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Formation of Monohydrocalcite in the Microbialites From Laguna De Los Cisnes (Isla Grande De Tierra del Fuego, Chile)

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Abstract:

Monohydrocalcite ($CaCO_3 \cdot H2O$) is a mineral rarely found in natural environments. Here we report finding of this mineral in the composition of the microbialites from a saline alkaline lake Laguna de los Cisnes (Isla Grande, Chile). We have made a structural and mineralogical description of these microbialites with the use of light and scanning electron microscopy, infrared spectroscopy and X-ray analysis. The predominantly carbonate composition of microbialites was revealed. Carbonates were represented mainly by high-magnesium calcites and monohydrocalcite. The yellowish-brown surface layer of microbialites consists of numerous crystals within a mineralized exopolysaccharide (EPS) matrix. A large number of unicellular and filamentous algae, as well as areas of released EPS, are also seen here. Below is a slimy green layer. This layer is not mineralized, it represents an "algal-bacterial mat" consisting of algae, cyanobacteria, and diatoms developed in EPS. Chisel-shaped crystals of monohydrocalcite and its amorphous spherical precursors are numerous in these upper layers. Thus, monohydrocalcite occurs in the upper layers of the microbialites being one of the main mineral components. As in other lacustrine localities it is formed in the presence of algae and cyanobacteria. To our knowledge this is the first report on the discovery of monohydrocalcite in South America.

Keywords: monohydrocalcite; microbialites; saline alkaline lake; algae; South America.

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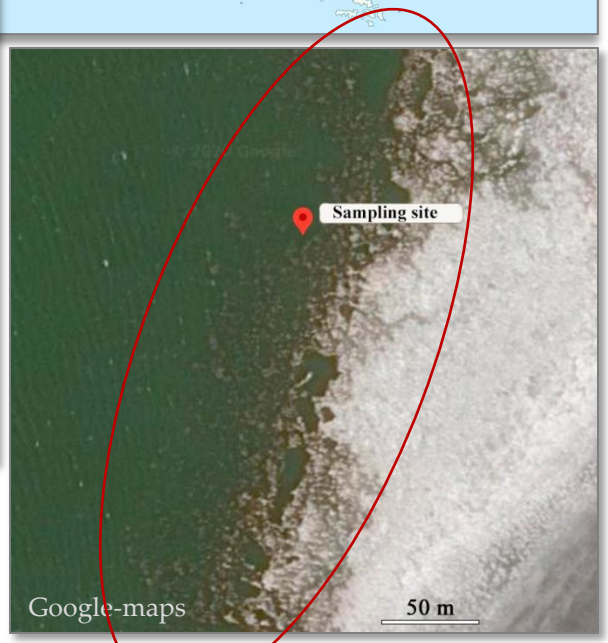
Results and Discussion

Laguna de Los Cisnes

Geographic location:

Chile,
Isla Grande
de Tierra del Fuego,
Porvenir,
53°14'24.0"S, 70°20'38.8"W



Numerous microbialites develop on the coastline of the lake.

Hydrochemical parameters:

Temperature (ºC)		16.4
pH		9.42
Conductivity (µS)		78 400
Salinity: refractometer (‰) sum of ions (g/l)		50 76.8
Total alkalinity(mM)		415
Cations (mg/l):	Na^+	17 230
	K^+	550
	Mg^{2+}	750
	Ca^{2+}	12.5
Anions (mg/l):	Cl^-	35 000
	HCO_3^-	12 505
	CO_3^{2-}	6 300
	SO_4^{2-}	4 441
	NO_3^-	5

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Microbialites from Laguna de Los Cisnes represent numerous carbonate structures in the form of oblong domes, hollow inside and elongated perpendicular to the coast.

Carbonate domes located in the lake water, have a yellowish-brown surface color. They are living and growing microbialites.

