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VASHEGYITE, A SHEET ALUMINUM PHOSPHATE: NEW DATA

Z. JOHAN

Centre de Recherches sur la Synthèse et la Chimie des Minéraux, GIS BRGM-CNRS, 1A, rue de la Férollerie, 45045 Orléans, France

E. SLANSKY

Geological and Mining Museum, Geological Survey of New South Wales, 36 George Street, Sydney 2000, Australia

P. POVONDRA

Institute of Geological Sciences, Charles University, Albertov 6, Prague, 128 43 Czechoslovakia

ABSTRACT

Examination of specimens from the type locality (Vashegy, now Železník, Czechoslovakia) and two other occurrences shows that vashegyite is an orthorhombic sheet phosphate with variable properties. This mineral is biaxial negative, $2V$ 67-74°, α 1.470-1.479, β 1.477-1.488, γ 1.482-1.490; $X = c$, $Y = b$, $Z = a$. Its ideal composition corresponds to $Al_{11}(PO_4)_9(OH)_6 \bullet 38H_2O$ (type locality) and $Al_6(PO_4)_5(OH)_3 \bullet 23H_2O$ (Chvaletice, Czechoslovakia). The main dehydration occurs between 140 and 190°C (DTA). Some dehydration curves show two maxima, and recrystallization to $AlPO_4$ is observed in the form of an exothermic peak at 860°C. Loss-of-weight curves indicate that OH groups are expelled immediately before recrystallization. Infrared-absorption spectra resemble those of variscite. Unit-cell dimensions vary with water content; for the specimen from Chvaletice (air dried; Weissenberg and powder photographs), a 10.754(3), b 14.971(5), c 22.675(6) Å, space group *Pnam* or *Pna*2$_1$, $Z = 4$, ρ_{calc} 2.005, ρ_{meas} 1.994(2) g/cm^3. For the specimen from Železník (Vashegy), a 10.773(3), b 14.971(5), c 20.626(6) Å, $Z = 2$, ρ_{calc} 1.934, ρ_{meas} 1.930(1) g/cm^3. Under vacuum, the c parameter becomes 19.0(1) Å. Differences in stacking, possibly irregular, are deemed responsible for the observed variations of properties. The sheet structure is indicated by Weissenberg photographs and the flaky habit accompanied by perfect (001) cleavage visible in SEM. A polytypoid relationship for the varieties is suggested; sasaite and vashegyite are possibly identical phases.

Keywords: vashegyite, sheet Al phosphate, crystallography, thermal analysis, optical properties, polytypoids, sasaite, Chvaletice, Železník(Vashegy), Czechoslovakia.

SOMMAIRE

L'étude des échantillons provenant du gisement-type (Vashegy, actuellement Železník en Tchécoslovaquie) et de deux autres occurrences montre que la vashegyite est un phosphate à structure en feuillets, de symétrie orthorhombique, à propriétés variables. Cette espèce est biaxe négative, $2V$ 67-74°, α 1.470-1.479, β 1.477-1.488, γ 1.482-1.490; $X = c$, $Y = b$, $Z = a$. Les analyses chimiques correspondent aux formules idéales suivantes: $Al_{11}(PO_4)_9(OH)_6 \bullet 38H_2O$ (gisement-type) et $Al_6(PO_4)_5(OH)_3 \bullet 23H_2O$ (Chvaletice, Tchécoslovaquie). L'ATD révèle une déshydratation majeure avec maximum entre 140 et 190°C. Sur certaines courbes, le départ d'eau se produit en deux étapes, et l'on observe une recristallisation en $AlPO_4$ indiquée par un maximum exothermique à 860°C. La perte en poids permet de situer le départ de OH juste avant la recristallisation. Le spectre d'absorption infrarouge ressemble à celui de la variscite. Les paramètres de la maille varient avec la teneur en H_2O; pour l'échantillon de Chvaletice (pression ambiante; clichés de Weissenberg et diagramme de poudre), a 10.754(3), b 14.971(5), c 22.675(6) Å, groupe spatial *Pnam* ou *Pna*2$_1$, Z = 4, ρ_{calc} 2.005, ρ_{mes} 1.994(2). Pour l'échantillon de Železník (Vashegy), a 10.773(3), b 14.971(5), c 20.626(6) Å, $Z = 2$, ρ_{calc} 1.934, ρ_{mes} 1.930(1). Sous vide, le paramètre c devient 19.0(1) Å. La variation des propriétés indique un empilement de couches peut-être irrégulier, différant d'un échantillon à l'autre. La structure en feuillets est révélée par les clichés de Weissenberg et le faciès micacé des cristaux de vashegyite, avec clivage parfait suivant (001), observable au MEB. Les variations entre différents échantillons seraient celles de polytypoïdes. Il se peut que la sasaïte soit identique à la vashegyite.

Mots-clés: vashegyite, phosphate-Al en feuillets, cristallographie, analyse thermique, propriété optiques, polytypoïdes, sasaïte, Chvaletice, Železník (Vashegy), Tchécoslovaquie.

INTRODUCTION

The mineral *vashegyite* was discovered by Zimanyi (1909) in the oxidation zone of the siderite-ankerite deposit at Vashegy, Hungary (now Železník in Czechoslovakia). The original description of this mineral is limited to some data on physical properties and a chemical analysis carried out by J. Loczka. Additional data on vashegyite from the type locality were published by Ulrich (1922), who noticed that the mineral is predominantly isotropic under the microscope and hence probably amorphous, although it displays incipient crystallization in places. Ulrich, in the same paper, also mentioned a new occurrence of vashegyite at Chvaletice, Czechoslovakia.

