GYPSUM AND BASSANITE IN THE BAT GUANO DEPOSIT FROM THE "DRY" CIOCLOVINA CAVE (SUREANU MOUNTAINS, ROMANIA)

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The "dry" Cioclovina Cave is located in the southern part of the Sureanu Mountains (Southern Carpathians), at about 16 km east-southeast of Haţeg, on Luncanilor Valley. The cave, known since 1873 and famous as the type locality for ardealite (Schadler, 1932), was extensively exploited for phosphates because the huge bat guano deposit inside. The mined part of the cave consists in a nearby sub-horizontal gallery with some short divergent passages, measuring on their all about 900 m. The cave is developed in Tithonic - Neocomian algal micritic limestones with calacrenite levels.

Phosphates from this famous guano deposit were subjected to minute investigation (*e.g.*, Constantinescu *et al*., 1999; Marincea *et al*., 2002; Marincea & Dumitraş, 2003; Dumitraş *et al*., 2004) and are the best documented from the 29 mineral species described in the cave. As a note, Onac *et al*. (2002) and Onac & White (2003) reported the presence of some exotic mineral species, such as berlinite, burbankite, churchite, chlorellestadite, foggite, paratacamite, collinsite and sampleite, but their occurrence is not enough substantiated.

During recent investigations, two Ca sulfates were also identified in the deposit: gypsum and bassanite. In Sample D 115, the two species occur as finely intergrown phases, with the dominant mineral being bassanite. Many other samples consist in pure gypsum. As far as the authors are aware, this is only the third report of bassanite in a Romanian cave and the first submitted to a minute mineralogical study.

The present paper aims to report new physical, chemical, X-ray and infrared absorption data on the two sulfate species, gypsum and bassanite. The information herein is based on scanning electron microscopy coupled with energy-dispersive scans, X-ray powder diffraction (Cu Kα, λ = 1.54056 Å) and Fourier-transform infrared absorption spectrometry. All the analytical facilities, procedures and experimental details are similar to those described by Dumitraş *et al*. (2004).

Gypsum is one of the most common sulfates in the bat guano deposits from the caves (*e.g.*, Hill & Forti, 1997). At Cioclovina, the mineral generally forms parallel aggregates of minute bladed crystals up to 100 µm in length. It occurs as tiny individuals, flattened on {010} and elongated toward [001]. Stacking aggregates of crystals grown subparallel or parallel to (010) are common.

The unit-cell parameters determined for representative samples after "n" cycles of least-squares refinement based on "N" well-resolved X-ray powder diffraction lines are given in Table 1. The refinements were carried out accepting the monoclinic symmetry, space group I2/c, of the mineral (Cole & Lancucki, 1974).

Table 1. Unit-cell parameters of selected samples of gypsum from the "dry" Cioclovina Cave

Sample	a (Å)	b (Å)	c (Å)	V (Å^3)	β (^{o})	n	N
D 25 II	6.513(3)	15.185(7)	5.684(2)	494.71(3)	118.37(2)	8	49
D 31 A	6.518(7)	15.184(1)	5.669(4)	494.77(7)	118.15(5)	3	24
D 32 A	6.519(3)	15.190(7)	5.678(3)	495.48(3)	118.21(2)	3	47
D 37 A	6.507(1)	15.221(3)	5.683(7)	495.78(1)	118.25(1)	6	28
D 38 A	6.513(2)	15.187(5)	5.672(2)	493.87(2)	118.33(2)	10	32
D 68 A	6.521(4)	15.202(9)	5.675(3)	494.53(3)	118.46(1)	7	83
D 81	6.523(8)	15.202(2)	5.679(7)	495.09(7)	118.46(1)	7	71
D 115	6.513(3)	15.152(9)	5.675(3)	493.20(3)	118.30(3)	7	51

The calculated density of a selected sample of gypsum from Cioclovina (sample D 115) with the ideal formula $(Ca_{0.998}K_{0.001}Na_{0.003})(SO_4)\cdot2H_2O$ (see below), is, for $Z = 4$, $D_x = 2.318$ g/cm^3. This value is in good agreement with the density of the "light" fraction obtained by heavy liquid separation, measured by suspension in methylene iodide diluted with toluene, which is $D = 2.32(1)$ g/cm^3 for a mean refraction index $n = 1.52(1)$. Calculations from the chemical data and the physical parameters (n and D_x), using the Gladstone-Dale constants of Mandarino (1981), gave "superior" compatibility (compatibility index = - 0.0112).

Bassanite occurs as pseudomorphs after gypsum, whose perfect cleavage parallel to {010} is always observable. The SEM study shows that bassanite occurs as clustered acicular crystals that parallels the [001] axis of gypsum. They currently show parallel growth along the longest axis. Crystals are of the order of no more than 5 μm in length and often much less than this.

The gypsum + bassanite association occurs as decimeter-sized, white nodules of earthy or chalky appearance, included by the guano mass. No fluorescence has been observed for these nodules under either short-wave (254 nm) or long-wave (366 nm) ultraviolet radiation. The analyzed sample (D 115) was taken off from an excavation that parallels the northern wall of a passage preceding the Bivouac Room. Restricted to this sample, associated minerals include brushite, minor quartz and illite 2*M*1. In order to avoid supplementary gypsum dehydration, samples were stored after collection in sealed plastic bags, at room temperature. As a result of the finely intergrown nature of the aggregates, it was not possible to obtain pure mineral separates.

