

VARISCITE (AIPO₄·2H₂O) FROM CIOCLOVINA CAVE (ȘUREANU MOUNTAINS, ROMANIA): A TALE OF A MISSING PHOSPHATE

BOGDAN P. ONAC¹, JOE KEARNS², RADU BREBAN³,
SIMONA CÎNTĂ PÂNZARU⁴

ABSTRACT. Recent investigations on a phosphatized sediment sequence in the Cioclovina Cave led to the identification of a second occurrence in Romania (first time in the cave environment) of variscite, AIPO₄·2H₂O. The mineral exists as dull-white, tiny crusts and veinlets within the thick argillaceous material accumulated on the cave floor. Under scanning electron microscope (SEM) variscite appears as subhedral to euhedral micron-size crystals. The {111} pseudo-octahedral form is rather common. Variscite was further characterized by means of X-ray diffraction, thermal, vibrational FT-IR and FT-Raman spectroscopy, and by SEM energy-dispersive spectrometry (EDS). The calculated orthorhombic cell parameters are $a = 9.823(4)$, $b = 8.562(9)$, $c = 9.620(5)$ Å, and $V = 809.167(6)$ Å³. The ED spectrum of variscite shows well-resolved Al and P lines confirming thus the presence of the major elements in our compound. The formation of variscite is attributed to the reaction between the phosphate-rich leachates derived from guano and the underlying clay sediments.

Keywords: phosphate minerals, variscite, Cioclovina Cave, Romania.

GENERAL DATA

The Cioclovina Cave is located 40 km southeast of the city of Hunedoara, in the west-southwest side of Șureanu Mountains, Romania (Fig. 1, inset), at an altitude of 770 m asl. The investigated part of the cave develops in reef limestone of Lower Cretaceous age (Stilla, 1981; Pop et al., 1985). The total length of the cave is 1400 m (Breban et al., 2003), but only the first 450 m (Fig. 1) are of great interest with respect to the occurrence of authigenic phosphate minerals.

Mining operations undertaken in this cave during the first half of the 20th century have exposed impressive outcrops of interstratified alluvial sediments (clay, sand, and gravels) that were subsequently phosphatized through the action of P-rich solutions provided by the breakdown of guano and bones. Depending on whether the percolating water passing through guano reacts with carbonate rocks or clay minerals, Ca-, Mg-, and Al-rich, or K-Fe phosphates have been deposited.

Over the last five years, several descriptive and/or detailed mineralogical investigations were undertaken, each of them pointing out a remarkable rich and diverse assemblage of authigenic phosphate minerals. So far, 15 phosphate minerals were described by Schadler (1929, 1932), Halla (1931), Constantinescu et al. (1999), Dumitraș & Marincea (2000), Marincea et al. (2002, 2003), Breban (2002), Onac et al. (2002), Onac & White (2003), and Dumitraș et al. (2004a, b).

¹ Department of Mineralogy, „Babeș-Bolyai” University & “Emil Racoviță” Institute of Speleology, Clinicilor 5, 400006, Cluj, Romania (bonac@bioge.ubbcluj.ro).

² Materials Research Institute, The Pennsylvania State University, University Park, PA 16801, U.S.A.

³ S.C. Roșia Montană Gold Corporation S. A., Roșia Montană, Romania.

⁴ Department of Molecular Spectroscopy, „Babeș-Bolyai” University, Kogălniceanu 1, 400084, Cluj, Romania.

Variscite, ideally ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), is a relatively common cave mineral (Nriagu & Moore, 1984; Hill & Forti, 1997), but its presence in the Cioclovina Cave was not reported so far in any of the previous studies, although, five other Al-rich phosphates have been documented from this cave. When berlinite (AlPO_4) was identified, the authors hypothesized the possibility that variscite acted as precursor and its dehydration/calcination (due to guano combustion) ultimately led to berlinite (Onac & White, 2003). However, the identification of variscite in the phosphate association close to the berlinite occurrence, failed, and therefore its presence was simply a tale. The focus of the present paper is to characterize the variscite sample we recently identified in Cioclovina Cave. The only other identified occurrence of variscite in Romania is from the Iacobeni manganese deposit (Bălan, 1976) hence, this study is the first to report variscite in a Romanian cave environment.

OCCURRENCE AND PHYSICAL PROPERTIES

In the room located just across the place where the artificial gallery penetrates the cave (Fig. 1), a huge deposit of phosphatized argillaceous material (clays and silty-clays) was exposed during the mining activities. On the upper part of this outcrop, within the clay-rich sequence, crusts and veinlets of dull white clay-like aggregates, intimately associated with detrital quartz were sampled. The mineral is brittle, shows waxy luster, possesses a splintery fracture, and white streak. The thickness of these occurrences never exceeds 3-4 mm.