Koch & Sarudi (1963) examined vashegyite from Železník by electron microscopy and performed chemical analyses; they postulated that the mineral is amorphous despite the appearance of their electron micrographs, which indicate stacks of parallel units separated, possibly, by cleavage traces. This discrepancy was also observed by McConnell (1974). An X-ray-diffraction or electron-diffraction study was not attempted by Koch & Sarudi (1963). These authors also proposed to attribute the name vashegyite to an Al-phosphate accompanying *vashegyite,* noted already by Zimanyi (1909), arguing that the analyses of this mineral gave more congruent results. This mineral had been determined by Ulrich (1922) as wavellite on the basis of a microscopic study. Koch & Sarudi (1963) ascribed the formula $Al_3(PO_4)_3{\cdot}AlO{\cdot}OH{\cdot}12H_2O$ to this mineral, which is rather unusual and hardly warranted because their chemical data correspond without much difficulty to $Al_3(PO_4)_2(OH)_3{\cdot}6H_2O$, *i.e.,* to the formula of wavellite as given by Fu (1966). This formula, which has one molecule of water more than normally reported for wavellite, is not unfounded, in view of the chemical composition of some wavellite samples (Bouška & Povondra 1969). Thus it appears that Ulrich's identification of the mineral is correct, even if it is impossible to confirm at this stage. In any case, the suggestion of Koch & Sarudi has to be rejected.

In an attempt to demonstrate the existence of sheet phosphates, McConnell (1974) studied vashegyite by X-ray powder diffraction using a specimen from the British Museum of Natural History. His X-ray powder-diffraction data differ somewhat from the first powder pattern of vashegyite produced by the British Museum and available in the powder-diffraction file since 1944 (PDF 2–0040). Assuming a crystal structure analogous to that of kaolinite, McConnell succeeded in indexing the powder pattern of vashegyite using a large orthorhombic cell. However, it has to be pointed out that some of McConnell's speculations are founded on the data of Koch & Sarudi, and in particular on the chemical formula for their "vashegyite" (which is, in fact, wavellite, as mentioned above).

The examination of vashegyite presented in this paper arose from an X-ray identification of vashegyite from Chvaletice (Ulrich 1922, Slavík 1928), during which it was realized that the present state of knowledge of this mineral clearly is inadequate.

SAMPLES STUDIED

The following specimens were used in this investigation: (1) Vashegy (Železník), Czechoslovakia: British Museum of Natural History (BMNH), London (specimen 1910, 101). This specimen, sent to the Museum by Zimanyi, can be considered as a cotype; the type specimen was destroyed in Budapest in 1956. (2) Železník, Czechoslovakia: mineral collection of the Department of Mineralogy and Crystallography, Charles University, Prague, Czechoslovakia (DMUC, specimen 10188). (3) Železník, Czechoslovakia: mineral collection of F. Souček, Prague. (4) Vashegy (Železník), Czechoslovakia: mineral collection of Ecole Nationale Supérieure des Mines, Paris (ENSMP, specimen 18544). (5) Fish Creek Range, Nevada, U.S.A.: mineral collection of Ecole Nationale Supérieure des Mines, Paris (ENSMP, specimen 18916). (6) Chvaletice, Czechoslovakia: private collection of P. Povondra.

X-ray examination showed that specimen 18544 is amorphous to X rays. Other specimens gave X-ray powder-diffraction patterns of different quality consistent with their respective degree of crystallinity; after a preliminary examination, our attention was thus focused on a detailed study of specimens BMNH 1910, 101, DMUC 10188 and vashegyite from Chvaletice.

PHYSICAL PROPERTIES

In Železník (Vashegy), vashegyite always occurs as chalky white polycrystalline aggregates filling cavities in a limonitic boxwork. It is often associated with variscite. The specimen from Chvaletice occurs in the form of small, millimetre-sized, pale greenish white crystals arranged in hemispheric aggregates with radial structure. The crystals possess a perfect basal cleavage. The homogeneity of the specimens BMNH 1910, 101 and DMUC 10188 was checked by selected-area electron diffraction: a hexagonal phase with $a = 9.2$ Å and rare irregular particles giving a strong diffraction maximum at 3.5 Å, were revealed as impurities. The hexagonal phase was attributed to a mineral of the apatite group, whereas the second phase was tentatively identified as a member of the smectite group. Under the microscope, we observed tiny particles of iron hydroxide finely dispersed on cleavage planes of vashegyite, particularly in specimen DMUC 10188. The specific gravity was measured several times by degassing specimens immersed in carbon tetrachloride in a vacuum and then weighing them in carbon tetrachloride. The results are as follows: BMNH 1910, 101: 1.930(1), DMUC 10188: 1.980(1), Chvaletice: 1.994(2).

Whereas specimens BMNH 1910, 101 and Chvaletice are very pure, specimen DMUC 10188 contains 2 wt.% FeOOH and 0.6 wt.% apatite (Table 1). After subtracting the density of these impurities (ρ of goethite 4.3, ρ of apatite 3.09 g/cm^3), the value for DMUC 10188 becomes 1.926, which is very close to the value for BMNH 1910, 101. A similar correction can be applied to the value 1.964 g/cm^3 measured on the type specimen by Zimanyi (1909), as the chemical composition in his paper indicates the presence of 1.32 wt.% FeOOH. The corrected value is 1.933 g/cm^3. We can therefore con-

TABLE 1. CHEMICAL COMPOSITION OF VASHEGYITE SPECIMENS

Specimen	Chvaletice		BMNH 1910,101			DMUC 10188			
	1	2	1	2	3	1	1a	2	3
Al_2O_3	27.09	5.956	29.01	6.099	11.089	28.22	29.11	6.027	10.958
Fe_2O_3	0.12	0.017	0.04	0.004	0.007	1.81			
CaO						0.33			
P_2O_5	31.83	5.027	32.43	4.897	8.904	32.67	33.44	4.973	9.042
H_2O	40.01	49.787*	37.72	44.881*	81.602*	36.54	37.45	43.882*	79.785*
insol.	0.50								
Total	99.55		99.20			99.57	100.00		

1.wt.% (P.Povondra, analyst);1a. after subtracting CaO and P_2O_5 of apatite and Fe_2O_3 of goethite;recalculated to 100%;2.number of atoms calculated on the basis of 11(Al+Fe+P);3. number of atoms calculated on the basis of 20(Al+Fe+P);*expressed as OH.

clude that the specific gravity of vashegyite from the type locality is 1.93, a value that is lower than the specific gravity of the specimen from Chvaletice.

