# THE NEW DATA OF THE FORMATION OF CALCITE SKELETAL CRYSTALS IN KARST CAVITIES

Dmitry I. Krinov, Yuliya V. Azarova
*JSC "Leading Scientific-Research Institute of Chemical Technology",*
*Moscow, krinov67@mail.ru, azarova_yu@mail.ru*

Morphologically rare skeletal crystals of calcite from karst cavities in limestones of the Kaluga region are described. The new data of the morphology and the internal structure of skeletal crystals were obtained using a scanning electron microscope and optical methods. Acicular individuals evolves to "tower" and "bastion" aggregates of skeletal crystals; the formation model of these aggregates is proposed.
The aggregates studied here are of various shades of yellow, and less frequent pink, blue, and green. Any shade changes to dirty-white if colored specimens are stored in low-humidity environment. The relationship between calcite colour and adsorbed water is suggested.
The karst system, where skeletal crystals have been formed is of interest. Daily (5 – 10°C) and seasonal (30 – 40°C) temperature variations have been recorded, The observed significant seasonal fluctuations of the system debit are not typical of karst. It is suggested that these features account for by unusual active ventilation of this karst system.
4 figures, 9 references.
Keywords: calcite, "tower" aggregates, "bastion" aggregates, skeletal crystals, Brontsy, Kaluga region, karst, morphology of crystals.

## Introduction

Skeletal growth of crystals in the nature is one of the most interesting parts of mineral ontogeny. In spite of more than semicentennial study of its laws (Shafranovsky, Mokievsky 1956), morphological features and growth conditions of of skeletal crystals from rather large properties are poor documented until the present time. Previously not studied morphology and structure of skeletal segregations of calcite (Fig. 1) from the karst cavities opened by quarries near villages Kol`tsovo and Brontsy, Kaluga region are reported in this article[1].

## General geology of the karst cavities near villages Kol`tsovo and Brontsy, Kaluga region

The karst cavities srudied is a dense network of small (0.01 – 1.0 m in size) elongated jointed cavities penetrating a sequence of stongly fractured not dolomitized light limstone. The karst system ranges from 15 to 30 m in thickness; its observable extent is longer than 10 km. The whole system of the karst cavities is divided conditionally in two parts (upper and lower) separated by thin (about 10 cm) layer of dark brown clay with rare lenses of glauconite. This clay layer, being a waterproof layer in not fractured rocks, is the basis of accumulation zone of karst solutions in the lower horizon of the upper karst system,. Solutions penetrate the lower karst system through fractures of this layer. Average thickness of each part of this system is about 15 m. The karst cavities are vertically zoned due to action of karst solutions (dissolution and precipitation of dissolved material). Active infiltration of karst-forming solutions without newly formed solid phases is typical of the upper horizons of both parts of the system.

Various newly formed calcite segregations are in the central horizons (up to 6 – 7 m in thickness) of the upper and lower parts of the karst system: stalactite and stalagmite , "shore ice", and echelons previously reported in the literature of karst mineral formation (Godovikov, 1961; Dorofeyev, 1979; Ikornikova, 1968; Lebedev, Stepanov, 1955; Lebedev, 1964; Moroshkin, 1984; Churakov, 1912).

Along with crystallictites and flowstones, aggregates of skeletal calcite crystals studied here were found in the bothe parts of the karst system.

## Morphology of aggregates of calcite skeletal crystals

Aggregates of calcite skeletal crystals are formed on the roof and walls of differently slopped karst cavities. The size of individuals and aggregates varies depending upon orientation of substrate and skeletal individuals. Individuals growing vertically downwards develop more intensive. Crystallictites and

[1] – It should be noted that the article presented here has already been accepted to the publication in 1990th in journal «New data on minerals». However, owing to the break in publications of this journal, it was not issued. It is nice to own that the article is accepted by the editorial board of journal «New data on minerals», which has renewed its activity.

onyx are formed on horizontal foreparts and bottom of cavities. Skeletal individuals and aggregates are formed directly on limestone, flowstones, and earlier skeletal aggregates (second, third and subsequent generations). The structure of aggregates of calcite skeletal crystals and individuals resemble towers and fortresses; therefore, such segregations are called "tower" and "bastion" according on their shape. Skeletal segregations of the hollow polyhedron type with a gaping cavity (Shafranovsky, 1956) are attributed to the "bastions" . The segragations with insignificant size of channels in comparison with the size of the individuals or without these channels are attributed to the "towers" .

The aggregates are elongated along axis [0001] of calcite crystals. The cross-section of these aggregates corresponds to that of trigonal prism. "Tower" individuals reach 8 cm in length and 3 cm in diameter, and "bastion" individuals, 10 and 20 cm, respectively.

The examined material was determined as calcite according to electron microprobe and X-ray diffraction study. The X-ray diffraction patterns of its samples are similar to those given for calcite in literature.

