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SLAVÍKITE — A REVIEW SLAVÍKIT — PŘEHLED VÝZKUMŮ

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Introduction

Slavíkite is a supergene yellowish green basic iron sulfate, first reported from Czechoslovakia and up to now recorded from nearly twenty localities, half of them in Czechoslovakia. It occurs in minute hexagonal lamellae as a weathering product of pyritic rocks.

The original paper in 1926¹² provided chemical and optical data, but some of them were rather strongly amended in later years. A controversy arose about the chemical composition. The original analysis reported alkali metals (2,2 % Na₂O and K₂O), a low water loss (3,1 %) at 110 °C and the absence of magnesium. Further analyses performed on the type material (slavíkite from Valachov Hill, Rakovník, Bohemia) in 1940²⁸ and 1949³⁷ and also on material from other localities, established a constant presence of magnesium and an important loss of water even at low temperature; furthermore the alkali metals were discarded from the formula. S. G. Gordon's investigation, in 1941, "permitted of redefining the mineral as to its composition". Accurate crystallographic data became available by optical goniometer measurements in 1941⁹ and by single-crystal X-ray diffraction in 1949³⁷.

Name and synonymy

The mineral name slavíkite was coined in 1926 by two Czech mineralogists, R. Jirkovský and F. Ulrich, in honour of Professor František Slavík (1876—1957) of the Charles University of Prague.¹⁾ Although named slavíkite in 1926, the same mineral was recognized²⁹ in the substance described by J. Klvaňa, in 1881, as paracoquimbite. On the other hand a polymorph substance of coquimbite was also named paracoquimbite by H. Ungemach in 1935. R. Rost argued in 1941 that paracoquimbite Klvaňa 1881, although having priority, should better be dropped as a synonym, because paracoquimbite Ungemach 1935 is a justified name for a polymorph mineral and because slavíkite was already largely used in literature.

The incorrect chemical data of the 1926 description and the inavailability of scientific papers (S. G. Gordon 1941, R. Rost 1940 and 1941) during World War II years, led the present author to distinguish the original slavíkite (1926) from a magnesium iron sulfate from Franquénies, Brabant, Belgium, and to describe this compound as franquenite in 1944. Further study performed in 1949 on material from different localities concluded to the identity of slavíkite and franquenite and, in this way, the name franquenite could be dropped as a species name³⁷ or used as variety name¹⁰.

Occurrences

Slavíkite is reported up to now from 19 localities: 17 in Europe and 2 on the American continent (Argentina and Canada).²⁾ Among the European occurrences 10 are known in Czechoslovakia, 3 in Austria³⁾ and 3 in Belgium, stressing the influence of authors' interest. From the field observations it is obvious that slavíkite, although only occasionally recorded, is not a rare mineral, but it may commonly be overlooked and taken for sulphur, jarosites or other iron sulfates, or even not stimulate mineralogists' interest.

In Table I the different known occurrences are tabulated together with the deposit conditions and associated secondary sulfates. As seen from this table, slavíkite occurs in association with several other sulfates, which can render separation sometimes very difficult. P. Černý (1956) established the following succession in the formation of the iron sulfates: halotrichite — melanterite — epsomite — copiapite — botryogene — fibroferrite and last slavíkite.

¹⁾ Kutina, J., 1958, Memorial of František Slavík. Amer. Miner., 43, 325—330.

²⁾ The Canadian occurrence is unpublished. The material was collected by J. P. Perry in 1964 and identified by J. L. Jambor the same year. The occurrence became known too late to be incorporated in Boyle's paper², where dozens of supergene minerals are reported (Private communication of W. H. Poole, 15. 4. 1970). Canadian slavíkite is not recorded in R. J. Traill's "A catalogue of Canadian Minerals" (Paper 69—45, Geol. Survey of Canada, 1970).

³⁾ The occurrence at Aigen, Eanstal, is new. Prof. H. Meixner kindly authorized its publication (Private communications 20. 10. 71 and 15. 1. 72).