Under the microscope, in transmitted light, vashegyite is colorless, and its crystals are generally so small that the determination of optical properties is impossible in most cases. Optical determinations were only carried out on specimen DMUC 10188 and the one from Chvaletice. Lozenge-shaped platy crystals flattened along the basal plane display straight extinction. The indices of refraction in γ_{Na} are given in Table 2. A larger range in error for specimen DMUC 10188 is due to the small crystals; it is of the same order as is the error of the measurement of α, carried out on sections along (010) or (100) rendered extremely thin by the (001) cleavage, on the specimen from Chvaletice.

Vashegyite is biaxial negative, $X = c$, $Y = b$, $Z = a$. The axial plane is parallel to (010). The optical orientation is represented in Figure 1.

CHEMICAL DATA

After dissolving purified specimens used for the specific gravity determination (200 to 400 mg) in 0.6M HCl and separating cations from anions by an ion-exchange resin, Al was determined by chelatometric titration, Fe by photometry, Ca by atomic absorption; P_2O_5 and H_2O were done by gravimetric analyses. The results of chemical analyses of the three selected specimens are given in Table 1.

TABLE 2. UNIT-CELL DATA AND OPTICAL PROPERTIES OF VASHEGYITE

SAMPLE	A	B	C	D
a*	10.754(3)	10.764(3)	10.773(3)	10.757(3)
b	14.971(5)	14.954(5)	14.971(5)	14.991(5)
c	22.675(6)	20.526(6)	20.626(6)	20.604(6)
V (Å³)	3650.6	3303.9	3326.6	3322.6
sp.gr.	Pnam;$Pna2_1$	?	?	?
Z	4	2	2	2
ρ_{calc}	2.005	1.948	1.934	1.937
a**	10.725(3)	10.814(3)	10.762(3)	
b	14.988(5)	14.960(5)	14.968(5)	
c	19.038(6)	19.135(6)	18.931(6)	
V (Å³)	3060.0	3095.6	3049.5	
α	1.470(8)	1.479(8)		
β	1.477(2)	1.488(5)		
γ	1.482(2)	1.490(5)		
$\gamma - \alpha$	0.016	0.011		
2V(-)†	74±5°	67±5°		

A. Chvaletice,B. BMNH 1910,101, C. DMUC 10188, D.coll.Souček;*76.4mm Debye-Scherrer camera,**evacuated Guinier camera,†measured on universal stage

For vashegyite from Chvaletice, the most probable chemical formula that can be derived from these data [on the basis of 11(Al + Fe + P)] is$(Al_{5.956}Fe^{3+}{}_{0.017})(PO_4)_{5.027}(OH)_{2.838}{\bullet}23.47H_2O$, which is very close to $Al_6(PO_4)_5(OH)_3{\bullet}23H_2O$. This formula is in good agreement with unit-cell dimensions (Table 2) and the measured specific gravity. The calculated specific gravity for $Z = 4$ is 2.005, compared with the measured value of 1.994. For vashegyite from Železník, the formulae calculated on the same basis are: $(Al_{6.009}Fe^{3+}{}_{0.004})(PO_4)_{4.897}(OH)_{3.618}{\bullet}20.63H_2O$ and $Al_{6.027}(PO_4)_{4.973}(OH)_{3.162}{\bullet}20.36H_2O$ for specimens BMNH 1910, 101 and DMUC 10188, respectively. Unfortunately, for $Z = 4$ and the unit-cell dimensions of Table 2, the calculated densities are 2.136 (BMNH 1910, 101) and 2.095 g/cm³ (DMUC 10188). These values disagree with the measured density, which is close to 1.930 g/cm³.

For a 6:5 ratio of Al and P, the closest agreement is obtained for the formula $Al_6(PO_4)_5(OH)_3{\bullet}16H_2O$, which leads to a ρ_{calc} of 1.948 g/cm³. Not only is this value far from the measured value but the theoretical chemical composition corresponding to this formula (Al_2O_3 31.34, P_2O_5 36.36, H_2O 32.30 wt.%) is also vastly different from the actual composition (Table 1). The difference is so great that it cannot be accepted unless we postulate in the specimens the presence of a great quantity of an amorphous phosphate having the same Al/P ratio and a higher water content than vashegyite. The amount of this substance, then, should be constant in all specimens investigated, which is obviously an untenable proposition.

On the basis of 20(Al + Fe + P), the formulae become $(Al_{11.089}Fe^{3+}{}_{0.007})(PO_4)_{8.904}(OH)_{6.576}{\bullet}37.51H_2O$, $Al_{10.958}(PO_4)_{9.042}(OH)_{5.748}{\bullet}37.02H_2O$ and, ideally, $Al_{11}(PO_4)_9(OH)_6{\bullet}37\text{–}38H_2O$. Then, assuming $Z = 2$ and $V = 3326.6$ Å³ (Table 2), the calculated density for the ideal formula with $38H_2O$, as above, is

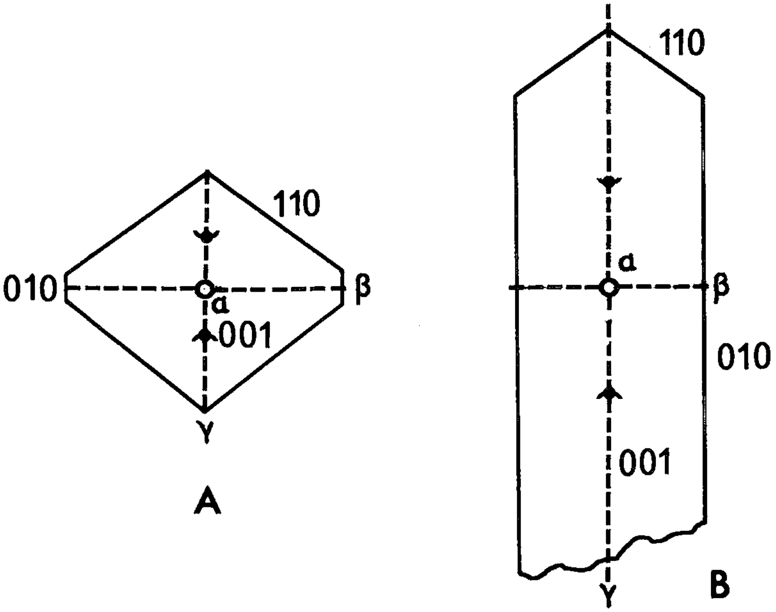

FIG. 1. Optical orientation of vashegyite. A. Železník (Vashegy), B. Chvaletice.