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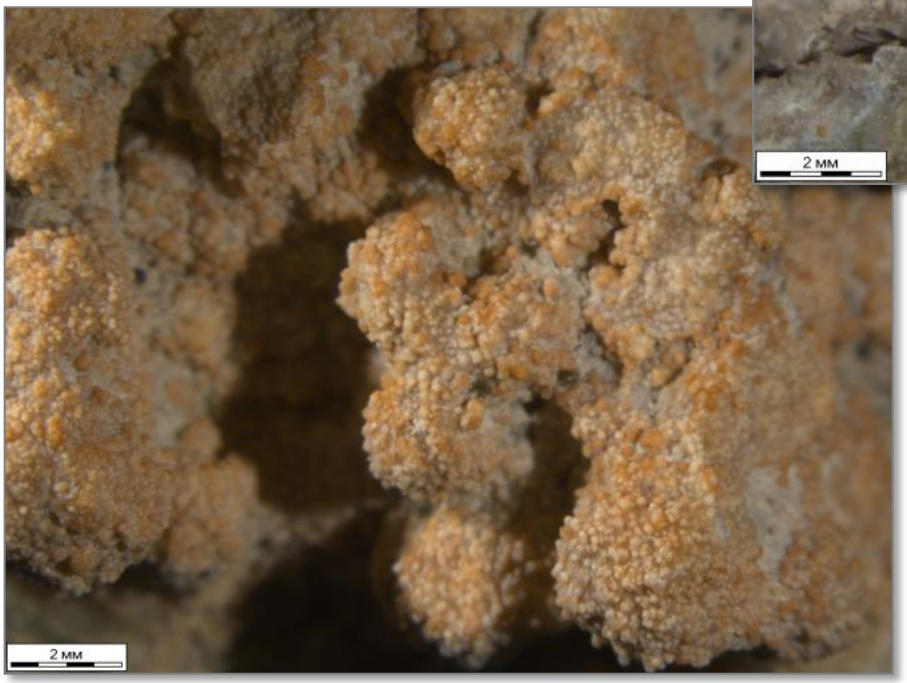
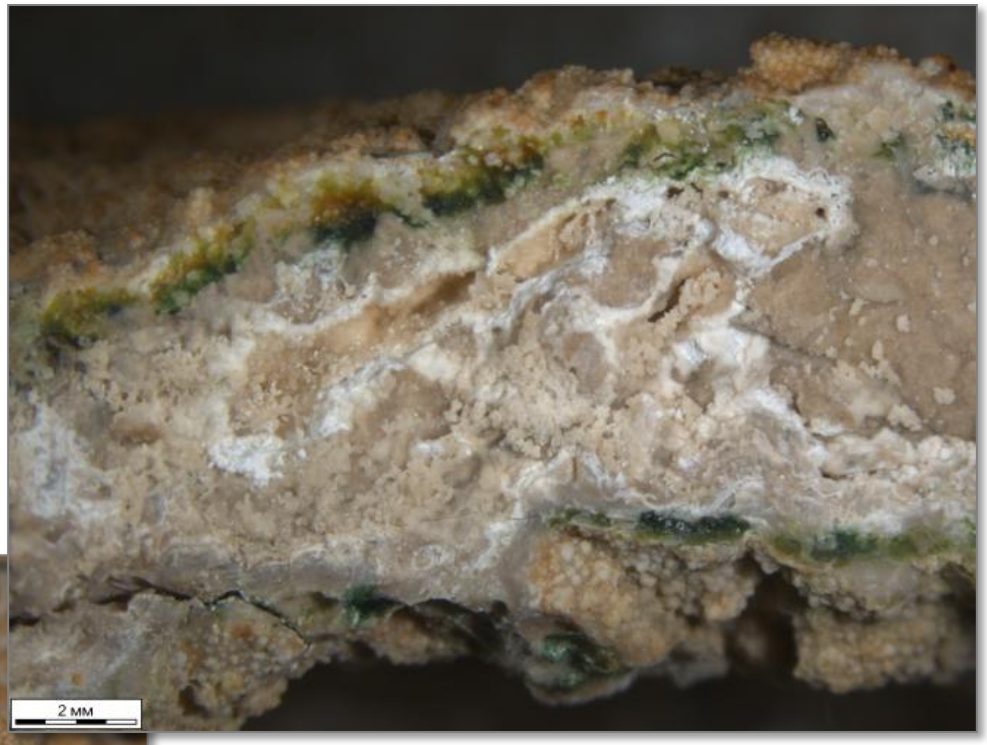
The microbialtes have a surface consisting of numerous “cones” of various sizes and locations relative to each other. It most resembles cauliflower inflorescences.





