Crisite - a new minerai species found in the Bolhac cave
(Pǎdurea Craiului mountains, Romana)

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Abstract

A white, sometimes yellow-brownish, gelatinous sediment found in the Bolhac cave was studied in laboratory (microscopy, chemical composition, X-ray analysis, IR spectroscopy, therm o-analysis). It is a new amorphous minerai assigned to the group of hydrated aluminium sulphate-silicates and should be called "crisite".

Résumé

Dans la grotte de Bolhac, on a trouvé un sédiment gélatineux de couleur blanche, parfois jaune-brunâtre. Divers échantillons en ont été observés en laboratoire. La microscopie, l'analyse chimique, la diffractométrie, le spectre infra-rouge et la thermo-analyse suggèrent qu'il s'agit d'un minéral nouveau, amorphe, du groupe des silicates-sulfates hydratés d'aluminium. Il devrait être appelé "crisite".

I. GENERAL DATA

The Bolhac cave is located in the northern part of the Pǎdurea Craiului mountains, 2.5 km upstream from uncuiu . The entrance, situated only 1 m above the level of Cri ul Repede River, is an impressive arcade of 33 x 20 m, opening in the left bank of the river, at the altitude of 307 m.

The cave is cut in marblish white Ladinian limestone (Fig. 1). The limestone is unconformably and transgressively overlain by Liassic sandstone and quartzitic microconglomerates within which lens-shaped kaolinitic clays, sometimes associated with pyrite and marcasite, are to be found.

H. MORPHOGENETIC OUTLINE OF THE CAVE

The Bolhac cave has a length of 554 m (WǍLENŞ & IURKIEWICZ, 1981) out of which 320.5 m belong to the main passage (Fig. 2). There is an underground stream, 195 m long, with no affluents, for which we assume an infiltrational source along the limestone/sandstone boundary. The collecting area is in fact a swamp formed by the waters coming from old mining galleries, in the slope of Grosu hill. The pH of these waters is strongly acid (3.3-5.1), uncharacteristic for the karstic sources in the area.
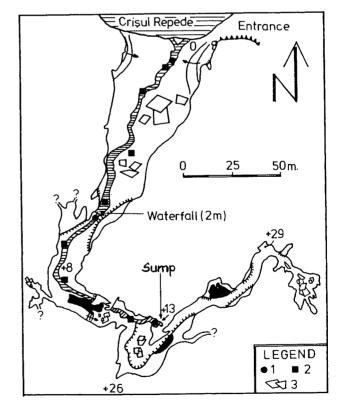

Figure 1 : Map of Bolhac cave (simplified after & IURKIEWICZ, 1978-1980)

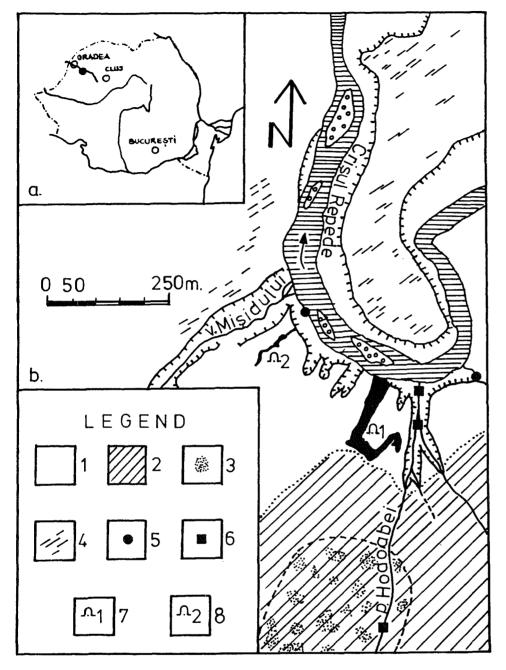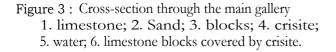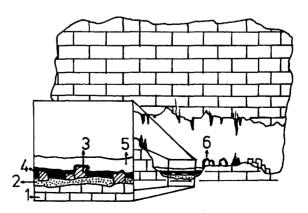1 water samples; 2 *crisite* samples; 3 limestone blocks