The data of structural features and symmetry of the samples studied have been initially obtained with the Laue method. However, strong fracturing of the samples caused by numerous chips on the cleavage planes prevents unambiguous interpretation of the Laue patterns because the slightly extended arrangement of reflections corresponding to the symmetry of mineral accounts for both a displacement along cleavage planes and block structure of crystals.

The study of optical properties in oriented samples and surface features of the individuals and chips of these individuals with scanning electron microscope provides thr major conclusions of the structure of skeletal individuals. Optical and scanning electron microscopy provides the distigushing separate repeated units of calcite individuls and aggregates of these individuals which are reflected in both internal and external structure (Fig. 2).The unit element of the structure of a skeletal crystal is an acicular subindividual elongated along axis [0001]. The size of this subindividual is 0.01 mm across and 1.0 – 15.0 mm in length.

## Ontogeny

The study of specimens and oriented samples provides tracing of the evolution of acicular individuals.. The relation of of acicular crystals composing oriented parallel intergrowths is observable in the sections of individuals perpendicular to the axis of symmetry (axis of elongation). Initial acicular crystal (described above as unit element of skeletal crystal) is directly overgrown by the similar crystals. The edge of previous crystal is overgrown by subsequent parallel crystal. Next lateral subindividuals overgrow simultaneously with growth of individual along long axis. It should be noted that this growth cannot be named auto-epitactic, because newly formed and previously formed individuals are growing simultenelously (Figs. 3, 4). Cyclicity and sequence of such overgrowth is supported by separate formed areas of individuals decorated with fine clay particles (Fig. 2). It allows determination of the formation sequence of separate elements of a skeletal crystal. Nonsystematic character of such decoration accounts for heterogeneous distribution and infrequent presence of clay particles in the karst solutions. As a result of growth from a seepage solution, skeletal individuals and aggregates of the hollow polyhedron type (Shafranovskiy, 1956) are formed simultaneously with new unit crystals.

## Chemical composition

According to electron microprobe measurement and semi-quantity spectral analysis, the examined calcite is extremely pure (total

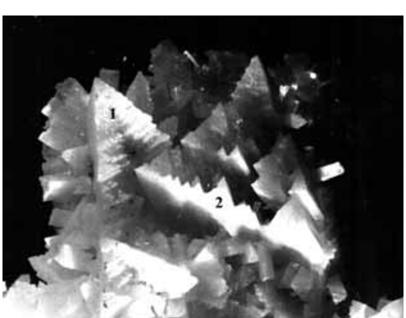


*Fig.1. Aggregate of calcite skeletal crystals (scale 1:1) from cavities of the Ferzikov quarry (Brontsy village, Kaluga region, Russia): (1) "tower" (1) and (2) "bastion".*

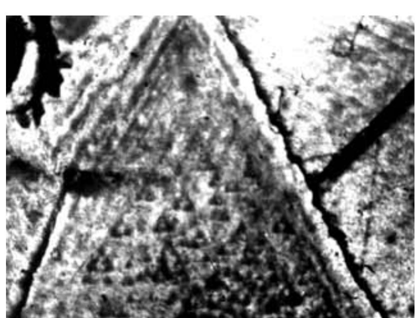

*Fig. 2. Internal structure of the "bastion" calcite . Oriented sample. Magnification ×25.*

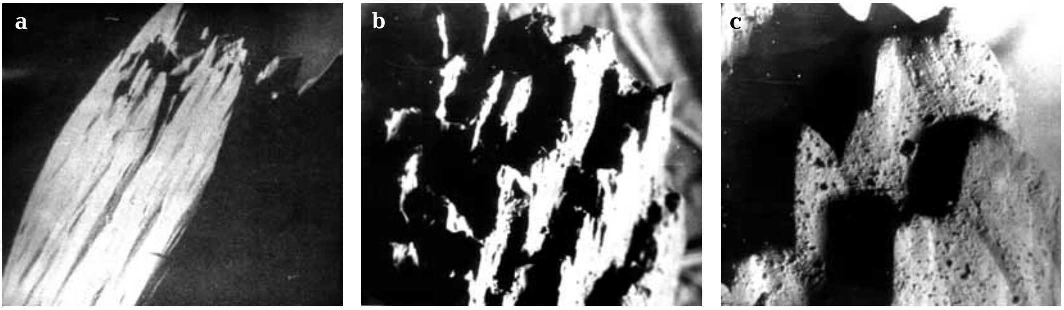


*Fig. 3. Scanning electron image of rows of acicular calcite crystals on the growth front of crystal individual:*
*(a) top of the "bastion" crystal, heads of fine axicular individuals are seen (magnification ×300);*
*(b) rows of acicular crystals (magnification ×300);*
*(c) rows of acicular crystals (magnification ×1000).*