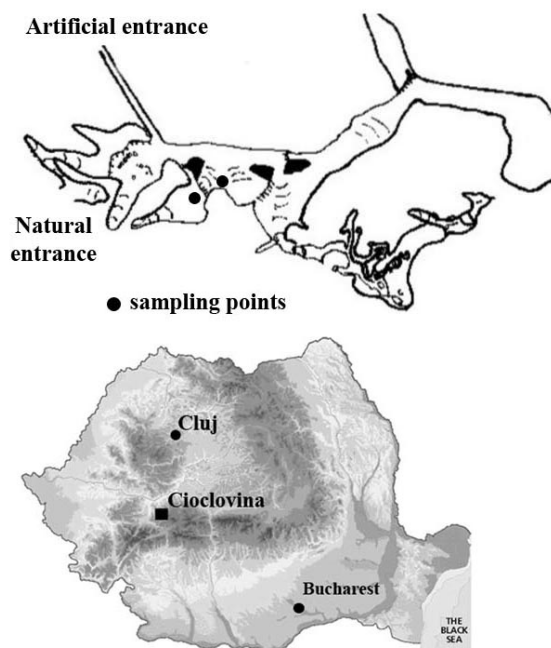


Fig. 1. Location of the Cioclovina Cave (inset) and the map of the near-entrance cave passage showing the location of the sampling points.

VARISCITE ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) FROM CIOCLOVINA CAVE (ȘUREANU MOUNTAINS, ROMANIA)

Carbon-coated fragments of variscite samples examined by a JEOL JSM 5510LV scanning electron microscope (SEM) showed the aggregates are generally composed of tiny euhedral and subhedral crystals that never exceed $2\ \mu\text{m}$ across (measured along the c axis) (Fig. 2, left). Nicely developed individual crystals having pseudo-octahedral habit $\{111\}$ can also be observed (Fig. 2, right).

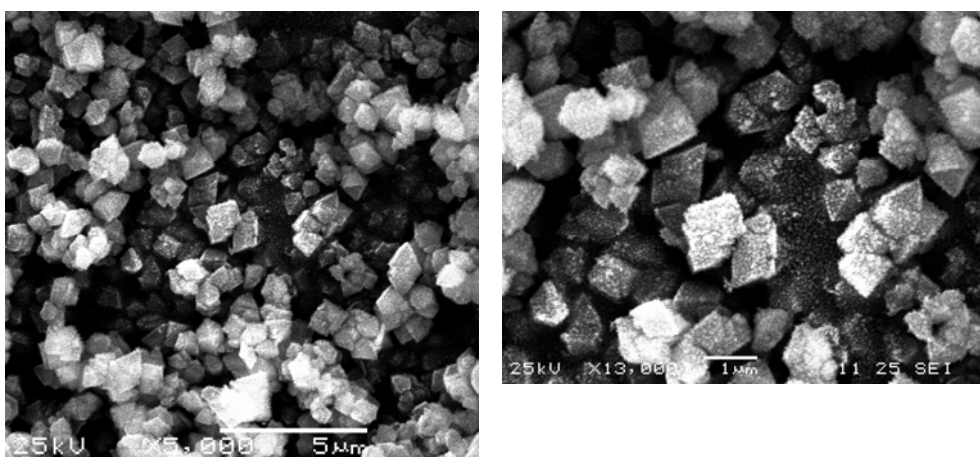


Fig. 2. General SEM image of variscite masses (left) and details of well developed pseudo-octahedral $\{111\}$ crystals (right).

Several qualitative chemical analyses were performed using the energy-dispersive X-ray spectrometer facility of the SEM. Invariably, the obtained spectra showed well-resolved Al and P lines (Fig. 3). Because the only possible ambiguity between $K\alpha$ lines of these elements is that with $L\alpha$ lines of Br and Zr, respectively, we are confident our compound is an aluminum phosphate. The Si peak it is not surprising considering the material with which the investigated mineral is intermixed.

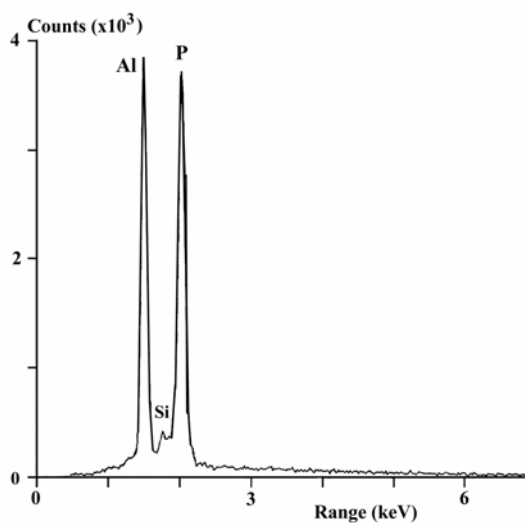


Fig. 3. ED spectrum of variscite.