Differently colored layers are clearly seen on the vertical splits: yellowish-brown surface, slimy green subsurface layer (sometimes also with a purple layer) and light-brown inner layer.

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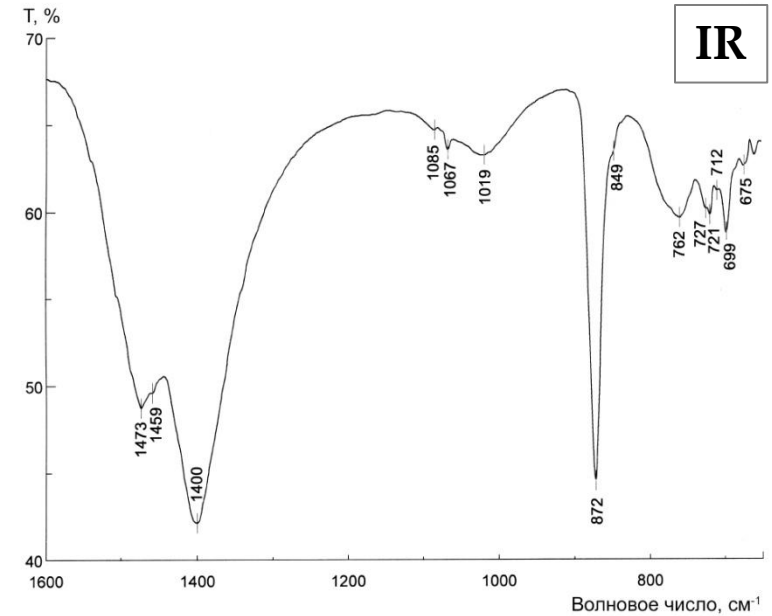

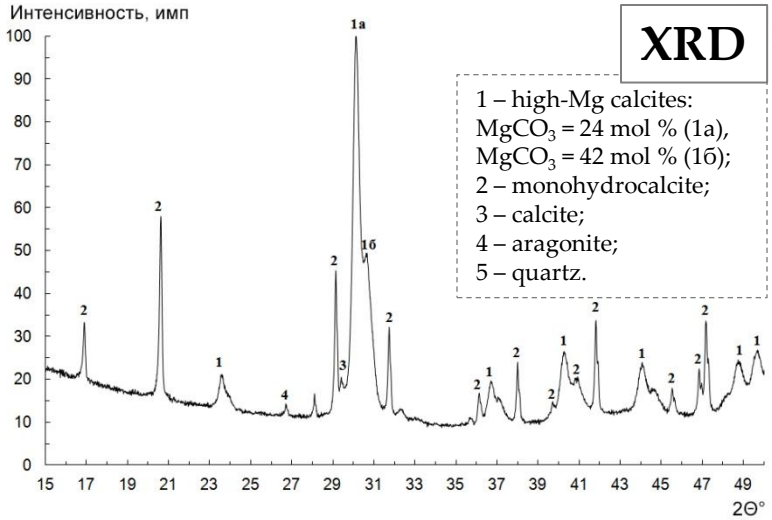

The predominantly carbonate composition of microbialites was revealed using infrared spectroscopy (IR) and X-ray diffractometry (XRD). Carbonates are represented mainly by high-magnesium calcites and monohydrocalcite. Calcite and aragonite are found in minor quantities. In addition, a small amount of silicates and amorphous hydromagnesite are found.

The IR spectrum of the mineral monohydrocalcite is characterized by absorption bands with maxima at 1408 and 1487 (doublet), 1068 and 760 cm^{-1}. The studied microbialites contain other carbonate minerals, which affect the position of the absorption band maxima in its IR spectrum. Thus, the positions of the absorption band maxima of monohydrocalcite in a total spectrum of the sample has the following values: 1400 and 1473 (doublet), 1067 and 762 cm^{-1}.

XRD shows the presence of monohydrocalcite with d(Å) 4.31, 3.06, 1.93, 2.16, 2.37 (ICSD 200820, PDF 29-306).

