

GYP SUM SPELEOTHEMS OF FREEZING ORIGIN

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Seasonal freezing affects the development of gypsum speleothems in caves of the Pinega area of the Russian European North including two types of deposits not previously described. One type, called gypsum yozh (hedgehog), grows in dense clay sediment within a high supersaturation environment. Originally growing in a direction away from the freezing front, they later enlarge almost symmetrically. Their shapes and characteristics are dependent on various factors and provide interesting comparisons with gypsum roses from arid regions. A second, very rare, type of gypsum speleothem appears to be produced from concretions of gypsum powder accumulated in cavities within an underground ice body. Recrystallization of the gypsum is controlled by fluctuating local temperature and seasonal freezing in an environment of low supersaturation.

The Pinega Karst is a north-trending region of sulfate and carbonate karstified rocks 600 km long and 100-200 km wide in the Arkhangel'sk Region of the Russian European North. The most interesting and best-studied caves are located on the territory of the Pinega State Nature Reservation and adjacent protected territories at the southeast border of the Belomor-Kuloi Plateau (Fig. 1). The karstified rocks are Lower Permian gypsum and anhydrite of the Assel to Lower Sackmar Stages with layers of dolomite with a thickness up to 150 m. The caves are mostly located on the banks of rivers and canyons in the lower part of the gypsum deposits. A great variety of cave morphology is caused by a complex geologic history, including glacial epochs and sea transgressions, as well as often-changing modern hydrologic conditions. In modern caves and canyons, ancient caves filled by clay deposits have opened in places. The longest cave of the area is the Kulogorskaya System, 16.1 km in length.

The average annual temperature of the area is 0.5°C, which causes an abundance of ice speleothems and deposits in the caves. The temperature in remote parts of the caves varies near 1°-2°C and in near-entrance parts does not exceed 4°C in the summer and minus 10°-20°C in the winter (Pinega State Reservation, 1996).

The caves of the region are mostly horizontal, supplied with water from an abundance of underground rivers, sometimes very powerful during spring floods (up to 200-300 L/s). The variety of cave-forming processes and conditions, such as deep-phreatic, shallow-phreatic, temporarily flooded, oscillating water-table, glacial, subaerial, lake, stream, vertical-flow, and others, caused a diversity in cave morphologies. Collapse, abundance of clay deposits, and ice speleothems are typical.

The most diverse and plentiful speleothems in these caves are made of ice. Perfectly transparent ice crusts cover hundreds of meters of underground lakes overgrown with "bamboo" stalagmites. Ice crystals of both winter and summer gen-



Figure 1. Sketch map of the Arkhangel'sk Region of the Russian European North.

eration cover all walls and ceilings of large chambers and also create complex formations. Monocrystalline labyrinthine hexagonal formations of skeletal crystals grown during tens of years can reach 30-40 cm in width. Ice flowers (antholites) and ice needles grow in the autumn-winter season; needles can reach 40 cm in length. Different stalactites, flowstone, draperies, spur helictites, as well as underwater and water-table crystals are widely distributed, especially in the wintertime. Some specific speleothems, for example ice "snakes," have never been described. A moving underground ice mass (2-3 cm/yr) in Ledyanaya Volna (Ice Wave) Cave is fed by both surficial-ice and cave-infiltration.

Gypsum and calcite speleothems are varied, although not abundant. Besides well-known gypsum (corallite, crystal

brush) and calcite (crust, crystal druse, soda-straw and other stalactite, stalagmite, flowstone, gour, corallite, conulite) speleothems that are widely distributed around the world, a low average surficial temperature causes rarer speleothems, some previously undescribed, whose origin is connected with seasonal or year-round frozen material.

GYPSUM POWDER OR PASTE

White powder is distributed in many of the Pinega caves that contain seasonally frozen material, covering cave ice masses (icing), frozen lakes, and other ice speleothems that are produced from water with a high gypsum content. During freezing of the water, small needle-like crystals of gypsum (up to 0.1 mm in length), together with ice crystals, grow mostly in a direction perpendicular to the surface. After sublimation of the ice during the winter-spring season, gypsum crystals remain as a porous layer on the surface of the ice. During melting of the ice, gypsum powder is gathered into hollows on the ice, increasing the speed of melting at those places and the growth of the cavities. The length and depth of the cavities in the ice with paste-like wet gypsum on the bottom can reach tens of centimeters. In relatively dry places, especially after removing any ice, slightly recrystallized gypsum powder can remain as very porous gypsum aggregates, called katyshki (pellets), which have a definite shape and structure and are not destroyed if removed carefully (Fig. 2).