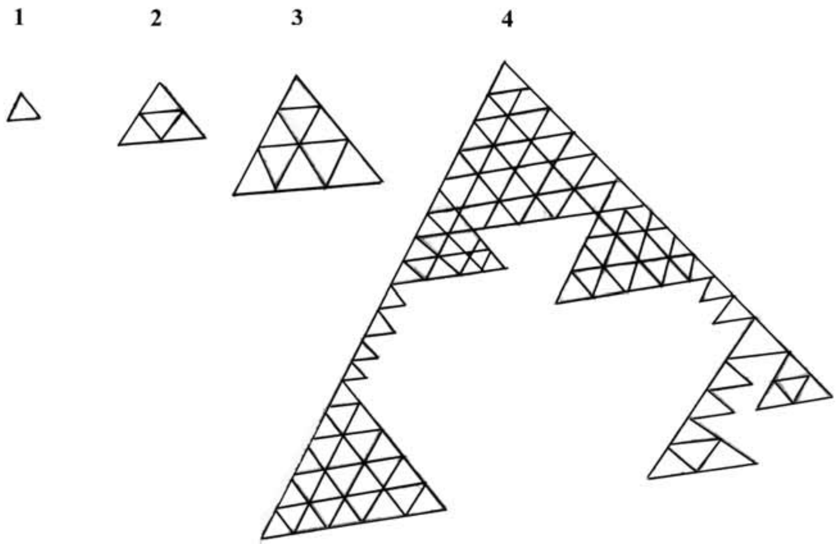


*Fig. 4. Sketch of evolution of skeletal crystals from (1) acicular (1) through (2, 3) "tower" to "bastion" habit.*

admixture is less than 0.01 wt.%) that is unusual for karst. According to electron paramagnetic resonance spectroscopy, neither centers nor chemical admixtures affecting color are found. However, the reported calcite segregations are characterized by unusual color changing under ambient conditions during a short period (a few hours) to dirty white. Fresh aggregates are of various yellow shades . Aggregates with pink, blue and green shades are occasional.

The samples studied, being storedat stable low humidity, do not change color for a long period (up to 15–20 days). Nevertheless, any sample becomes dirty white after this period.

In the case of long storage (one month and longer) at slowly and fradually decreasing high humidity, yellow color of the samples was not changing. In similar environment, green shade is seldom retained , whereas pink and blue shades are never retained.

Fast change of color without artificial maintenance of the storage mode (samples are bleached for the first hours) prevents the preparation of the samples for IR-spectroscopic study. The nature of colouring of the described samples is unclear . Dependence of the aggregates color stability on humidity and storage conditions suggests that color is determined in any way by adsorbed water.

## Formation conditions of skeletal crystals

Unusualness of the karst system, where the described skeletal crystals are formed is of special interest. Daily (5 – 10°C) and seasonal (30—40°C) temperature variations were recorded during obserbation of many years. Significant seasonal fluctuations of the system debit, which are not typical of karst, were also recorded. In addition, Besides, the described karst system is characterized by an active ventilation that results in the abovementioned features.

As is known, the crystallization from the seepage solutions is affected by fatal changes in mineral-forming system because of the temperature variations. The described calcite aggregates are formed from seeped solutions that get in the zone of crystallization as drops and aqueous films supplying the growing aggregate.

Churakov (1912) reported the similar mechanism of crystallization for stalactite in the system with constant debit and temperature. As a result of seepageinfiltration, the solution is diluted in the zone of crystallization leading to the formation of helictites and/or hollow stalactites under isothermic conditions. Strong and drastic temperature fluctuations, active ventilation, and changing debit of the systems are resulted in the formation of skeletal crystals.

## References

*Churakov A.N.* To the problem of the structure and growth of tubular stalactites. // Trudy St.Petersburg Soc. Naturalists. **1912**. Vol. XXXV. No 5. P. 1155 – 1161 (in Russian).

*Dorofeyev E.P.* Ice crystals in the lakes of the Kungur cave. Priroda. **1970**. No 4. P. 54 – 56 (in Russian).

*Godovikov A.A.* On the calcite from the quarry near the Amerovo village, Moscow region. Tr. Mineral. Museum. **1961**. Vol. 12. P. 57—69 (in Russian).

*Ikornikova N.Yu.* Formation and growth of crystals of trigonal carbonates. In: Hydrothermal synthesis of crystals. Nauka, Moscow. P. 123 – 137 (in Russian).

*Lebedev L.M.* Metacolloids in endogenic deposits. Nauka, Moscow. **1964**. (in Russian).

*Lebedev L.M., Stepanov V.I.* Nikel-bearing calcite from the Podolsk. Tr. Mineral. Museum. **1955**. Vol. 7. P. 167 – 170 (in Russian).

*Moroshkin V.V.* (1984): Minerals of the Kugitang caves. Priroda. No 3. P. 51. (in Russian).

*Shafranovskiy I.I., Mokievskiy V.A.* Conditions of growth, geometry and symmetry of skeletal crystals. Zapiski VMO. **1956**. Vol. 85. N 2. P. 171 – 186 (in Russian).

*Shustov A.V.* Elemental mechanism of setting and goniometry of large calcite crystals. Zapiski VMO. **1966**. Vol. 95. No 1. P. 465 – 467 (in Russian).