1.935 g/cm^3 (1.926 for $37.5H_2O$), which is in very good agreement with the measured value.

For the specimen from Chvaletice the calculation carried out on the basis of 20(Al + Fe + P) gives $(Al_{10.829}Fe^{3+}_{0.031})(PO_4)_{9.140}(OH)_{5.160}{\bullet}42.68H_2O$ which, if one assumes the ideal formula $Al_{11}(PO_4)_9(OH)_6{\bullet}43H_2O$, yields a ρ_{calc} of 1.844 g/cm^3. This value is completely incompatible with the measured value.

All this indicates that the chemical compositions of vashegyite from Chvaletice and from Železník are very close but not identical. This discrepancy can be explained on the basis of an X-ray study, as is shown later.

The comparison of physical specific refractivity K_P for specimens DMUC 10188 and Chvaletice with their chemical specific refractivity K_C, calculated using 0.195 (Al_2O_3), 0.183 (P_2O_5) and 0.340 (H_2O) as Gladstone–Dale constants (Mandarino 1981), gives a compatibility index $1-(K_P/K_C)$ of 0.033 and 0.032, respectively, in the "excellent" category of compatibility on the scale proposed by Mandarino (1979).

THERMAL ANALYSIS

All three specimens were analyzed by differential thermal analysis, and the resulting curves are presented in Figure 2. The specimen BMNH 1910, 101 was available only in very small quantity, and the thermal analysis was thus carried out in a micro-DTA apparatus using 10 mg of the sample. This explains a somewhat different format of the curve A in comparison with the other curves, which were obtained with a conventional device (Erdey, Paulik & Paulik derivatograph). All three curves are simple and similar to curves of other hydrated aluminum phosphates such as variscite, wavellite and evansite Čech & Slansky 1965, Ivanova *et al.* 1974); all display one large endothermic reaction in the low-temperature range. This reaction starts almost immediately after the temperature begins to rise during heating and stops between 300 and 350°C. The peak temperature varies from 150°C (BMNH 1910, 101) to 190°C (DMUC 10188). The specimen from Chvaletice shows two maxima, one at 140°C and the other at 170°C (curve D). These maxima are well resolved on the differential thermogravimetric curve (E) of the specimen. A similar feature is also poorly distinguishable on the differential thermogravimetric curve of specimen DMUC 10188 (C).

The endothermic reaction signifies the removal of water molecules from the specimens. This loss of water may occur in two stages, most of the water being expelled at the higher temperature. Another feature is an exothermic maximum at 860°C clearly visible on curve D (Chvaletice) and absent on the other curves. This effect, when taking into consideration the differential thermogravimetric (E) and thermogravimetric (not illustrated) curves, appears to correspond to two reactions: the expulsion of OH groups and the simultaneous recrystallization producing $AlPO_4$, which has the tridymite structure. The escape of OH groups is accompanied by a loss of 2.8% (by weight), which is in good agreement with the theoretical value (2.45 wt.%) calculated from the chemical formula (Table 1). The formation of $AlPO_4$ was established by X-ray powder diffraction.

INFRARED ABSORPTION SPECTRA

Owing to a lack of material, only two specimens were analyzed, BMNH 1910, 101 and Chvaletice. The infrared absorption curves (Fig. 3) were obtained with a Beckmann spectrometer using 0.1 wt.% of sample in a KBr pellet. The interpretation of the absorption spectra is given in Table 3. The assignments are based on the data of several authors, compiled by Ross (1974). It is apparent from Figure 3 and