Figure 2 :
a) location of the studied area on the map of Romania
b) geological map of the investigated area :
1. limestone (Ladinian) ; 2. sandstone (Hettangian-Sinemurian) ; 3. pyritization ; 4. lapies ; 5. spring; 6. water samples ; 7. Bolhac cave ; 8. Napiștileu rave

Figure 3 : Cross-section through the main gallery
    1. limestone; 2. Sand; 3. blocks; 4. crisite;
    5. water; 6. limestone blocks covered by crisite.

For example, the waters of the Napiștileu cave (195 m long, with a 71 m long underground stream), located in the close vicinity, have a pH of 6.5. This high acidity is caused by the oxidation of pyrite and marcasite, fairly abundant in the sandstone cut by the stream.

III. DESCRIPTION OF THE GELATINOUS DEPOSIT

All along the underground stream bed, covering both sandy alluvia and its limestone borders, a layer of white, sometimes yellow-brownish sediment can be observed (Fig. 3).

The material of which the sediment is formed is jelly-like in the water, easily dispersing when sampled. The thickness of the sediment is of 1-3 cm on the river bed white the submerged blocks are covered only with 3-5 mm of the same material. The emerged blocks have also an 1-3 mm thick crust formed by under-water deposition during floods (Fig. 3). The above mentioned moonmilk-type sediment also covers the bed of a 2 m high waterfall.

Detailed observations showed that the sediment is thicker in the lower third of the underground stream and in the arecs with pools; even the pools are close to the sump which makes the source of the subterranean stream. This indicates a transport of the material in suspension during floods, from the upper to the lower, flatter, sections of the cave, and also explains the thicker deposits from the lower third, as well as their presence on the emerged borders of the stream.

Figure 4 : Globular cluster of Crisite

Figure 5 : Globular cluster of Crisite; goethite

IV. LABORATORY DATA

The analysis performed on samples collected from varions locations in the cave (Fig. 2) showed the following :

A. Microscopy

Under polarized light, the material behaves like an isotropic, earthy mass, due to the very small size of granules. TEM (transmission electronic microscope) analysis shows a homogenous mass (more than 90%) made up of agglomerates of tiny spheres, rarely ovoids, with diameters ranging from 0.02 to 0.2 μm, specific for colomorphous minerals (Fig. 4, 5). Rare (3-5%) xenomorphous equally thick and semitransparent to electron beams lamellae, have also been noticed ; only 2-3% of these lamellae revealed to have a reticular structure when checked bv electron diffraction. The diffraction pattern produced by individual crystals, is characteristic for phylosilicates with pseudohexagonal symmetry (probably illite). Goethite prisms (1 - 2 %) are also present (0.2-1 pm).

B. Chemical composition

The chemical analysis revealed high contents of Al_2O_3 and notable amounts of SO_3, SiO_2 and H_2O+ (as main components of the mineral) and $1(_2O$, mainly as adsorbing ion. The rest of the oxides are present in negligible amounts, and are considered to corne from impurities (Table 1). The problem arising here is : are the three main components gathered in one compound or in distinct phases? An answer could be provided by microprobe analysis (Fig. 6-8).