If removed by a powerful flood, the gypsum powder can become a principal part of gypsum "foam" (which also includes some clay and organic matter) deposited on shelves and on the banks of streams. The thickness of this foam can



Figure 2. Concretions of gypsum powder in Ledyanaya Volna Cave. The second author provides scale.

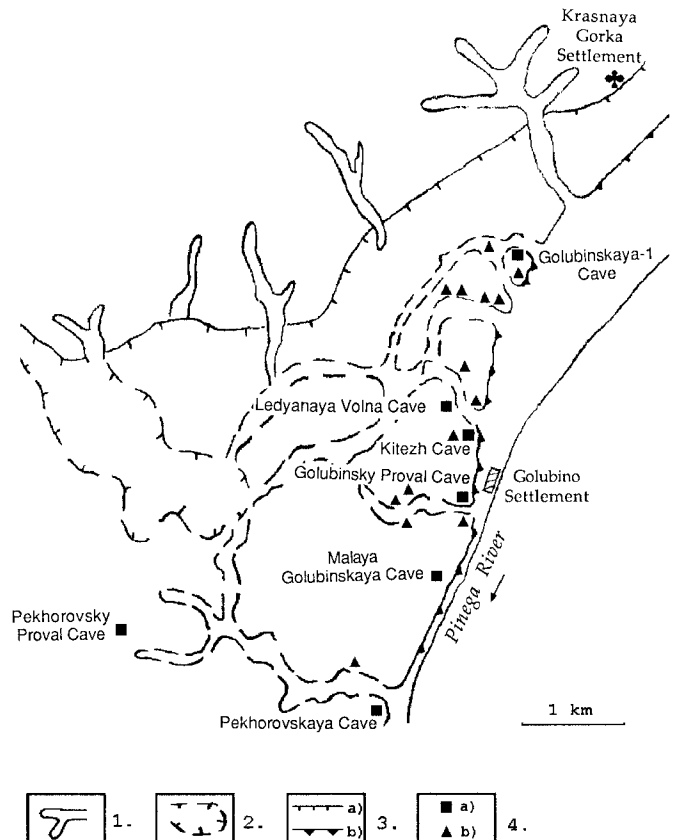


Figure 3. Sketch map of the Golubino District showing the caves mentioned in the text. 1, karst hollow; 2, shallow depression; 3a, margin of Upper Permian terra rossa; 3b, margin of gypsum rock along the Pinega River; 4a, cave containing gypsum yozh; 4b, other cave.

reach 0.5 m. Gypsum "beards" of flood origin also sometimes appear.

Two other types of speleothems, both called yozh (hedgehog), have thus far been found only in the Pinega Region.

NORMAL GYPSUM YOZH

This kind of yozh has been found in six caves in the Golubino District: Bolshaya Golubinskaya, Golubinskaya-1, Golubinsky Proval, Kitez, Malaya Golubinskaya, and Pekhorovsky Proval (Fig. 3). One sample of yozh, found on the bank of the Sotka River, evidently came from one of the nearby caves. This kind of speleothem has not been described before, and only once has been noted in the literature (Malkov & Shavrina, 1991). This yozh consists of several crystals that are split to resemble opened books with fanned lens-shaped pages 3-7 mm long perpendicular to the surface. The color of the white to brown speleothems depends on the content of clay inclusions. Morphologically they can be divided into four groups:

1. Rather spherical in shape (ellipsoid-like, clam-like), dis-



Figure 4. Gypsum yozh that has grown inside of frozen clay.

tributed in thick clay sediment. Normally 2-4 cm but up to 10 cm in diameter. These clearly are the purest kind and almost always have a little cavity inside (1-4 cm, up to 15 mm), sometimes with a stone in the cavity that rattles when shaken. The degree of splitting varies widely and, based upon its distribution in these caves, is probably controlled by supersaturation (Russo 1981) (i.e. by the velocity of freezing, Fig. 4).

2. Hemispherical, found in thick clay sediment in contact with ceilings or walls. They are similar to the first group, but the cavities are open to the outside and often are small or absent.
3. Relatively flat, often with an extremely irregular morphology. The most widely distributed shape is similar to some mushroom caps with a flat cavity on the bottom. They are observed in thin (up to 10 cm) clay deposits, and reach 30 cm in length if a few have accreted together. Normally they have a great quantity of clay inclusions.
4. In the clay filling of fissures in cave walls, they follow the shape and curvature of the fissures. The crystals are normally bigger and less (or not) split as in the other groups, probably due to lower supersaturation caused by better heat exchange to the wall rocks. They reach 20 cm long.