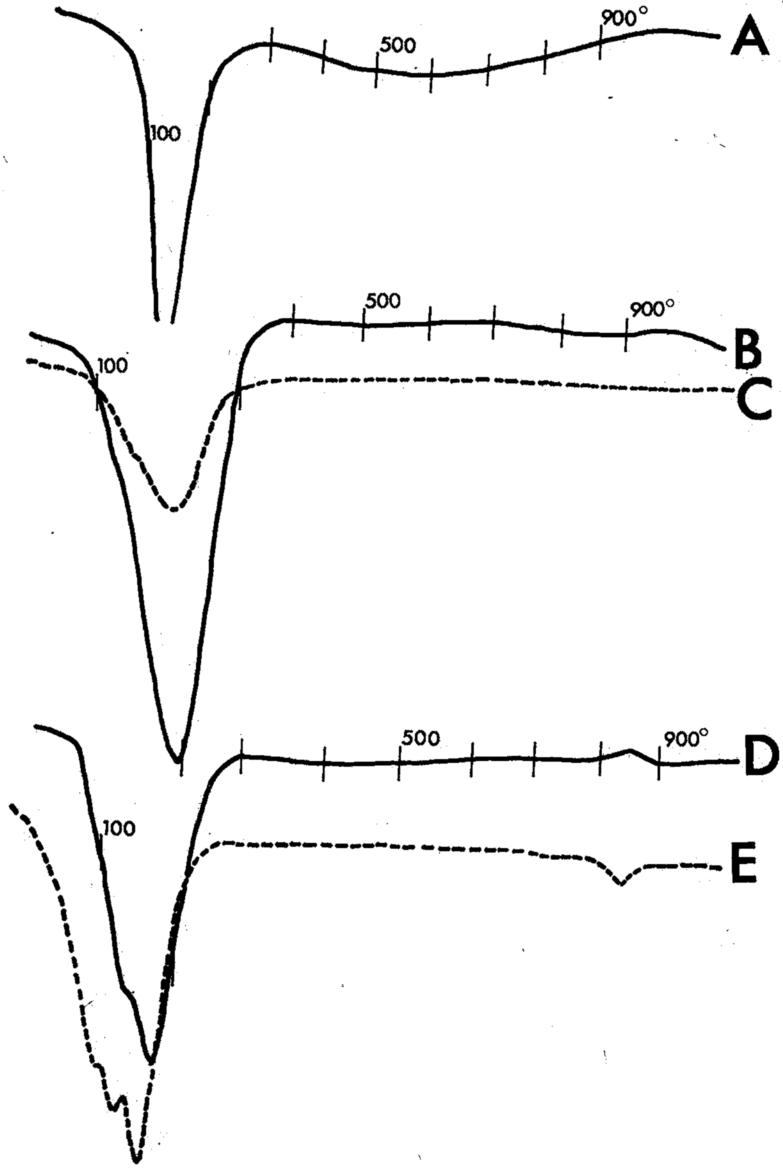

FIG. 2. Results of thermal analyses of vashegyite. A. DTA analysis of the specimen BMNH 1910, 101 (Železník), B. DTA analysis of the specimen DMUC 10188 (Železník), C. differential thermogravimetric analysis of the same specimen, D. DTA of the specimen from Chvaletice, and E. differential thermogravimetric analysis of the same specimen.

TABLE 3. INFRARED ABSORPTION SPECTRA OF VASHEGYITE

Frequency (cm^{-1})		Assignment
BMNH 1910,101	Chvalet.	
3400 (large band)	3400 3200	H_2O,OH:stretching vibrations
1635	1635	H_2O:bending vibrations
1385	1383	OH: δ
1175	1173	
1110	1115	$PO_4:\nu_3$ (antisymmetric stretching)
1010	1015	
905	905	$PO_4:\nu_1$ (symmetric stretching)?
733	725	Al-OH_2 mode or OH bending
650	650	ditto?
600	605	
528	530	$PO_4:\nu_4$
482	485	
380	385	

Table 3 that the specimens produce almost identical spectra, which resemble those of other Al phosphates such as variscite (Čech & Slansky 1965).

CRYSTALLOGRAPHY

Scanning-electron-microscope (SEM) examination of vashegyite from Železník reveals that its microcrystalline aggregates consist of almost euhedral crystals flattened on (001) and showing {110}, {010} and {001} as the most prominent forms (Fig. 4a, b). Two different habits were distinguished on the sample from Chvaletice (Fig. 4c, d). The first, typical of microcrystalline aggregates, is characterized by diamond-shaped crystals, with {110} as the most prominent form (Fig. 4c). The second habit shows the combination of {110} with {010} very prominent, leading to crystals having [100] elongate (Fig. 4d). This axis is the radius direction of radiating aggregates whose surface exhibits {110} as the atypical form. Simple twins (100) were rarely observed.

The size of vashegyite flakes from Chvaletice made it possible to use single-crystal techniques. By carefully positioning a fragment of vashegyite in a Weissenberg camera, zero-, first- and second-level photographs were obtained using Ni-filtered Cu radiation. An orthorhombic unit-cell was obtained despite the poor quality of diffraction diagrams caused by the deformation of cleavage planes (Fig. 4d). The parameters of this unit cell were refined by the least-squares method using powder-diffraction data from a 76.4-mm-diameter Debye–Scherrer camera (Table 2). The following systematic extinctions were observed: $0kl$: $k + l = 2n$; $h0l$: $h = 2n$; $h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$, corresponding to space groups *Pnam* or $Pna2_1$. The $hk0$ reflections with $h + k = 2n + 1$ are very weak and appear only on strongly overexposed photographs. The distribution of intensities on 0- and 2-level photographs is identical.

Another single-crystal approach was electron diffraction. Selected-area diffraction on vashegyite flakes from Chvaletice and Železník with the beam direction parallel to [001] gave identical results. The electron-diffraction pattern a^*b^* shows, in accordance with the intensities observed on the Weissenberg photographs, only $hk0$ reflections with

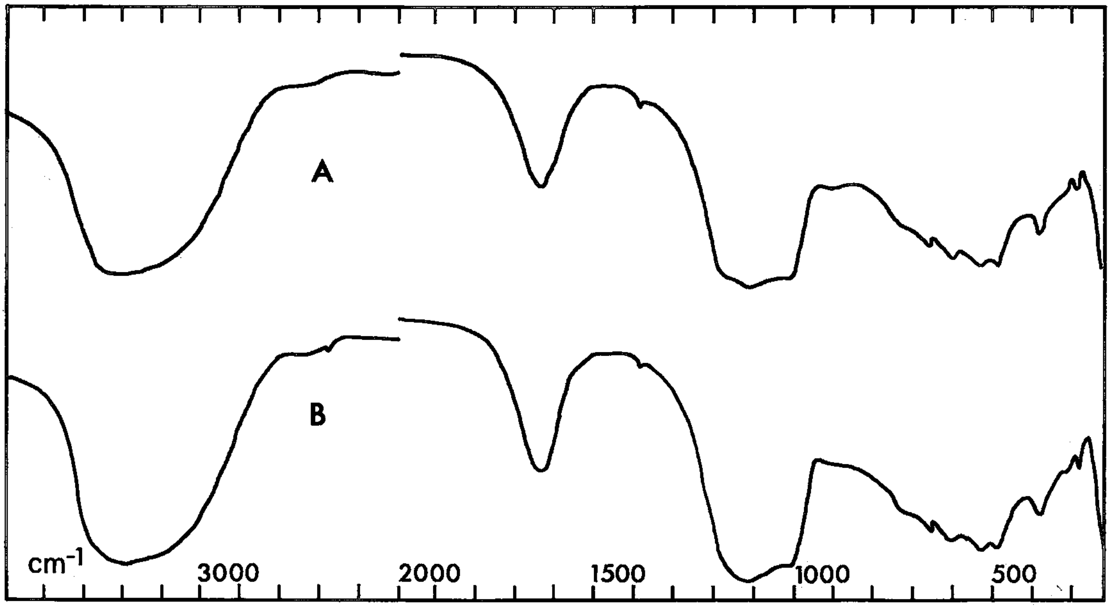

FIG. 3. Infrared absorption spectra of vashegyite. A. Železník BMNH 1910, 101, B. Chvaletice.

