composition of the host marbles (*a*), cryogenic calcite powder (*b*), corallite (*c*) and ikaite (*d*) from Aya (1), Mechta (2), Bolshaya Baidinskaya (3) and Malaya Baidinskaya (4) caves.

DISCUSSION

Ikaite ($CaCO_3 \cdot 6H_2O$) is a cryogenic cave mineral (CCM) which is common in the Baikal and the Urals regions [*Kadebskaya and Chaikovskiy, 2013*]. Both fine-grained CCMs (>5 μm) and large aggregates (up to 3 cm) precipitated after ikaite were found in the Pribaikalie region caves [*Bazarova et al., 2014*].

The composition of ground ice is largely governed by that of host rocks (Fig. 7). The CaO, MgO

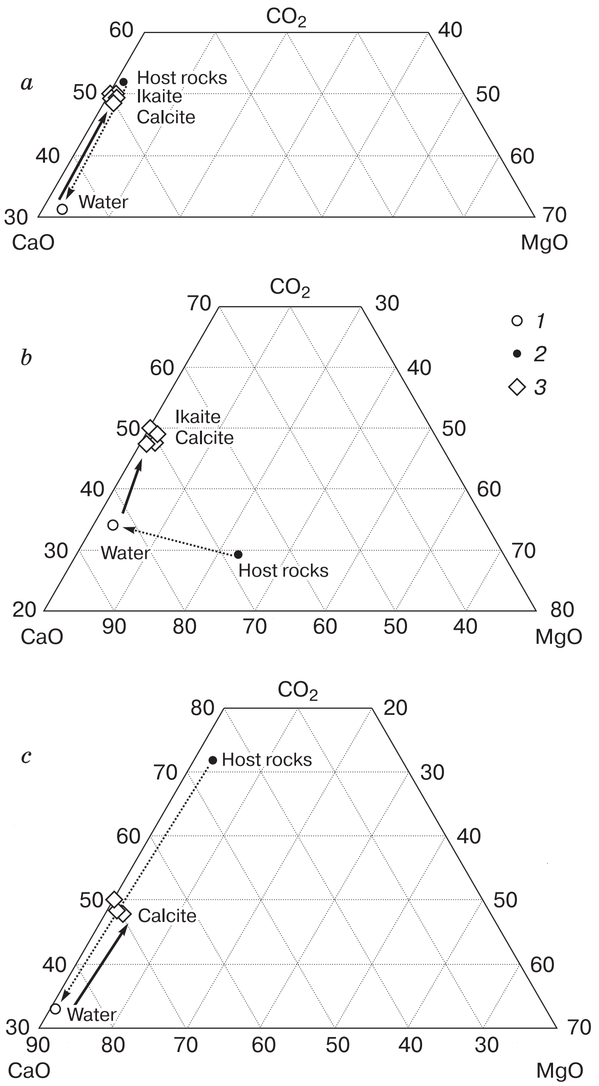

Fig. 7. Molecular ratio of CaO, MgO and CO_2 in the host rocks, aufeis formations and cryogenic minerals from Malaya Baidinskaya (*a*), Bolshaya Baidinskaya (*b*) and Mechta (*c*) caves:

1 – aufeis forming waters; *2* – host rocks; *3* – ikaite and calcite.

and CO_2 molecular ratios were calculated and plotted for the host rocks, ice and cryogenic minerals in these caves. Figure 7 shows that although amounts of CaO and MgO differ in compositions of their host rock, the composition of ice is characterized by almost identical CaO and MgO contents and by precipitation of similar minerals from the solutions. In B. and M. Baidinskaya caves, ikaite predominates in the composition of cryogenic formations, with its crystals measuring up to 1 cm. The experimental studies have shown that the degree of supersaturation of feed solutions, pH level, Mg^{2+} ion concentrations and the presence of impurities (e.g. organic substances) are critical factors in the crystallization of unstable forms of calcite [*Bots et al., 2012*]. Given small depths of underground cavities of B. and M. Baidinskaya caves, ikaite precipitation was probably affected by the contributions of the organic matter arriving to their groundwaters. Besides, precipitation of ikaite and, in particular, its large crystals, can be associated with slower freezing of the solution at temperatures around 0 °C and accumulation of thick perennial ice spanning several millennia.

As such, large aggregates of ikaite crystals were observed by the authors in Okhotnich'ya cave in place of melted multiyear aufeis found in the entrance part of the cave at a small depth from the surface [*Bazarova et al., 2014*]. Unlike in B. and M. Baidinskaya caves, cryogenic calcite powder formed over thin aufeis in Aya cave and on the ice stalagmite in Mechta cave, which was favored by lower temperature conditions during the so-called shock crystallization.

CONCLUSION

Multiyear aufeis widely developed in Mechta and Bolshaya and Malaya Baidinskaya caves is a product of congelation ice formation and sedimentary-metamorphic processes, while seasonal glaciation is more characteristic of Aya cave. Cryogenic mineral formations are dominantly localized both on the surfaces of aufeis in these caves and in place of its disappearance. The authors believe the progressive degradation of perennial ice in these caves to be largely affected by high anthropogenic pressures exerted on the caves during the high tourist seasons, rather than climate warming alone. Affected by ice melting and subsequent evaporation, both the volumes of cryogenic cave minerals (CCMs) and their morphology are subject to change.

The cryogenic origin of newly formed CCMs from Aya, Mechta, Bolshaya and Malaya Baidinskaya caves was inferred from the morphology of calcite and ikaite crystals and aggregates, and characteristic "shift" in their O (lightened) and C (heavying) isotope compositions, against "normal" drapery formations (speleothems), i.e. corallites, from these caves.

Calcite is a common cryogenic cave mineral in Aya and Mechta caves, whereas in Bolshaya and Malaya Baidinskaya caves ikaite is more widespread, along with gypsum and silica. The distinctions revealed in the morphology of cryogenic formations, are largely controlled by the cave conditions of CCMs formation (temperature, humidity). The calculation of the CaO, MgO and CO_2 molecular ratio for the host carbonate rocks, aufeis and cryogenic minerals in caves can provide insights about the formation of various forms of crystallohydrates (e.g. ikaite and lansfordite) [*Bazarova et al., 2016*], however this method appears insufficient for explaining the process of crystallization of unstable phases of calcite. Most likely, when interpreting the cases of ikaite precipitation instead of calcite, besides studying microelements concentrations, the feed solution should be analyzed in respect to the presence of organic substances in the process of crystallization and temperature characteristics during its freezing.

This research results revealed that the isotopic composition of calcite pseudomorphoses after ikaite can both show affinity with that of calcite powder and might as well differ significantly from it due to lighter oxygen and carbon isotope compositions. This remarkable distinction established in the composition of ikaite from Malaya Baidinskaya cave ($\delta^{18}O$ −22.3 ‰ and $\delta^{13}C$ −3.3 ‰) can be explained by the formation of ikaite during slow freezing of ice. Elucidation on the origin and reconstruction of the ikaite formation conditions in cave cavities still remain big questions in speleomineralogy necessitating therefore future research efforts.

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