Quantitative analyses were conducted with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Jobin-Yvon ULTIMA) for K, Mn, Mg, Na, Ti, and Fe and with a Jeol JSM-6310 (equipped with ED- and WD-spectrometer) electron microprobe (EMP-Oxford) for Al, P, Ca, Si, and Fe, operated at an acceleration voltage of 15 kV and a beam current of 10 nA with corundum (Al), YPO_4 (P), adular (K), apatite (Ca), and garnet (Fe) as standards. The crystal was analyzed at 5 different points. The results of the chemical analyses are listed in Table 1. The empirical formula for variscite is: $\text{Al}_{0.695}\text{P}_{0.683}\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Table 1

The composition of variscite as obtained from combined ICP-AES and EMP analyses (in brackets the standard deviations; n = 5).

	1	2	3
Al_2O_3	35.47	33.87-36.91 (0.1)	0.695
P_2O_5	48.47	44.25-49.57 (0.11)	0.683
CaO	1.54	0.67-2.21 (0.03)	0.055
SiO_2	0.57	0.43-0.69 (0.3)	0.019
FeO	0.69	0.42-0.84 (0.06)	0.019
MnO	0.04		0.001
MgO	0.27		0.013
K_2O	0.36		0.015
Na_2O	0.09		0.006
TiO_2	0.06		0.002
H_2O	10.61		2.219
Σ	98.18		
1. mean analytical results for variscite wt% (ICP-AES) 2. electron microprobe ranges 3. cations based on O = 4			

X-RAY CRYSTALLOGRAPHY

X-ray data on several samples were obtained by means of Scintag Pad V and Philips X-pert diffractometers using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). NBS 640b Si was used as internal standard. Peak positions were determined by fitting the numerical profiles with a Pearson VII function. Operating conditions were 40 kV and a beam current of 40 mA, and 40 kV at 30 mA, respectively. All samples were continuously scanned from 3 to 85° and 5 to 70° 2θ , with a step scan of 0.01° 2θ and 2s per step. The diffraction spectra obtained with both instruments are almost identical to the one illustrated in Fig. 4.

Cell dimensions were calculated as average of two least-square refinements of 45 corrected d values (Tab. 2) using the UnitCell Program of Holland & Redfern (1997). The orthorhombic unit cell (space group $Pbca$) was found to be: $a = 9.823(4)$, $b = 8.562(9)$, $c = 9.620(5) \text{ \AA}$ and $V = 809.167(6) \text{ \AA}^3$.

Table 2
Comparison between the powder diffraction pattern of Cioclovina variscite and the standard reference pattern from ICDD file 33-33.

Nr. crt.	Variscite (this study)			Variscite (ICDD card 33-33)	
	<i>d</i> _{meas.} (Å)	<i>d</i> _{calc.} (Å)	I/I ₀	<i>d</i> (Å)	I/I ₀
1	5.3604	5.3599	72	5.36	65
2	4.812	4.8102	43	4.815	25
3	4.269	4.2604	100	4.26	70
4	3.908	3.911	32	3.903	25
5	3.634	3.633	15	3.632	20
6	3.195	3.197	11	3.190	7
7	3.043	3.0408	55	3.041	100
8	2.914	2.914	22	2.914	45
9	2.877	2.8719	20	2.871	35
10	2.633	2.6358	24	2.633	25
11	2.566	2.566	9	2.564	9
12	2.475	2.483	15	2.483	20
13	2.449	2.455	8	2.457	12
14	2.4029	2.405	5	2.406	2
15	2.397	2.3903	5	2.390	8
16	2.337	2.336	6	2.337	12
17	2.2907	2.292	3	2.293	5
18	2.211	2.213	3	2.213	1
19	2.141	2.1405	8	2.1401	12
20	2.100	2.0996	4	2.097	4
21	2.085	2.0834	5	2.0839	13
22	2.054	2.0506	3	2.054	6
23	2.026	2.020	4	2.0202	6
24	1.962	1.9622	9	1.9608	14
25	1.945	1.947	7	1.947	10
26	1.917	1.918	5	1.918	10
27	1.845	1.8439	4	1.8447	6
28	1.784	1.786	3	1.786	3
29	1.753	1.755	6	1.755	13
30	1.727	1.7223	4	1.7225	4
31	1.651	1.644	1	1.644	2
32	1.6002	1.608	6	1.608	6
33	1.596	1.5919	6	1.591	18
34	1.578	1.5782	4	1.578	8
35	1.563	1.564	6	1.563	4
36	1.525	1.5251	7	1.5247	3
37	1.503	1.4989	3	1.497	4
38	1.4716	1.484	1	1.483	1
39	1.4447	1.447	7	1.446	13
40	1.432	1.431	4	1.4309	6
41	1.411	1.411	2	1.4109	4
42	1.4035	1.404	2	1.404	6
43	1.395	1.397	2	1.396	3
44	1.354	1.355	2	1.353	1
45	1.3434	1.342	3	1.3434	4