A wet-chemical analysis of a composite aggregate (sample D 115) gave (in wt.%): CaO = 35.05, MgO = 0.01, K$_2$O = 0.04, Na$_2$O = 0.06, P$_2$O$_5$ = 4.55, SO$_3$ = 45.02, H$_2$O$^+$ = 14.49, total = 99.22. The corresponding chemical-structural formula, calculated on the basis of 1 (P + S) per formula unit (*pfu*), is: $(Ca_{0.998}K_{0.001}Na_{0.003})(SO_4)_{0.898}(HPO_4)_{0.102}\cdot1.233H_2O$. Accepting that all the

sulfate ions are included in the formula of gypsum and bassanite and all the protonated phosphate pertain to the formula of brushite, the formula above corresponds to a mixture of 45.53 wt.% bassanite, 44.27 wt.% gypsum and 10.20 wt.% brushite. Supposing that the alkali cations are uniformly distributed within the three mineral species, which respect the stoichiometry as concerning the molecular water, the formula of bassanite is $(Ca_{0.998}K_{0.001}Na_{0.003})(SO_4) \cdot 0.5H_2O$.

Its unit-cell parameters, calculated after 6 cycles of least-squares refinement from 32 X-ray powder reflections attributable to bassanite in the sample, are: $a = 12.027(12)$ Å, $b = 6.906(7)$ Å, $c = 12.657(17)$ Å and $\beta = 90.27(6)°$. They were refined in the space group $I2$, accepted for the mineral by Ballirano $et\ al.$ (2001).

With Z = 12 (Ballirano $et\ al.$, 2001), the calculated density for the formula given before is $D_x = 2.751$ g/cm^3, which is close enough to the value measured for the "heavy" fraction in Sample D 115 by sink-float in methylene iodide diluted with toluene [D = 2.74(1) g/cm^3]. A mean index of refraction measured in Cargille oils for the same fraction, that apparently consists mainly in bassanite, is n = 1.56(1). Calculation of the Gladstone-Dale relationship using the calculated density and the constants of Mandarino (1981) yields superior compatibility (compatibility index = -0.0186).

An infrared spectrum recorded for the "heavy" fraction in Sample D 115 gave bands that are assumable to both gypsum + bassanite (gyp + bas) and brushite (brs). An attempt to assume these bands to specific vibrational modes of the structural groups in the three mineral species is given in Table 2, being largely based on data in literature. These assumptions ignore the tendency to overlap of the infrared bands and must be taken with caution.

Table 2. Positions and ideal assumptions of the infrared absorption bands of Sample D 115

Structural group	Vibrational mode	Wavenumber (cm^{-1})	Character, intensity[1]	Mineral species
H_2O	ν_3 antisymmetric stretching	3617	s, sh	bas
H_2O	ν_3 antisymmetric stretching	3561	s, sh	gyp, bas, brs
H_2O	ν_3' antisymmetric stretching	3431	s, b	gyp, bas, brs
H_2O	ν_1 symmetric stretching	3250	s, shd	gyp, bas, brs
$(HPO_4)^{2-}$	(P)O-H stretching	2935	s, shd	brs
H_2O	ν_4 in-plane H-O-H bending	1621	m, b	gyp, bas, brs
$(SO_4)^{2-}$	ν_3 antisymmetric stretching O-S-O	1158	vs, sh	bas
$(SO_4)^{2-}, (PO_4)^{3-}$	ν_3 antisymmetric stretching	1142	vs, sh	gyp, brs
$(SO_4)^{2-}, (PO_4)^{3-}$	ν_3' antisymmetric stretching	1138	vs, sh	gyp, bas, brs
$(SO_4)^{2-}$	ν_3 symmetric stretching O-S-O	1117	vs, sh	gyp, bas
$(SO_4)^{2-}$	ν_1 symmetric stretching	1011	m, sh	bas
$(SO_4)^{2-}, (PO_4)^{3-}$	ν_1 symmetric stretching	1007	m, sh	gyp, brs
$(HPO_4)^{2-}$	P-O(H) symmetric stretching	865	w, b	brs
$(HPO_4)^{2-}$	P-O-H out-of-plane bending	778	w, b	brs
$H_2O, (SO_4)^{2-}$	ν_2 H-O-H; ν_4 in-plane bending (O-S-O)	667	s, sh	brs; gyp, bas
$(SO_4)^{2-}$	ν_4' in-plane bending (O-S-O)	632	m, sh	gyp, bas
$(SO_4)^{2-}$	ν_4'' in-plane bending (O-S-O)	605	s, sh	gyp, bas

$(PO_4)^{3-}$	ν_4 in-plane bending (O-P-O)	576	w, sh	brs
$(PO_4)^{3-}$	ν_4' in-plane bending (O-P-O)	526	w, sh	brs
$(SO_4)^{2-}$	ν_2 out-of-plane bending (O-S-O)	492	w, sh	gyp, (bas)
$(SO_4)^{2-}$	ν_2' out-of-plane bending (O-S-O)	420	w, sh	gyp, bas
$(PO_4)^{3-}$	ν_2 out-of-plane bending (O-P-O)	410	w, shd	brs

(1) s = strong; m = medium; w = weak; vs = very strong; sh = sharp; b = broad; shd = shoulder.

The presence of $(SO_4)^{2-}$ in solution is clearly critical to the formation of gypsum at Cioclovina. The sulfate ions in the leaching waters, that may be strongly acidic, may derive both from the oxidation of the up-welling pyrite-bearing schists and from the oxidation of the organic matter in the guano itself. Bassanite formed during a later diagenetic stage, typical for the "dry" karst systems, and was found in the driest part of the cave.

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