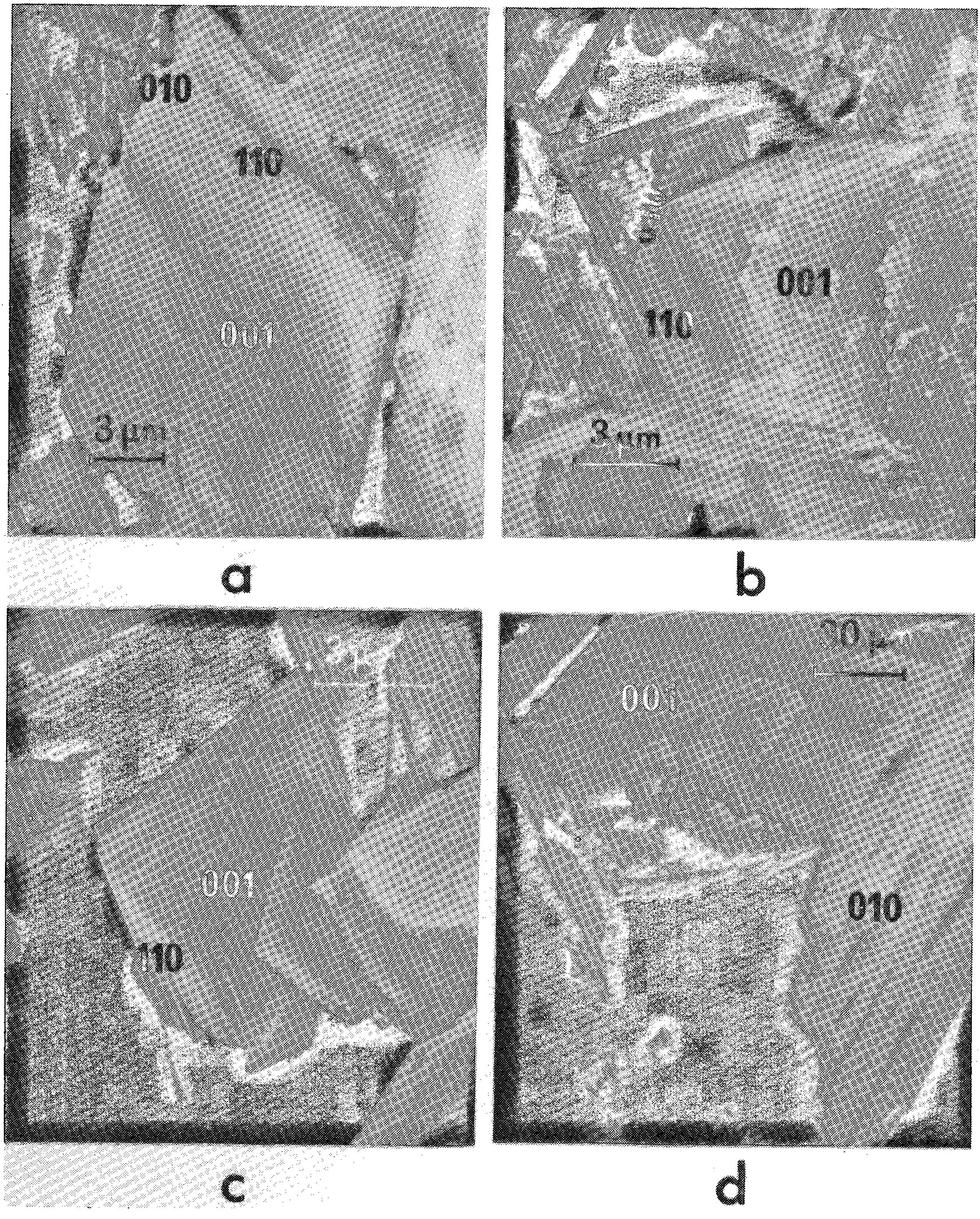

FIG. 4. Scanning electron photomicrographs of vashegyite crystals. a and b. Železník, collection of F. Souček; c. diamond-shaped crystals with {110} as the most prominent form, Chvaletice; d. macroscopic crystals elongated along [100]; Chvaletice, collection of P. Povondra.

TABLE 4. X-RAY POWDER DATA OF VASHEGYITE

Chvaletice				Železník							
				A		B		C			
I	d_{meas}	d_{calc}	hkl	I	d_{meas}	I	d_{meas}	I	d_{meas}	d_{calc}	hkl
10	11.3	11.34	002	10	10.3	9	10.2	10	10.1	10.31	002
				2	8.4	2	8.48			8.49	012
8	7.50	7.486	020	9	7.49	10	7.50	9	7.40	7.485	020
				9	7.04	7	6.99	9	7.02	7.036	021
3	6.90	6.919	112	3	6.41					6.670	112
7	6.26	6.247	022								
						1	5.93	2	5.93	5.891	121
1	5.62	5.669	004								
4	5.385	5.377	200	2	5.39	4	5.395	4	5.38	5.386	200
				4B	4.90					4.875	014
								2-3	4.505	4.528	130
1	4.351	4.367	220	4	4.437	5	4.373			4.372	220
						1	4.055			4.080	213
										4.039	033
						1	3.774	2	3.756	3.782	133
4	3.745	3.743	040							3.743	040
				3	3.699					3.725	204
3	3.460	3.459	224								
				5	3.455	2	3.464	6	3.460	3.450	232
6	3.297	3.332	312								
				4	3.269	1	3.277	4	3.268	3.275	106
				4	3.191			4	3.186	3.199	116
										3.183	303
1	3.169	3.166	313								
				2	3.062					3.074	240
				3	3.001			4	3.009	3.000	225
9	2.912	2.911	330	9	2.919	9	2.919	9	2.908	2.915	330
2	2.884	2.888	331								
		2.884	150								
4	2.834	2.834	008								
				3	2.808	4	2.776	4	2.791	2.805	332
										2.792	117
3	2.687	2.688	400	4	2.699	4	2.693	4	2.693	2.693	400
2	2.611	2.616	402			1	2.600	1	2.600	2.606	402
3	2.533	2.530	420	3	2.528	4	2.533	5	2.531	2.534	420
4	2.443	2.437	062	5	2.417	4	2.415	5	2.417	2.425	062
						1	2.291	1	2.301	2.300	350
4	2.280	2.284	064								
								1	2.237	2.244	352
2	2.183	2.183	440								
						2	2.175	1	2.175	2.174	441
2	2.136	2.129	510								
				5	2.125	3	2.124	4	2.125	2.127	247
										2.123	048
						2	2.084	3	2.085	2.083	443
2	2.045	2.049	513								
		2.042	319								