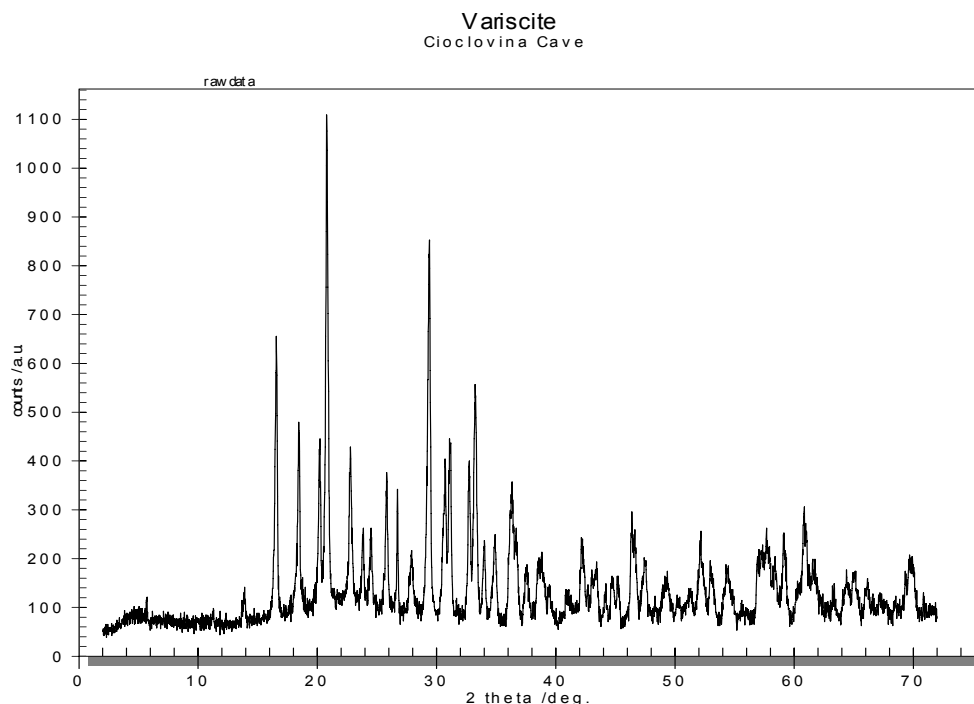


Fig. 4. X-ray diffraction pattern of variscite from the Cioclovina Cave.

THERMAL ANALYSIS

Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on about 21 mg of the sample in a Mettler Toledo instrument. The temperature ranged from 30 to 1000°C, using a constant flow of nitrogen (100 mL/min) and a heating rate of 5°C/min.

TGA/DTA trace obtained for variscite is reproduced in Fig. 5. The TG curve shows one single dehydration step. The weight loss of 10.0 % that occurs between 90 and 145°C was due to the expulsion of the two molecules of water. The corresponding endothermic effect appears at 120°C on the DTA curve (Fig. 5). Our TG analysis indicated a total amount of 2.1 H₂O groups per AlPO₄ unit, i.e., slightly more than the expected stoichiometric amount. This extra water (0.1) was attributed to water absorption on the particles' surface. A similar situation was observed by Reale & Scrosati (2003) when investigating strengite, FePO₄·2H₂O.

INFRARED ABSORPTION SPECTRUM

Fourier-transform infrared spectra were obtained with a Perkin-Elmer 1760X FT-IR spectrometer middle (NIR spectral range, 400 – 4000 cm⁻¹) using the KBr pellet technique. The spectral resolution was 2 cm⁻¹. FT-IR spectrum of the dull white phosphate material (Fig. 6) presents the characteristic bands assigned to variscite (Lehr et al., 1967).

VARISCITE ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) FROM CIOCLOVINA CAVE (ȘUREANU MOUNTAINS, ROMANIA)