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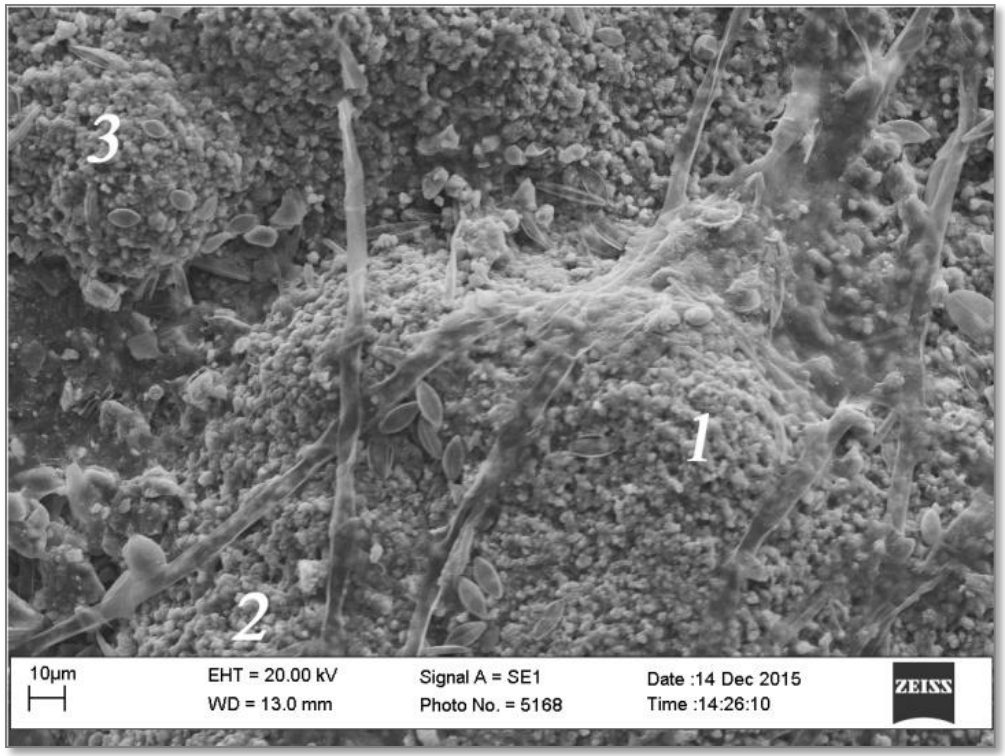
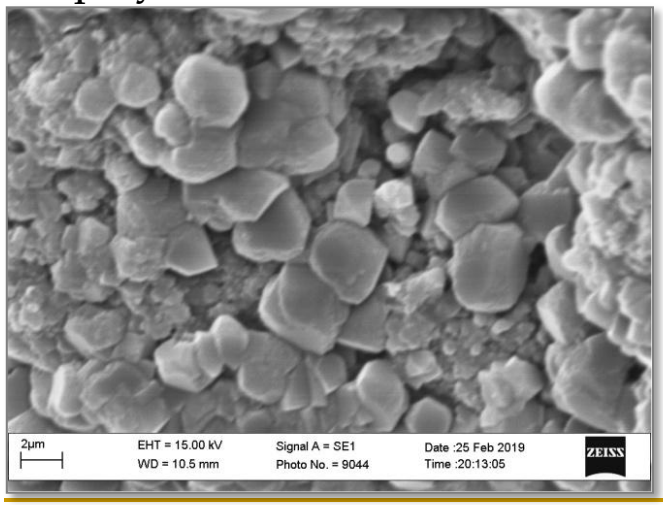
The yellowish-brown surface layer of microbialites consisted of numerous crystals connected by a mineralized polysaccharide matrix. Energy dispersive X-ray spectral microanalysis (EDX) of the surface areas revealed the predominance of calcium in the elemental composition of these crystals, confirming their assignment to monohydrocalcite. Numerous unicellular and filamentous algae were also visible here, as well as areas of free exopolysaccharide.





№	Atomic %							
	C	Na	Mg	Si	Cl	Ca	Fe	O
1	27.6	0.3	-	0.2	-	8.0	0.2	63.8
2	22.3	0.4	-	0.5	0.2	15.0	0.4	61.2
3	25.0	0.4	-	0.2	0.1	11.3	0.5	62.5

Crystals of monohydrocalcite were found mainly in the surface and near-surface layers. Their chisel-like shape is visible at higher magnification.