76.4mm Debye-Scherrer camera, Ni-filtered CuKα radiation;Intensities estimated visually; B = broad line; A.DMUC 10188;B. BMNH 1910,101; C. coll.Souček

TABLE 5. X-RAY POWDER DATA OF VASHEGYITE (GUINIER CAMERA)

Chvaletice				Železník							
				DMUC 10188				BMNH 1910,101			
I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl
				3	18.6	18.93	001				
								5	14.9	14.96	010
				8B	10.2	10.76	100				
10B	9.53	9.52	002	10VB	9.4	9.46	002	8VB	9.50	9.57	002
3	8.74	8.72	110					3	8.78	8.76	110
1	7.98	8.03	012	1	8.00	8.00	012	2	8.06	8.06	012
9B	7.485	7.494	020	9	7.49	7.484	020	10	7.51	7.480	020
				4VB	7.082	7.107	102				
7	6.979	6.973	021			6.960	021	7	7.00	6.970	021
3VB	6.486	6.431	112	2	6.425	6.420	112				
2	6.069	6.143	120	1	6.087	6.144	120				
8	5.366	5.363	200	7	5.387	5.381	200	7	5.412	5.407	200
1	4.656	4.672	202	1	4.661	4.678	202				
								2	4.392	4.407	131
1	4.360	4.361	220							4.382	220
2B	3.597	3.594	223								
				1	3.566	3.571	105				
						3.554	204	1	3.587	3.583	204
3	3.490	3.490	115								
5	3.472	3.477	310								
				3	3.441	3.434	034	1	3.453	3.452	034
1	3.425	3.421	311			3.431	311			3.447	311
								1	3.401	3.407	025
								1	3.323	3.315	142
								1	3.237	3.231	224
2	3.227	3.227	043								
2	3.173	3.173	006					2	3.187	3.189	006
5	3.086	3.071	240	3	3.072	3.072	240				
1	3.061	3.056	322								
4	3.040	3.043	106								
9	2.912	2.907	330	9	2.914	2.912	330	9	2.922	2.921	330
6	2.889	2.887	150	2	2.879	2.884	150	3	2.889	2.884	150
6	2.881	2.876	323								
		2.874	331								
3	2.856	2.854	151								
1	2.797	2.781	332					2	2.801	2.794	332
4	2.764	2.763	152								
								2	2.731	2.747	206
3	2.693	2.686	216								
4	2.677	2.681	400	5	2.690	2.690	400	4	2.703	2.703	400
1	2.578	2.581	402								
4	2.523	2.525	420	2	2.530	2.532	420	3	2.539	2.542	420
								2	2.525	2.520	421
1	2.458	2.462	325								
2	2.415	2.416	062	2	2.416	2.412	062	2	2.410	2.413	062
2	2.377	2.380	008								

Intensities estimated visually; evacuated Guinier camera, CoKα radiation
B = broad line; VB = very broad line

$h + k = 2n$. We must stress that obtaining electron-diffraction patterns of vashegyite was extremely difficult because of its rapid dehydration, followed by a complete destruction of its structure.

We obtained X-ray powder data (Tables 4, 5) with the aid of photographic techniques because these gave much better results in terms of the number and resolution of diffraction lines than diffractometer techniques. A conventional Debye–Scherrer camera (diameter of 76.4 mm) and a Guinier–de Wolff camera were used. There is a marked difference between the data from the two cameras; this discrepancy is attributed to a loss of water in the Guinier camera caused by evacuation. A similar phenomenon was observed by Martini (1978) in the course of an examination of sasaite, a mineral that is extremely close to vashegyite, as will be argued later.

The powder data were indexed on the basis of an orthorhombic unit-cell determined from Weissenberg photographs on vashegyite from Chvaletice. Taking into account the electron-diffraction patterns as well, we have to attribute the identical a^* and b^* unit-cell parameters to vashegyite from Železník; however, the periodicity along c^* for the latter was deduced from the analogy with vashegyite from Chvaletice and has not been confirmed by a single-crystal method.

The specimen from Chvaletice has a larger unit-cell than the three specimens from Železník (Vashegy). Whereas the a and b parameters remain identical, the value of c of the Chvaletice specimen is about 10% larger which, in turn, is partly commensurate with the increased water content of this specimen (Table 1). The unit-cell parameters obtained by least-squares refinement are listed in Table 2. The agreement between measured and calculated spacings is good, although not as good, perhaps, as in the case of better crystallized minerals.

X-ray-powder patterns (76.4 mm camera) of specimens from Železník are nearly identical (Table 4). The presence or absence of a few weak lines may be explained by variations in the crystallinity of material. However, X-ray-powder patterns of vashegyite from Chvaletice and from Železník (Table 4) reveal noticeable differences in intensities of several lines, particularly in the low-angle region. Besides the *hk*0 and 00*l* lines having the same intensities in all powder patterns considered, three lines (underlined) with forbidden indices in space groups *Pnam* and $Pna2_1$ (0*kl*: $k + l = 2n + 1$; *h*0*l*: $= 2n + 1$) appear in the powder patterns of vashegyite from Železník. One of these lines, with d = 7.04 Å, is very strong. On the other hand, the strong 022 diffraction line with d = 6.26 Å in the powder pattern of vashegyite from Chvaletice is systematically missing in the X-ray powder diagrams of specimens from Železník. These differences in X-ray powder diagrams indicate that vashegyite from Chvaletice and from Železník (Vashegy) have different space-groups.