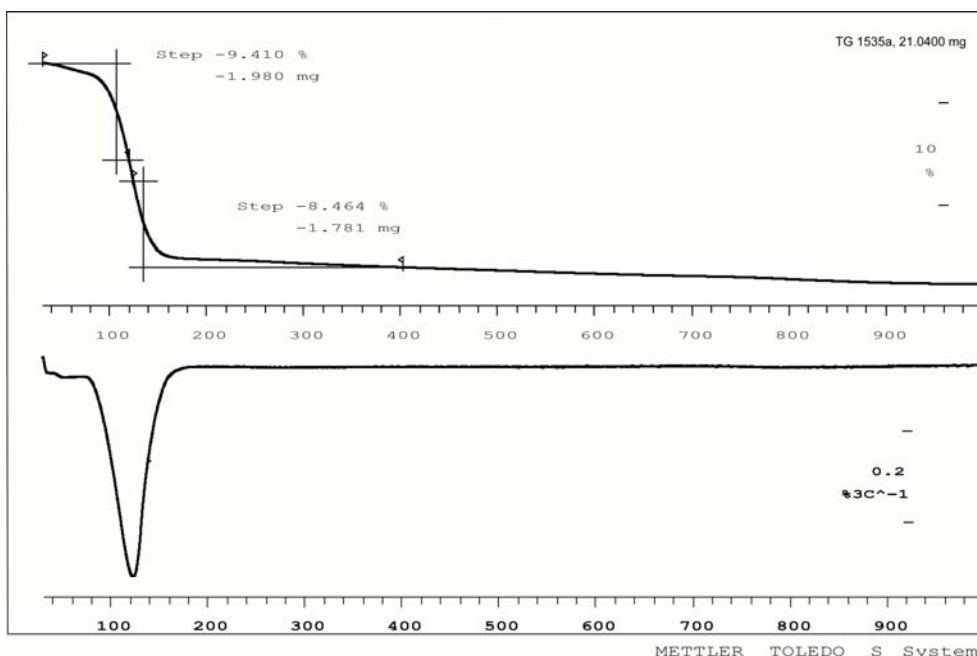


Fig. 5. TGA and DTA curves of variscite (sample #1535a) from Cioclovina Cave.

The bands observed in the spectral range between 2500 and 3500 cm^{-1} (3300 , 3195 , 3108 , and 2945) are due to symmetric or asymmetric O-H stretching of water (Ross, 1974; Socrates, 2001; Frost & Weier, 2004). The two very sharp peaks at 3583 cm^{-1} and 1384 cm^{-1} , respectively, can tentatively be ascribed to N-containing organic compounds (aromatic or aliphatic) that could be present as contaminants of the title compound. This last band is a stretching mode specific for the -C=N- bonds or C-N-C from aromatic rings. Amine/amide-containing organic compounds exhibit also strong bands in IR spectra in the $3100\text{-}3500\text{ cm}^{-1}$ spectral range, assigned as N-H stretching modes, whereas the bending modes are located around 1600 cm^{-1} . They are weak to medium in the Raman spectra.

Variscite absorption bands at ~ 1600 and 1574 cm^{-1} are located in the water deformation region, and their presence was interpreted by Salvador & Fayos (1972) as indicating the existence of two different types of water molecules. The nature of the two water molecules in variscite has always been of special interest to scientists (Kniep et al., 1977; Falk, 1984). However, in our variscite sample the DTA and TG curves do not show a two-step water loss so that this assumption is not substantiated. It seems more likely to accept Pâques-Ledent & Tarte (1969) opinion that suggests the presence of OH^- and H_3O^+ in the variscite structure.

The accuracy in precisely locating the hydrogen atoms is very poor and usually the $\text{O}_{\text{water}}\text{-H}$ distances are shorter than the theoretical one ($\sim 0.96\text{ \AA}$). It is believed that three of the H atoms form single hydrogen bonds to phosphate O atoms, whereas the fourth does not participate in a hydrogen bond (Kniep et al., 1977). Considering our case if we assume that the 1575 cm^{-1} bending mode and

one of the 2500 to 3500 cm^{-1} stretching mode bands are associated to the same water molecules, at least one of its two hydrogen atoms should not be bonded to the structure. Such an interpretation is in good agreement with the studies undertaken for the isotopic indium and gallium analogs of variscite (Mooney-Slater, 1961, 1966; Loiseau et al., 1998), and with the more recent investigations on hydrogen bond lengths (Libowitzky, 1999) and valence bond calculations (Brese & O'Keeffe, 1991; Huminiki & Hawthorne, 2002).