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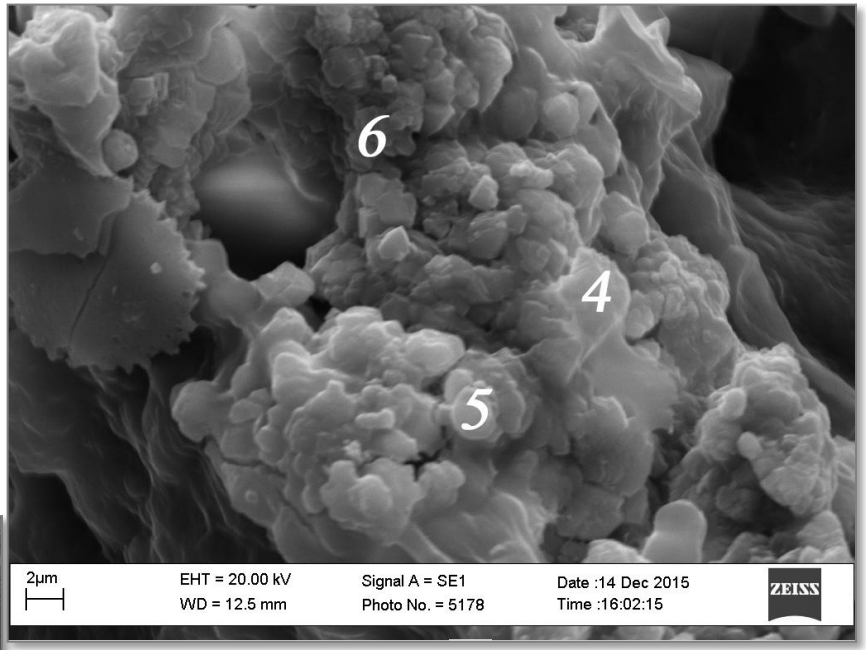
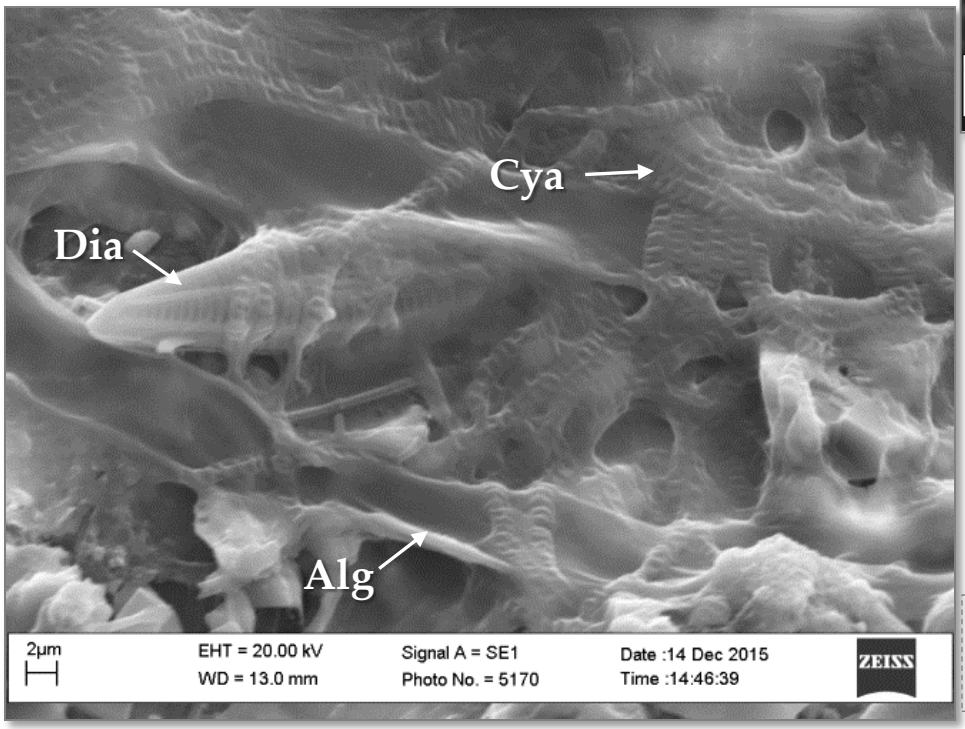
Below was a slimy green layer. This layer was not mineralized and represented an "algal-bacterial mat" consisting of an exopolysaccharide (EPS) matrix with filaments of algae and cyanobacteria, as well as diatoms. Various chemical elements indicating the precipitation of sodium and potassium chlorides, sodium carbonates and Ma-Ca carbonates from the lake water were detected in the EPS of this layer using EDX (*data not shown*).