Chemical composition (★)				Interpretation	
Oxides	%	Impurities	crisite	Chemical formula	
SiO_2	8.51	3.11	5.40	Chemical coefficients	
TiO_2	0.26	0.26	-	Si	1.06
Al_2O_3	48.17	0.98	47.19	Al	10.94
Fe_2O_3	1.26	1.26		K	0.36
MnO	0.12	0.12	-	S	2.00
MgO	0.15	0.15	-	OH	25.10
CaO	0.49	0.49	-	H_2O	2.03
K_2O	1.50	0.06	1.44	Chemical formula :	
Na_2O	0.20	0.20	-	$K_{0.3}Al_{10.9}(OH)_{25}(SO_4)SiO_42H_2O$	
P_2O_5	0.18	0.18	-	Mineral impurities computed by normative method	
I.L.	39.36				
Total	100.20			Silica	2.07
SO_3	13.55		13.55	Hydromicas	2.84
CO_2	0.22	0.22	-	Calcium phosphate	0.40
Data from thermal analysis Ignition loss				Calcite	0.49
°C				Fe, Mn, Ti oxides and hydroxides	1.79
50-110	3.1	(H_2O)	3.1	Total impurities	7.59
110-400	19.7	(OH⁻) 0.58	19.12	(★) The analysis was performed at the chemistry laboratory of ICPMSN Cluj-Napoca by Monica Bengeanu	
400-750	3.2	(SO_3, OH⁻)	-		
750-1000	10.4	(SO_3, CO_2)	-		
Total	36.4				

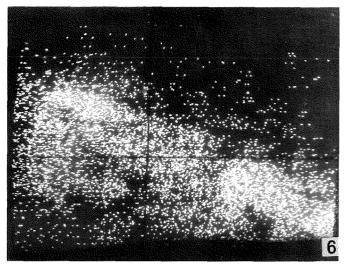**Table 1 :** Chemical composition and thermic behaviour of the crisite.

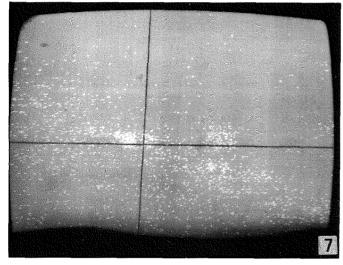**Figure 6 :** Electron microprobe analysis.
Al repartition

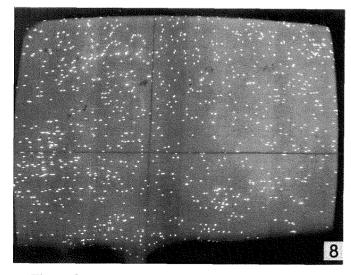**Figure 7 :** Electron microprobe analysis.
Si repartition

Figure 8 : Electron microprobe analysis. S repartition

It must be mentioned that the investigated layer is made-up of superposed spherulites, therefore the data obtained can not be rigorously assigned to a unique phase. Silicon distribution in respect to aluminium is relatively uniform, excepting some agglomerates, very poor in aluminium, that we considered to be opal and illite. We estimate opal does not exceed 1-2% in the sample. An argument for the presence of SiO_4^{4-} in the formula of the minerai is given by the presence of mullite in the sample heated at 1000°C. Although the uniform distribution of sulphur in the "X-ray image" indicates the Jack of correlation between SO_4^{2-} and Al^{3+} ions, we consider that SO_4^{2-} is actually part of the minerai formula, on the ground of the endotherms at 830°C and 880°C, characteristic of the decomposing of aluminium sulphate.

The formula of the minerai is :

$$K_{0.3} Al_{10.9} [(OH)_{25} (SO_4) (SiO_4)] 2H_2O$$

The amount of water lost until 110°C varies according to the dryness of the sample, ranging from 2 to 4 H_2O.

C. X-ray analysis
The X-ray analysis (diffractometry) shows the a-morphous character of the sample. After heating at 1000°C, we obtained a spectrum characteristic of mullite (Table 2) and probably for i-Al_2O_3 (FOSTER, 1959).

D. IR spectroscopy

The IR spectrum clearly shows the presence of H_2O and OH^-. Absorption bands characteristic of SO_4^{2-} compounds, as well as of Si-O-Al and of Al-OH bands, were also obtained. The line at 1445 cm^{-1} was assigned to calcite (Fig. 9).

E. Thermie analysis
The DTA curve shows a double endotherm effect at 100°C, and 200°C respectively, and two close linked endotherms at 830°C and 880°C, followed by the exotherm at 940°C that marks the formation of mullite. The fast two endotherms are the result of water release, the following two ones marking the release of OR, SO_3 and small amounts of CO_2 (Fig. 10).