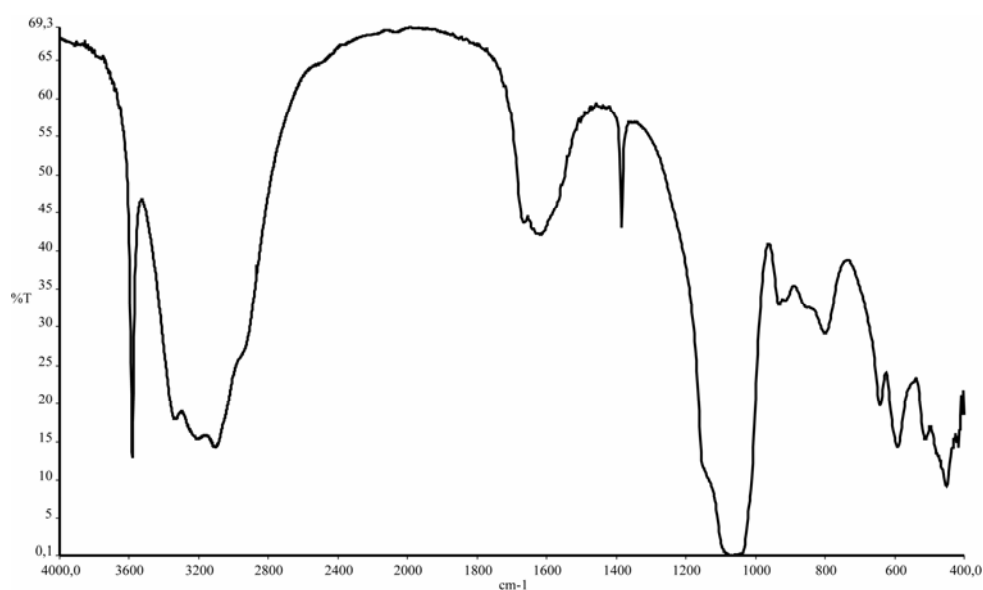


Fig. 6. FT-IR spectrum of variscite (sample #1535a).

Variscite absorption bands at 1160, 1063, and 934 cm^{-1} are comparable in position and intensity to other Al-phosphates compiled by Lehr et al. (1967) and Ross (1974). According to Adler (1964, 1968) the number of infrared-active modes in this part of the spectrum depends on the PO_4^{3-} group symmetry. The two bands at 1160 and 1063 cm^{-1} assignable to the PO_4^{3-} : ν_3 asymmetric mode, and a unique band at 934 cm^{-1} (PO_4^{3-} : ν_1 symmetric stretching) may indicate a C_{3v} symmetry for at least one of the two independent PO_4^{3-} anions. The following four significant absorption bands occur at 866, 799, 646, and 574 cm^{-1} . These wave numbers correspond to vibrational modes involving M-OH₂, but PO_4^{3-} : ν_4 can also contribute to bands between 500 and 600 cm^{-1} (Tarte, 1967; Salvador & Fayos, 1972; Ross, 1974). The IR absorption spectrum between 550 and 400 cm^{-1} is dominated by bands at 514, 449, 422, and cm^{-1} , which were interpreted (based on comparison with other published data) as being due to O-P-O (ν_4 in-plane; ν_2 out-of plane) bending modes.

RAMAN SPECTROSCOPY OF VARISCITE

The FT-Raman spectrum of variscite was recorded using an Equinox 55 FT-IR Bruker spectrometer with an integrated FRA 106 S Raman module. For the excitation of the spectra the 1064 nm line from a Nd:YAG laser was used with an output power of 350 mW. The InGaAs detector was used. For each spectrum 200 scans were accumulated. The spectral resolution was 4 cm⁻¹. Table 3 lists the wavenumbers, intensity, and the assignments of the identified bands. The positions of the bands observed on the variscite spectrum are in agreement with the characteristic Raman data of the phosphates (Socrates, 2001).

Table 3

Vibrational Raman data of variscite /cm⁻¹ and their assignment (s-strong, m-medium, w-weak, sh-shoulder).

Wavenumber (cm ⁻¹) & Intensity	Assignments	Wavenumber (cm ⁻¹)	Assignments
3400-3100 broad band	OH asym, sym, stretch, Water stretching modes	1079 sh	PO ₄ ³⁻ , often complex, broad P=O stretch
1634 wm	OH bend, water bending mode	1055 m	P-O stretch, depending on the inductive effect of the substituent
		1026 m	P-O stretch
		605 w	Phosphate bending
		562 w	
		434 m-s	
		225 m	
		168 sh	Lattice vibrations
		144 m	Lattice vibrations

The most intense bands in the stretching vibrations region of the PO₄³⁻ units (all assigned to the ν_3) are at 1023 cm⁻¹ and 1055 cm⁻¹ with less defined other component bands. According to Frost et al. (2004), the number of bands observed in the stretching (symmetric and antisymmetric vibrations) regions of the PO₄³⁻ units indicates a combination of two effects: symmetry reduction and multiple PO₄³⁻ species. Based on the later one, individual crystals of the variscite mineral group (but not only) can readily be determined by Raman spectroscopy.

CONCLUSIONS

The formation of variscite is attributed to the reaction between the phosphate-rich leachates derived from thick guano deposits and the underlying Al-rich residual or water-laid sediments under acid conditions. With continued leaching and in the presence of excess alkali, crandallite may be the dominant phase. In fact, there are evidences from different locations worldwide that variscite is replaced by crandallite (Altschuler, 1973). Therefore, a similar scenario could be applicable to the geochemical situation within the Cioclovina Cave, where crandallite has already been identified by Constantinescu et al. (1999).

Powder X-ray diffraction of the dull white crusts and veinlets recovered from a phosphatized sequence indicate the presence of variscite, of which orthorhombic cell was found to be in good agreement with other published results on this mineral. The presence of this Al-phosphate was also confirmed by a set of qualitative (EDS) and quantitative (ICP-AES and EMP) analyses. Additionally, the SEM investigations on crystal morphology, along with thermal and vibrational IR and Raman analyses confirm the existence of variscite in this unique Romanian cave.