This type of yozh is always found inside of clay deposits, or as a residue after clay removal from the floor, ceiling, and walls of caves, and in wall fissures in near-entrance areas that have undergone winter seasonal freezing. The purest samples (with little clay inclusion) were found relatively far from entrances, in places with a smooth change of temperature.

Sometimes their content of sediment reaches 40%.

These speleothems grow due to supersaturation with respect to gypsum during the freezing of clay sediment in areas of seasonal freezing. Growth appears to start around a little cavity inside the clay. At first, the preferred direction of development is opposite to the front of freezing, according to the highest gradient of supersaturation. Following this, these speleothems have a mostly symmetrical growth, controlled by high supersaturation (5 to 10 times) at the surface (Russo, 1981) caused by the low permeability of compact clay.

At the beginning of the spring floods, water remains saturated with respect to gypsum for 1-2 weeks. This is a reason why these gypsum formations do not dissolve when the clay has been filled by flood water.

These speleothems are rather similar to desert gypsum roses, which have grown in friable sediment in arid regions, and also with gypsum roses in caves in arid regions. The term desert rose includes many different aggregates with a great variety of morphologies of both individual crystals and structures of aggregates. Cave gypsum rose is also a vague term, including both aggregates growing in cave sediment as well as subaerially growing speleothems, clearly corallites. Unlike the above described yozh, desert roses, in most cases, consist of unsplit, relatively isometric tabular, acicular, or lens-shaped crystals, that show a very low degree of supersaturation (1 to 1.5 times). Studies of gypsum crystal growth show that equidimensional tabular crystals grow slowly under conditions of low supersaturation, and elongated needle-like crystals grow rapidly under high supersaturation (Russo, 1981). The same is true for any crystal: Quick growth forms dendrites, whereas near-equilibrium crystallization forms crystals with minimum surface energy, which are close to equidimensional in appearance (Gregor'ev, 1961).

Previously described similar cave formations are obviously single crystals or simple crystal accretions, and appear to grow in thick sediment of drying clay in dry but periodically flooded cave areas (Hill & Forti, 1986, 1997; Maltsev, 1993; Rogozhnikov, 1984). Evidently, freezing of clay sediment can cause a much higher degree of supersaturation than drying of clay or changes in the temperature of a moving capillary solution.

Another characteristic feature of this type of yozh is the internal cavity (1 to 15 mm in diameter), sometimes with a stone inside the cavity that can rattle when shaken. Possibly there are two main reasons for this phenomenon that work together:

1. Growth preference toward a higher temperature gradient. A fact that the heat conductivity of wet clay is higher than that of gypsum can cause growth not only toward the surface of the clay deposit, but also, and even more, so along the edges of the formation, causing a "tucking up" of the edges, similar to a mushroom. This is clearly visible for the relatively flat subtype of yozh.

2. During freezing of the surface of the clay, water filling intergranular volumes of the yozh would be drawn out by capillary forces to areas of higher supersaturation, especially if ice crystallization inside the cavity is absent. Examination of frozen clay deposits shows that there are few centers of crystallization of ice under these conditions, and there is a low probability of the appearance of an ice center inside a cavity. During the spring-summer season, clay would be filled by slightly undersaturated water causing recrystallization and an enlargement of the internal cavity.

It is easy to estimate that these formations can be formed during hundreds to a few thousands of years. The content of water in dense clay ranges from 20 to 25% and averages 22%. The content of water in frozen clay (excluding ice veins) is 3-5%. Hence about 20% of the water is crystallized as ice veins, crystals, lenses, and antholites. The solubility of gypsum in water near the freezing point is about 2 g/L. The content of gypsum in ice veins and flowers in frozen clay is about 1.2 grams per kilogram of ice. The typical content of gypsum formations in clay is 5-10%.

Let's reckon the upper limit of annual growth of gypsum yozh in 1 kg of the clay as $M = 0.2 \times 1000 \text{ g/yr} \times (2 - 1.2 \text{ g}) / 1000 \text{ g} = 0.16 \text{ g/yr}$, meaning that a content of 10 wt% of gypsum yozh in the clay could be reached during $T = 0.1 \times 1000 \text{ g} / 0.16 \text{ g/yr} = 625 \text{ yr}$.