When testing the pH of the samples collected along the underground Stream (Table 3), a slight neutralization due to the buffer-effect of the limestone was noticed, this parameter varying from 3.8 (at the sump) to 4.6 (at the entrance), favouring thus the precipitation of the *Crisite* from solution.

d	I	Mullite 15-776		ℓ -Al$_2$O$_3$ 12-537	
		d	I	d	I
6.347	2	-	-	-	-
5.453	50	5.39	50	5.45	100
4.234	1	-	-	-	-
4.018	1	-	-	-	-
3.814	3	3.774	8	-	-
3.482	30	-	-	3.47	100
-	-	3.428	95	-	-
3.429	100	3.390	100	-	-
3.348	40	-	-	-	-
3.289	1	-	-	-	-
3.161	1	-	-	-	-
3.076	1	-	-	-	-
2.900	25	-	-	2.92	20
2.882	20	2.886	20	-	-
2.708	50	2.694	40	2.72	80
2.561	40	-	-	2.59	80
2.547	45	2.542	50	-	-
2.446	15	-	-	2.46	5
2.329	5	-	-	2.34	80
2.307	30	2.292	20	-	-
2.212	55	2.206	60	2.24	80
2.131	25	-	-	2.15	40
2.125	24	2.121	25	-	-

Table 2 : X-ray diffraction spectrum of crisite, heated at 1000 $^\circ$C.

Place	Analysis					
	pH	Ca^{2+}	Mg^{2+}	SO$_4^{2-}$	Cl$^-$	Total
				(mg/l)		
SUMP	3.80	48.5	22.4	264.3	2.6	337.8
WATERFALL	4.00	52.1	21.8	254.3	2.8	331.0
ENTRANCE	4.60	75.4	20.1	241.5	3.1	340.1

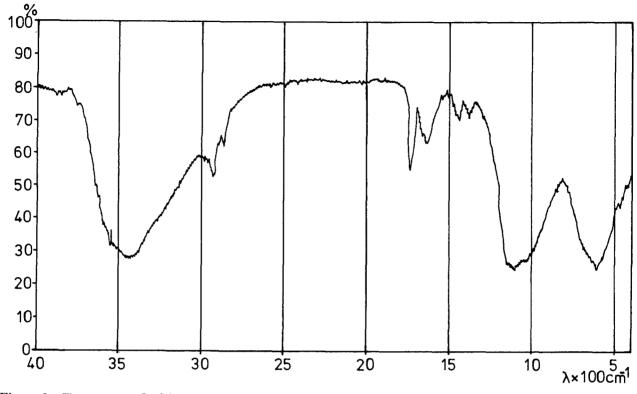Table 3 : Chemical analysis of the water samples from Bolhac cave.
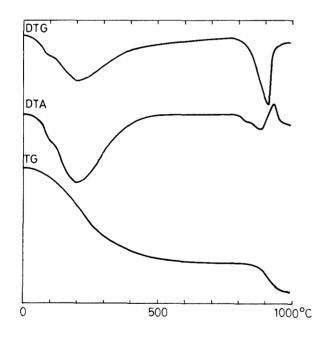
Figure 9 : IR spectrum of crisite

V. CONCLUSIONS

The analysis to which the white-yellowish minerai in the Bolhac cave has been subjected, negate the presence of allophane as we first thought. The chemical formula, the thermie analysis, the electron microscopy, microprobe and 1R spectroscopy are pleading for the existence of a new amorphous minerai, assigned to the group of hydrated aluminium sulphate-silicates, which we propose to be called *CRISITE* ; it derives from the latin naine of the Cri șul Repede River - *Crisis*. The first, and up to now the only, occurrence of this minerai is the Bolhac cave, which opens on the left bank of this river.

The *crisite* sample was deposited at the Mineralogy Museum of the "Babeș-Bolyai" University in Cluj—Napoca, Romania.

Figure 10 : Thermal analysis of crisite

VI. REFERENCES

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