Acknowledgements. Permission for entering and sampling the Cioclovina Cave phosphate deposit was granted by the Romanian Academy through the Romanian Commission of Natural Protection. Part of this research was supported by MEC-CNCSIS grants 101/1696 to B. P. Onac. L. Zaharia first tested the FT-IR spectrum of variscite at Institute of Mineralogy and Crystallography, University of Wien. D. Keravis and D. Vereş are thanked for the ICP-AES analyses at Institute des Sciences de la Terre, Université d'Orléans (CNRS). The EMP analyses were conducted at the Institute of Mineralogy and Petrology in Graz by the senior author. The help of K. Ettinger with EMP analyses is acknowledged. Useful suggestions were provided by two anonymous referees during the review process. Variscite specimen is preserved in the *Cave Minerals* collection of the Mineralogical Museum, "Babeş-Bolyai" University in Cluj.

REFERENCES

- Adler, H. H. 1964, Infrared spectra of phosphate minerals: symmetry and substitutional effects in the pyromorphite series. *The American Mineralogist*, 49: 1002-1015.
- Adler, H. H. 1968, Infrared spectra of phosphate minerals: splitting and frequency shifts associated with substitution of PO_4 for AsO_4^{3-} in mimetite. *The American Mineralogist*, 53: 1740-1744.
- Altschuler, Z. S. 1973, The weathering of phosphate deposits-geochemical and environment aspects. In *Environmental phosphorus handbook* (Griffith, E. J., Beeton, A., Spencer, J. M., Mitchell, D. T., Eds.), New York: John Wiley & Sons, 33-96.
- Bălan, M. 1976, *Mineralogia zăcămintelor manganifere de la Iacobeni*. Ed. Academiei R. S. România, Bucureşti, 124 pp.
- Breban, R. C. 2002. *Studiul fosfaţilor din Peştera Ciclovina Uscată (Munţii Şureanu)*. B.Sc. Thesis. University of Cluj, 92 pp.
- Breban, R., Şerban, M., Viehmann, I., Băicoană, M. (Eds.) 2003, *Istoria exploatării de guano-fosfat şi a descoperirii omului fosil din peşterile de la Ciclovina (Hunedoara)*. Clubul de Speologie Proteus, Hunedoara, 138 pp.
- Brese, N. E., O'Keeffe, M. 1991, Bond-valence parameters for solids. *Acta Cryst.*, B47: 192-197.
- Constantinescu, E., Marincea, Ş., Crăciun, C. 1999, Crandallite in the phosphate association from Cioclovina cave (Şureanu Mts., Romania). In *Mineralogy in the system of the earth sciences* (Anastasiu, N., Ilinca, G., Eds.), London: Imperial College Press, 1-5.

VARISCITE ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) FROM CIOCLOVINA CAVE (ȘUREANU MOUNTAINS, ROMANIA)