This result means that all these speleothems can have grown during post-glacial time (the past 8000 yr). Of course, this reckoning does not take into account the solubility of gypsum in residual supersaturated capillary solution. The relationship between capillary and constitutional water is unknown, but a half year seems to be enough time for diffusion of most of this water.

ANOTHER TYPE OF YOZH

Another speleothem has now been found only in Ledianaya Volna Cave in the Golubino District. Only two samples have been collected for the museum of the Pinega State Nature Reservation. They are nearly spherical porous accretions, 6-8 cm in diameter, consisting of radial gypsum, very thin needle-like split crystals of the sheaf type, of which sub-individuals are 0.1-0.3 mm wide and 1-4 cm long. These white to light yellow speleothems are very delicate. Also, they are very porous and can absorb water nearly twice their weight (Fig. 5).

It is necessary to note that the sheaf type of splitting is not typical for gypsum and is not described in common reference books, so it is impossible to strictly estimate the degree of supersaturation. However, based on the shape of the crystals and not taking into account splitting (which is not so evident), it is possible to suppose a degree of supersaturation near 2-3 times, lower than for the first type of yozh, and close to that of needle-like unsplit crystals.



Figure 5. Another type of gypsum yozh that appears to have grown inside of a cave ice body.

A difference in structure and features might be caused not only by the degree of supersaturation, but also by other factors. Type and degree of splitting obviously depend on isomorphous inclusions in the crystals (i.e. on the composition of the solution) (Grigor'ev, 1961). Gypsum deposits as well as clay deposits contain much organic matter, which also could be a reason for the shape of individual crystals.

Pressure, which can become enormous during freezing, also seems to be a prominent influencing agent affecting the shape of individual crystal and the structure of aggregates. The first type of yozh seems to have grown under high pressure conditions, unlike this type.

The genesis of this type of yozh is not clear, but it appears to be controlled by a narrow seasonal change of temperature inside the large cave ice body (which is, in effect, a small underground glacier). Probably they have grown due to secondary recrystallization from thick deposits of gypsum powder or paste, as described above, that accumulated in cup-like cavities in the ice body. The location of speleothems found on a large block in the train of a degrading underground ice body supports this idea. Growth of needle-like gypsum crystals and their aggregates from gypsum paste of a different origin (often called moonmilk) have been described by some authors (Hill & Forti, 1986). Also, some small acicular transistor-shaped and hedgehog-shaped accretions of gypsum needles, which have grown from similar gypsum paste, were found in Kungur Ice Cave in the Ural Region of Russia (Andreichouk, 1989).

In the winter of 1997, one more sample of these speleothems was found: there is a spherical accretion 1.5-2.0 cm in diameter of needle-like crystals, exposed on the surface of the ice body of Ledianaya Volna Cave due to warm air flow (Fig. 6). This find strongly supports our idea about the gene-



Figure 6. Small concretion of needle-like gypsum crystals exposed by the shrinking of a cave ice body.

sis of this kind of speleothem.

The age of these formations could be estimated very roughly by the velocity of ice-body movement as not to exceed 3000-4000 years.

REFERENCES

- Andreichouk, V.N. (1989). Several specific deposits in Kungur Ice Cave connected with its freezing (in Russian). *Mineraly i otlozheniya peshcher i ikh prakticheskoye znachenije*. Perm University thesis: 22-23.
- Grigor'ev, D.P. (1961). *Ontogeny of Minerals: Individuals* (in Russian). L'vovskogo University: 250 p.
- Hill, C. & Forti, P. (1986; 1997). *Cave Minerals of the World*, ed. 2, Huntsville, National Speleological Society: 463 p.
- Malkov, V.N. & Shavrina, E.V. (1991). Golubino Caves on the Pinega River (in Russian). *Sotsyal'no-ekonomicheskie problemy Evropeiskogo Severa*, Arkhangel'sk: 175-191.
- Maltsev, V.A. (1993). Minerals of the Cupp-Coutunn Cave System (in Russian). *World of Stones* (2): 5-30.
- Pinega State Reservation (1996). *Reservation reference book* (in Russian). Arkhangel'sk.
- Rogozhnikov, V.Y. (1984). Water-chemogenic deposits in karstic maze caves of Podol'e, Near-Dnestr Region (in Russian). *Peshchery* 19: 45-56.
- Russo, G.B. (1981). Splitting of gypsum crystals (in Russian). *Zapiski Vsesoyuz. Mineral. Obsch.* 110(2): 167-171.