Morphology

Slavíkite occurs in hexagonal plates, generally from 10 to 30 μ , showing a pinacoid and faces of rhombohedra. Jirkovský and Ulrich (1926) reported crystals of max. 0,5 mm, but this dimension was not further observed for material from the same locality, neither in 1939²⁰, nor in 1949³⁷. The material from Argentina provided the best developed crystals, ranging to one millimeter and even more in diameter⁹. Dimension data of slavíkite crystals are grouped in Table II.

Table I. — Occurrences of slavíkite

Locality	Environment	Accompanying secondary sulfates	
		Iron sulfates	Other sulfates
Czechoslovakia			
1. Valachov, Rakovník, near Skřivani, Bohemia ^{11, 12}	Algonkian pyritic shales	halotrichite, melanterite, botryogene, fibroferrite, natrojarosite, szomolnokite	gypsum, pickeringite, epsomite, keramohalite, tschermigite, glockerite
2. Luka near Medník, south of Prague ²⁸	Euler zone shales	halotrichite	gypsum, epsomite, pickeringite
3. Vrané, south of Prague ²⁸	Algonkian pyritic shales	id.	id.
4. Štěchovice, south of Prague ²⁸	id.	id.	id.
5. Jarov, near Štěchovice, south of Prague ²⁸	id.	id.	id.
6. Troja, near Prague ^{15, 29, 37}	id.	halotrichite, fibroferrite	pickeringite, epsomite, keramohalite
7. Mandát, near Davle, north of Štěchovice, south of Prague ^{15, 37}	id.	halotrichite, natrojarosite	gypsum, pickeringite, epsomite
8. Branná, Moravia ⁵⁰	Pyritic rocks		
9. Smolník, eastern Slovakia ⁵	Pyritic lenses in chloritic sericitic phyllites	halotrichite, melanterite, botryogene, fibroferrite, natrojarosite, copiapite	gypsum, pickeringite, epsomite
10. Medzev, near Košice, eastern Slovakia ¹⁹	Pyritic veins in sericitic phyllites	fibroferrite, jarosite	gypsum, pickeringite, epsomite

Locality	Environment	Accompanying secondary sulfates	
		Iron sulfates	Other sulfates
Austria			
1. Pöham, Salzburg ²⁰	Pyritic shales	melanterite, fibroferrite, jarosite, copiapite	gypsum, epsomite
2. St Peter ob Rennweg, Liesertal, Kärnten ^{21, 22}	Graphitic pyritic shales	fibroferrite	gypsum, epsomite ? pickeringite
3. Aigen, Ennstal, Steiermark (new locality)			
4. Doubtful occurrence: Kalwang, Steier- mark ^{8, 20} „Botryogene“ Freyn	Graphitic shales	? copiapite	
Belgium			
1. Franquénies, near Mousty, prov. Brabant ^{36, 37}	Graphitic pyritic and arsenopyritic shales	ferroan pickeringite, melanterite, fibroferrite	gypsum
2. Stavelot, prov. Liège ³⁸	Pyritic Cambrian shales	jarosite	gypsum, pickeringite,
3. Val-Dieu, prov. Liège ³⁸	Micaceous Upper Devo- nian sandstone with coal layer	jarosite	gypsum, pickeringite,
France			
St Cyprien-sur-Dourdou, district Kaymar, Aveyron ¹⁶	Carbonaceous pyritic micaschists		gypsum
Argentina			
Mina „Santa Elena“, Alcaparrosa, dep. Barreal, prov. San-Juan ^{9, 37}	Pyritic veins in diabase	botryogene, fibroferrite, copiapite, szomolnokite, calingastite	gypsum, pickeringite, epsomite, aluns, hohmannite
Canada			
Galena Hill, near Porcupine Creek, Yukon (new locality)	Greenstone interlayered with quartzite, graphi- tic phyllite and fine- grained schists	presumably many ²	gypsum, presumably many others ²