- Dumitraș, D., Marincea, Ș. 2000, Phosphates in the bat guano deposit from the "Dry" Cioclovina Cave, Șureanu Mountains, Romania. *Rom. J. Mineral. Dep.*, 79 (1): 43-45.
- Dumitraș, D. G., Marincea, Ș., Fransolet, A. M. 2004 a, Brushite in the bat guano deposit from the "dry" Cioclovina Cave (Șureanu Mountains, Romania). *N. Jb. Miner. Abh.*, 180 (1): 45-64.
- Dumitraș, D.-G., Hatert, F., Bilal, E., Marincea, Ș. 2004 b, Gypsum and bassanite in the bat guano deposit from the "Dry" Cioclovina Cave (Șureanu Mountains, Romania). *Rom. J. Mineral. Dep.*, 81: 84-87.
- Falk, M. 1984, The frequency of the H---O---H bending fundamental in solids and liquids. *Spectrochimica Acta*, A40: 43-48.
- Frost, R. L., Weier, M. L. 2004, Vibrational spectroscopy of natural augelite. *Journal of Molecular Structure*, 697: 207-211.
- Frost, R. L., Weier, M. L., Erikson, K. L., Carmody, O., Mills, S. J. 2004, Raman spectroscopy of phosphates of the variscite mineral group. *J. Raman Spectrosc.*, 35 (12): 1047-1055.
- Halla, F. 1931, Isomorphe Beziehungen und Doppelsalzbildung zwischen Gips und Brushit. *Z. Krist.*, 80: 349-352.
- Hill, C. A., Forti, P. 1997. *Cave minerals of the world* (2nd ed.) National Speleological Society, Huntsville, Alabama, pp. 163-176.
- Holland, T. J. B., Redfern, S. A. T. 1997, Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineral. Mag.*, 61: 65-77.
- Huminicki, D. M. C., Hawthorne, F. C. 2002, The crystal structure of the phosphate minerals. In *Phosphates - geochemical, geobiological, and materials importance* (Kohn, M. J., Rakovan, J., Hughes, J. M., Eds.), In *Reviews in Mineralogy & Geochemistry* 48, Washington: Mineralogical Society of America / Geochemical Society, 123-253.
- Johan, Z., Slansky, E., Povondra, P. 1983, Vashegyite, a sheet aluminum phosphate: new data. *The Canadian Mineralogist*, 21: 489-498.
- Kniep, R., Mootz, D., Vegas, A. 1977, Variscite. *Acta Cryst.*, B33: 263-265.
- Lehr, J. R., Brown, E. H., Frazier, A. W., Smith, J. P., Thrasher, R. D. 1967. *Crystallographic properties of fertilizer compounds*. National Fertilizer Development Center, Muscle Shoals, AB., 166 pp.
- Libowitzky, E. 1999, Correlation of O-H stretching frequencies and O-H...O hydrogen bond length in mineral. *Monatshefte für Chemie*, 130: 1047-1059.
- Loiseau, T., Paulet, C., Férey, G. 1998, Crystal structure determination of the hydrated gallium phosphate $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$, analog of variscite. *C. R. Acad. Sc. Paris*, II(1): 667-674.
- Marincea, Ș., Dumitraș, D. G. 2003, The occurrence of taranakite in the "dry" Cioclovina Cave (Șureanu Mountains, Romania). *N. Jb. Miner. Mh.*, 2003 (3): 127-144.
- Marincea, Ș., Dumitraș, D., Gibert, R. 2002, Tinsleyite in the "dry" Cioclovina Cave (Șureanu Mountains, Romania): the second occurrence. *Eur. J. Mineral.*, 14: 157-164.
- Mooney-Slater, R. C. L. 1961, X-ray diffraction study of indium phosphate dihydrate and isostructural thallic compounds. *Acta Cryst.*, 14: 1140-1146.
- Mooney-Slater, R. C. L. 1966, The crystal structure of hydrated gallium phosphate of composition $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$. *Acta Cryst.*, 20: 526-534.
- Nriagu, J. O., Moore, P. B. (Eds.) 1984, *Phosphate minerals*. Springer-Verlag, Berlin, 442 pp.

- Onac, B. P., Breban, R., Kearns, J., Tămaș, T. 2002, Unusual minerals related to phosphate deposits in Cioclovina Cave, Șureanu Mts. (Romania). *Theor. Appl. Karstol.*, 15: 27-34.
- Onac, B. P., White, W. B. 2003, First reported sedimentary occurrence of berlinite (AlPO₄) in phosphate-bearing sediments from Cioclovina Cave, Romania. *The American Mineralogist*, 88: 1395-1397.
- Pâques-Ledent, M. T., Tarte, P. 1969, Spectre infra-rouge et structure des composés GaPO₄·2H₂O et GaAsO₄·2H₂O. *Spectrochimica Acta*, 25 (6): 1115-1125.
- Pop, G., Hârtoapanu, I., Hârtoapanu, P., Szasz, L., Ion, L., Popescu, G., Bandrabur, T., Stela, I., Stela, G., Mihăilescu, N., Ungureanu, N., Moiescu, V., Kräutner, H., Kräutner, H., 1985, Foaia Pui, Harta geologică a R. S. Romania, 1:50000. Inst. Geol. Geofiz., București
- Reale, P., Scrosati, B. 2003, Synthesis and thermal behavior of crystalline hydrated iron(III) phosphates of interest as positive electrodes in Li batteries. *Chem. Mater.*, 15: 5051-5058.
- Ross, S. D. 1974, Phosphates and other oxy-anions of group V. In *The infrared spectra of minerals* (Farmer, V. C., Ed.), London: Mineralogical Society, Monograph 4, 383-422.
- Salvador, P. S., Fayos, J. 1972, Some aspects of the structural relationship between "Messbach-type" and "Lucin-type" variscites. *The American Mineralogist*, 57: 36-44.
- Schadler, J. 1929, Mineralogische-petrographische charakteristik der Phosphat ablagerung in der Cioclovina-höhle bie Pui. *Publ. Muz. Hunedoara*, 5: 642.
- Schadler, J. 1932, Ardealit, ein neues Mineral CaHPO₄ CaSO₄ +4H₂O. *Zentral-bl. Miner. A*: 40-41.
- Socrates, G. 2001, *Infrared and Raman characteristic group frequencies: tables and charts* (3rd ed.). John Wiley & Sons Ltd, New York.
- Stilla, A. 1981, Géologie de la région de Hateg-Ciclovină-Pui-Banita (Carpathes Meridionales). *An. Inst. geol. Geofiz.*, 66: 91-179.
- Tarte, P. 1967, Infra-red spectra of inorganic aluminates and characteristic vibrational frequencies of AlO₄ tetrahedra and AlO₆ octahedra. *Spectrochimica Acta*, 23 (7): 2127-2143.