The formation of crystals (including putative monohydrocalcite) within the EPS was also detected in some sectors.

№	Atomic %					
	C	Na	Mg	Cl	Ca	O
4	29.1	0.6	-	0.1	5.8	64.4
5	29.4	0.5	-	0.1	5.5	64.5
6	27.6	0.3	-	0.1	8.3	63.7

Dia – diatoms;
Cya – cyanobacteria;
Alg – filamentous algae.

The inner light-brown layer was mineralized and consisted predominantly of Mg-carbonates with varying degrees of Mg. Algae and cyanobacteria were decomposed or fossilized there (*data not shown*).

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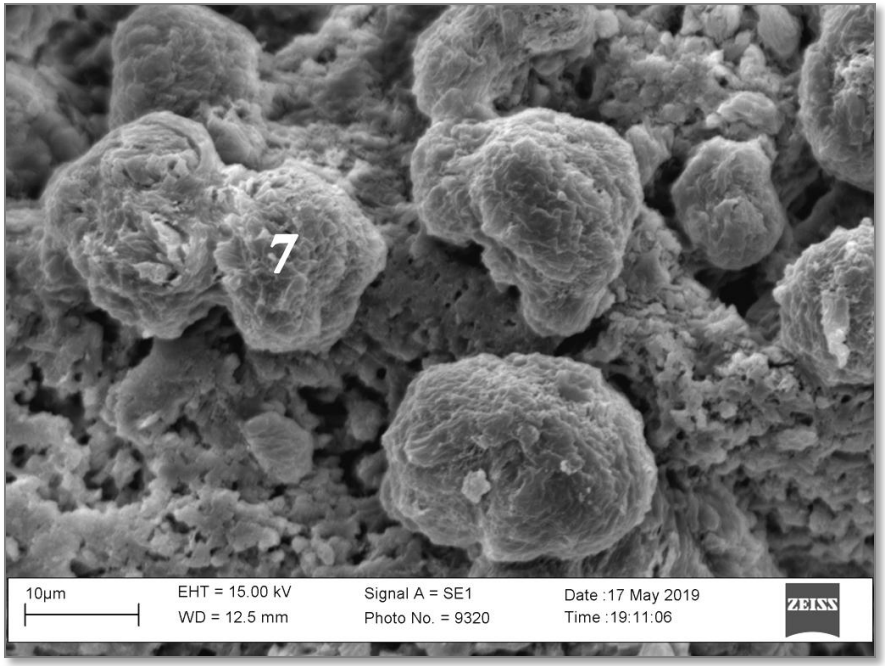

№	Atomic %					
	C	Na	Mg	Cl	Ca	O
7	30.4	0.6	0.8	0.3	3.0	64.9

It is supposed that monohydrocalcite crystallizes in a 4-stage process [Wang et al., 2015]. In the 1st stage of its nucleation, amorphous calcium carbonate (ACC) appears, forming spheres. At the 2nd stage, the spheres are crystallized with the formation of monohydrocalcite, at the 3rd stage maturation occurs, and at the 4th stage Mg releases from the structure of monohydrocalcite.

The studied microbialite samples contain areas of minerals with low ordering: with poorly crystallized fragments and globules. Numerous amorphous spherical formations of Mg-Ca-carbonate composition with $MgCO_3$ content from 10 to 23%, found in the composition of the surface layer of the studied microbiolite, can be precursors of monohydrocalcite.

Conclusion

Thus, monohydrocalcite occurs in the composition of the microbialites being one of the main mineral components. As in other lacustrine localities it is formed in the presence of algae and cyanobacteria. The influence of the metabolic activity and released organic compounds on the monohydrocalcite precipitation is still unclear.

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