Table II. — Dimensions of slavikite crystals

Locality	Max. dimension observed in mm	Current dimensions in mm
Valachov ¹²	0,5	0,03 —0,05
Valachov ^{20, 28}	0,07	0,01 —0,04
Luka ²⁸		0,02 —0,03
Troja ^{29, 37}	0,03	0,015—0,03
Mandát ³⁷	0,06	0,015—0,03
Smolník ³		0,01 —0,05
Medzev ¹⁹		0,003—0,03
Pöham ²⁰		mostly 0,01
Rennweg ²²	0,06	0,03 —0,05
Argentina ⁹	1 and more	0,2 —0,3
? Kalwang ²⁰		0,005
Franquenes ³³	0,03	0,008—0,015
Stavelot ³⁸	0,03	0,007—0,015
Val-Dieu ³⁸	0,03	0,007—0,015
Kaymar ¹⁶		0,01 —0,02
Yukon		0,01

Table III. — Goniometric data

Locality	Azimuth angle ρ	Number of measurements	Ratio c : a
Argentina ⁹	58°39' (from 58°12' to 59°07')	10	1,421 (1)
Valachov ⁹	58°38' (from 58°04' to 58°56')	3	1,420
Argentina ³⁷			2,85 (2)

(1) S. G. Gordon (1941) gave, with $c = \frac{1}{2} \sqrt{3} \tan \rho$, the value of 1,389 for $c : a$, which is incorrect for ρ 58°39'. In Dana's System²⁴ [p. 621] ρ is taken 58°03½' in order to satisfy $c : a = 1,389$. There is no reason for doing so, all the measured angles being above 58°03½'.

(2) Calculated from X-rays.

Under the microscope R. Jirkovský and F. Ulrich recognized¹² a rhombhedron forming an angle of $50 \pm 2^\circ$ with the basal plane and H. Meixner²⁰ also measured $\pm 50^\circ$. S. G. Gordon⁹ observed a basal pinacoid, a prominent developed rhombohedron and three other narrow rhombhedra. With the reflection goniometer he measured the values grouped in Table III, obtained on crystals from Argentina and on a 0,02 mm crystal from Valachov. According to X-rays the c-axis is to be doubled (the prominent rhombohedron {1011} of Gordon, with azimuth angle of 58°, becomes {1012}).

Optics

The optical data obtained on slavíkite from different localities are tabulated in Table IV. They are very similar, excepted for the observations of 1926¹² and 1940²⁸ indicating weaker birefringence. The data with n_o (yellow) = 1,531 and n_e (almost colourless) = 1,496, birefringence 0,035, uniaxial negative, appear most characteristic.

Table IV. — Optical data

Locality	Observed interference figure	Refractive indices			Reported pleochroism	
		n_o	n_e	$n_o - n_e$	n_o	n_e
Czechoslovakia						
Valachov ¹²	uniaxial. negat.	1,530	1,506	0,024	yellow	nearly colourless
Valachov ³⁷		1,432	1,497	0,035		
Luka ²⁸		1,530	1,506	0,024	yellow	colourless
Jarov ²⁸		1,530	1,506	0,024	yellow	colourless
Troja ¹³	uniaxial. negat.	—	—	—		
Troja ²⁹		1,532	1,496	0,036		
Troja ³⁷		1,531	1,497	0,034		
Mandát ³⁷		1,531	1,496	0,035		
Smolník ³	uniaxial. negat. biaxial $2V = \pm 5^\circ$	1,535	1,496	0,039	yellow	colourless
Medzev ¹⁹		1,531	1,495	0,036		
Austria						
Pöham ²⁰	uniaxial. negat.	1,537	1,498	0,039 0,037 (Berek)	yellow	colourless
Rennweg ²²	uniaxial. negat.	1,531	1,500	0,031		strong
Belgium						
Franquemies ³³		1,531	1,494	0,037		
Stavelot ³⁸		1,531	1,496	0,035		
Val-Dieu ³⁸		1,531	1,496	0,035		
France						
Kaymar ¹⁶	uniaxial. negat.	1,526 1,533	1,495 1,497	0,031 0,036	yellow green	colourless
Argentina ^{9, 37}	uniaxial. negat.	1,531	1,496	0,035		