Furthermore, there are noticeable variations in the powder patterns of the specimens from Železník, as revealed on powder photographs taken in a Guinier-de Wolff camera (Table 5). Of these, the most significant is the presence of reflections 001 and 100 on the powder pattern of specimen DMUC 10188, and the presence of reflection 010 on the powder pattern of specimen BMNH 1910, 101. This indicates changes in the symmetry of the unit cell, probably due to the irregular stacking of individual sheets. Whether this is the result of the generally poorly crystalline nature of the mineral or the consequence of a partial dehydration of the specimens in the vacuum of the Guinier camera is difficult to decide. In any case, this type of disorder leads to lowering of the symmetry of the unit cell and to an inconsistency in the assignment of a space group from one sample to another.

DISCUSSION

Our investigation shows that the specimens of vashegyite selected for study are a hydrated Al phosphate having a sheet structure. This type of structure is indicated by the distribution of intensities on Weissenberg photographs and by the flaky habit and perfect cleavage of crystals as seen in the SEM (Fig. 4). Thus the layer structure postulated for this mineral by McConnell (1974) is confirmed. However, no evidence has been found for his analogy with the crystal structure of kaolinite.

Vashegyite is orthorhombic; specimens show a variability in chemical composition that is related to variation in crystal structure. This is demonstrated by some differences in X-ray powder-diffraction patterns; a different space-group symmetry appears to be involved. The most probable reason for the variations is a somewhat different, possibly irregular manner of stacking the structural sheets in each specimen. Thus, among the hydrous Al phosphates examined, there exists a group of chemically and structurally similar phases which, for now, are best designated as vashegyite. Future research may show that the mutual relationship between the varieties of vashegyite is that of polytypoids as defined by Bailey *et al.* (1978).

A probable member of this group is the mineral sasaite described from West Driefontein Cave, Transvaal, South Africa by Martini (1978). This mineral has a chemical composition very similar to vashegyite, but with a much higher water content. Its chemical formula, given by Martini (1978) as $(Al,Fe^{3+})_{14}(PO_4)_{11}(SO_4)(OH)_7{\cdot}83H_2O$, can be rewritten, by analogy to vashegyite from Chvaletice, as $(Al,Fe)_6(SO_4)_{0.5}(PO_4)_{4.55}(OH)_{3.35}{\cdot}35H_2O$ or, more simply, $(Al,Fe)_6(PO_4,SO_4)_5(OH)_3{\cdot}35\text{–}36H_2O$.

TABLE 6. X-RAY DATA OF HYDRATED SASAITE (MARTINI 1978)*

I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl
100	11.52	11.51	004	5	3.368	3.373	046
10	10.74	10.750	100	15	3.315	3.322	229
		10.733	013			3.308	145
4	8.75	8.742	110	18	3.262	3.261	047
1	8.18	8.172	112			3.260	315
22	7.51	7.510	020	16	3.216	3.212	01.14
18	7.13	7.140	022			3.211	03.11
23	6.99	6.992	105	10	3.091	3.090	238
		6.961	114	14	3.066	3.071	241
21	6.30	6.289	024			3.069	12.13
7	5.95	5.947	122	3	2.985	2.981	318
7	5.78	5.767	116			2.980	326
		5.755	008	12	2.926	2.930	13.12
14	5.42	5.429	124			2.919	245
		5.375	200	42	2.901	2.908	331
1	5.24	5.255	117			2.902	327
		5.234	202	18	2.863	2.862	333
2	4.966	4.947	027	11	2.835	2.843	153
		4.943	212			2.841	02.15
5	4.881	4.892	032	7	2.810	2.809	118
		4.870	204	6	2.734	2.733	329
12	4.822	4.807	118	8	2.702	2.707	156
1	4.666	4.642	205			2.705	14.11
1	4.570	4.568	028	1	2.653	2.650	23.12
2	4.381	4.371	220	1	2.632	2.637	249
18	4.214	4.222	134			2.628	412
		4.204	223	2	2.603	2.604	14.12
2	4.104	4.086	224	6	2.542	2.543	415
2	3.935	3.934	129			2.542	13.15
		3.928	208	3	2.478	2.480	24.11
5	3.846	3.837	00.12	7	2.372	2.368	430
10	3.695	3.706	042	1	2.302	2.302	350;00.10
		3.705	209	2	2.250	2.251	10.10
13	3.518	3.513	11.12			2.250	33.13

Diffractometer, CoKα radiation;*indexed on the basis of a 10.75, b 15.02, c 46.03 Å

Martini's unit cell (hydrated form of sasaite) obviously is related to the unit cell of vashegyite in the following manner: $a/2_{sas} \simeq a_{vash}$; $b/2_{sas} \simeq b_{vash}$; $c/4_{sas} \simeq c_{vash}$ or 21.5/2 = 10.75; 30.04/2 = 15.02; 92.06/4 = 21.015. In Table 5, it can be seen that divided values of parameters of sasaite are extremely close to those of vashegyite from Chvaletice. In indexing the powder data for hydrated sasaite, the best fit was obtained with: *a* 10.75, *b* 15.02 and *c* 46.03 Å (Table 6). These parameters give twice the volume of the unit cell of vashegyite and, with Z = 6, give a calculated density of 1.780 g/cm^3. This value can be considered in fair agreement with the value of 1.75 determined by Martini (1978), taking into consideration the ease with which this mineral loses water. The calculated density given by Martini, 1.747 g/cm^3, is inconsistent with his Z value, which should obviously be doubled. Twenty formula units with $83H_2O$ per unit cell do not seem to be a probable suggestion. This, and the similarity with vashegyite, casts doubt on the validity of sasaite. However, without investigating the type material, a final decision as to the recommendation for the removal of sasaite from the list of valid mineral species cannot be reached.

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