Density

The density determinations are as follows:

Valachov ¹²	1,905
Argentina ⁹	1,99
Kaymar ¹⁶	1,945
Franquemies ³⁶	between 1,87 and 1,94
Calculated from X-rays ³⁷	2,10
(admitting $Z = 6$ in the hexagonal cell and Gordon's formula)	

Chemical composition

The chemical analyses have been interpreted in different ways. The three trends can be summarized in Table V.

Table V. — Chemical composition

Author	Alkali metals	Magnesium	Loss at 110 °C
1. Jirkovský and Ulrich, 1926 2. Rost, 1940 and 1941 3. Gordon, 1941; Van Tassel, 1944, 1949, 1956; Lenfant, 1964; Makovický and Streško, 1967; Klvaňa, 1881	present absent absent	absent absent present	small (3,10 %) important (\pm 26,5 %) important (between 23 and 30 %)

The original analysis published by R. Jirkovský and F. Ulrich in 1926 seems almost impossible to explain, although the treatment with absolute alcohol prior to the analysis may have altered the crystalline substance and although the contaminating jarosite may be responsible for some alkali metals and low H_2O^- content. R. Rost (1940) stated that the original analysis is difficult to explain with respect to water loss at 110 °C while the total water content is consistent with newer analyses. Professor F. Slavík wrote to the author in 1948⁴⁾ that the formula based on the first analysis appeared so complicated that doubt arose about the homogeneity and even about the existence of the species. Rost's interpretation²⁸ based on three other analyses (material from Luka and Jarov) and on the earlier analysis of Klvaňa led to a much simpler composition, but this interpretation seems to have oversimplified.

Table VI. — Chemistry of slavíkite in literature

Dana's System, 7th edit., 1951 ²⁴	$[\text{Na}, \text{K}]_2\text{Fe}^{++10}(\text{SO}_4)_{13}(\text{OH})_6 \cdot 63\text{H}_2\text{O} (?)$	(1)
Schüller A., 1954 ³¹	$\text{MgFe}^{++3}(\text{SO}_4)_4(\text{OH})_3 \cdot 18\text{H}_2\text{O}$ resp.	(3)
Hey M. H., 1955 ¹⁰	$[\text{Na}, \text{K}]_2\text{Fe}^{++10}(\text{SO}_4)_{13}(\text{OH})_6 \cdot 63\text{H}_2\text{O} (?)$	(1)
Betehtin A. G., 1964 ¹	$\text{MgFe}^{++3}(\text{SO}_4)_4(\text{OH})_3 \cdot 18\text{H}_2\text{O}$	(3)
(original edition of 1961)	$\text{Fe}^{++}(\text{OH}, \text{SO}_4) \cdot 8\text{H}_2\text{O} (?)$	(2)
Kostov I., 1968 ¹⁴	$\text{MgFe}^{++3}(\text{SO}_4)_4(\text{OH})_3 \cdot 18\text{H}_2\text{O}$	(3)
(original edition of 1966)	$\text{Fe}^{++}(\text{OH}, \text{SO}_4) \cdot 8\text{H}_2\text{O} (?)$	(2)
Strunz H., 1966 ³⁴	$\text{MgFe}^{3+}(\text{OH})_3/(\text{SO}_4)_4 \cdot 18\text{H}_2\text{O}$	(3)
id. 1970 ³⁵	$\text{Fe}^{++}(\text{OH}, \text{SO}_4) \cdot 8\text{H}_2\text{O} (?)$	(2)
Ramdohr P. and Strunz H., 1967 ²⁷	$\text{Fe}^{++}(\text{OH}, \text{SO}_4) \cdot 8\text{H}_2\text{O} (?)$	(2)

(1) refers to Jirkovský and Ulrich, 1926; (2) to Rost, 1940 and (3) to Gordon, 1941. The frequent use of the note of interrogation stresses the doubt in admitting the formula.

4) Private communication 8. 4. 1948.

M. H. Hey stated in 1955 that it appeared fairly clear that the original analysis which showed Na and K, but no Mg, was incorrect, that the mineral has also been formulated $\text{FeSO}_4 \cdot \text{OH} \cdot 4\text{H}_2\text{O}$, but, all the analyses showing $4\frac{1}{2}\%$ MgO, there can be little doubt that Mg is essential.

The complicated history of slavíkite's chemistry is responsible for the unfortunate situation that no chemical formula was unanimously accepted in recent handbooks and tables of mineralogy, as can be seen from the listing in Table VI.

The analytical data hitherto published for slavíkite are grouped in Table VII and completed with four unpublished analyses, made on three samples from Austria: Pöham, Rennweg and Aigen (new locality according to Prof. H. Meixner) and one from Canada (R. O. M. specimen №

Table VII. — Analytical data

	1	2	3	4	5	6	7	8	9	10
Na ₂ O	} 2,97	—	1,63	} 0,3	0,68	0,28	0,53	} tr	—	0,29
K ₂ O		—	0,57		0,26	0,13	0,16		—	
CaO		—	0,01		tr	0,42	2,38		0,87	—
MgO	3,44	—	—	4,1	4,40	4,54	4,63	—	—	4,40
MnO	—	—	—	—	—	—	tr	—	—	—
FeO	—	—	—	—	—	0,82	0,65	—	—	—
Fe ₂ O ₃	21,70	—	20,08	18,0	19,08	18,75	16,94	21,4	21,3	23,93
Al ₂ O ₃	2,02	—	4,29	4,3	2,79	1,77	3,52	—	—	—
SO ₃	32,22	35,3	34,06	33,2	34,70	34,61	34,23	—	33,7	34,62
H ₂ O -	} 36,65	26,7	3,10	27,2	} 36,65	} 36,58	} 38,46	—	19,1	} 37,21
H ₂ O +		—	35,66	—				—	—	
Residue	—	—	—	—	—	—	—	—	—	—
Total	100,00	—	99,92	—	98,98	99,86	99,99	—	—	100,45

	11	12	13	14	15	16	17	18	19	20
Na ₂ O	—	—	—	0,15	—	} < 0,3	} 0,3	—	—	—
K ₂ O	—	—	—	0,3	—			0,41	0,42	5,8
CaO	—	—	tr	0,0	0,95	3,90	3,63	3,3	4,4	4,0
MgO	4,3	4,23	4,6	2,8	3,7	0,89	0,04	—	—	—
MnO	—	—	—	—	—	0,0	0,0	—	—	—
FeO	0,2	1,0	—	0,6	—	—	—	—	—	—
Fe ₂ O ₃	24,7	14,84	22,5	14,0	19,4	22,98	17,45	19,1	22,8	20,4
Al ₂ O ₃	—	5,51	0,7	6,8	—	0,59	1,56	—	—	—
SO ₃	31,6	32,77	32,8	32,2	33,0	31,87	31,20	35,5	32,2	33,1
H ₂ O -	26,0	28,2	27,4	26,2	} 34,8	} 35,72	} 35,74	25,0	26,7	27,8
H ₂ O +	12,5	12,5	11,2	11,9				—	—	—
Residue	—	—	—	5,8	—	4,08	10,50	0,4	1	1
Total	99,3	99,05	99,2	100,75	—	100,59	100,55	—	—	—

1. Troja¹³, 2,97 by difference. 2. Troja³⁷, contaminating fibroferrite observed. Sample provided by the National Museum, Prague. 3. Valachov¹². 4. Valachov³⁷; sample collected in 1926 and provided by the National Museum, Prague. 5. Luka²⁸, after deducting 16,22 % insoluble. 6. Jarov²⁸, after deducting 4,68 % insoluble. 7. Jarov²⁸, after deducting 2,20 % insoluble. 8. Pöham. 9. Pöham. Sample provided by H. Meixner. New analysis. Contaminating gypsum and jarosite observed. 10. Argentina⁹. 11. Argentina³⁷. Sample provided by S. G. Gordon. 12. Franquénies³⁶. 13. Mandat³⁷. Sample provided by the National Museum, Prague. 14. Stavelot³⁶. Contaminating fibroferrite observed. 15. Kaymar¹⁶. 5—6 % insoluble to be added. 16. Medzev¹⁹. 17. Medzev¹⁹. 18. Yukon (unpublished analysis). Contaminating gypsum observed. Sample ROM № M 29225. 19. St Peter, Rennweg (unpublished analysis). Sample H. Meixner. 20. Aigen, Ennstal (unpublished analysis). Sample H. Meixner.

M 29225). The identification of the Austrian slavíkites is due to H. Meixner and of the Canadian material to J. L. Jambor (Geol. Surv. of Canada, film 24128, 1964).⁵⁾

For comparison purposes the analytical data of Table VII are calculated on the basis of a constant molecular quotient for SO₃, CaO being deducted as gypsum and alkali metals neglected. In many cases the experimental ratio MgO : Fe₂O₃ : SO₃ : H₂O is not entirely convincing, although the general trend is in favour of the admitted formula MgFe₃(SO₄)₄(OH)₃ · 18H₂O (S. G. Gordon, 1941). The observed variability is presumably due to associated sulfates difficult or almost impossible to separate.

Interpreting the analytical data, R. Rost (1940, 1941) eliminated, from the composition of slavíkite, MgO as epsomite, FeO as halotrichite and (Na, K)₂O as jarosite, and concluded to a ratio Fe₂O₃ : SO₃ : H₂O = 1 : 2 : 9, based on analyses on material from Luka, Jarov and Troja, for which the respective ratios 1 : 2,30 : 9,81, 1 : 1,906 : 7,84, 1 : 1,908 : 8,74 and 1 : 2 : 9,5 were found. However, when maintaining MgO for the composition of slavíkite, ratios are found comparable to those for the admitted formula: 2MgO : 3Fe₂O₃ : 8SO₃ : 39H₂O. The most valuable data in this respect are obviously the values obtained on well crystallized slavíkite from Argentina, which can easily be isolated as a pure sample, excepted for the very tiny inclusions of jarosite. Analyses of this Argentine slavíkite undoubtedly supports the ratio MgO : Fe₂O₃ : SO₃ : H₂O = 2 : 3 : 8 : 38 — 42.

Spectrochemical analyses, suitable for small samples permitting better quality, were made on material from Argentina³⁷, Valachov³⁷, Mandat³⁷, Franquénies³⁷, Pöham, Rennweg and Aigen by the present author and for slavíkite from Medzev by E. Makovický and V. Streško (1967); in each case the presence of the main metals Fe and Mg was confirmed. Makovický and Streško assumed that Al₂O₃ generally does not enter into the composition of slavíkite in appreciable amounts on the basis of undetectable variation in refractive indices and X-ray data.

⁵⁾ The samples were most kindly provided by H. Meixner, Professor at the University of Salzburg, and by J. A. Mandarino, Curator of Mineralogy, Royal Ontario Museum, Department of Mineralogy, Canada. Identifications confirmed by X-rays.

Microprobe analysis of a carefully selected crystal of slavíkite from Argentina established undoubtedly that Mg belongs to the main components (a few percents).⁶⁾

It is obvious that synthetic material would be extremely helpful in settling the composition chemical. Unfortunately E. Makovický and V. Strěško (1967) gave no analytical data for their synthetic slavíkite and the present author was rather unsuccessful in synthesizing slavíkite.

Table VIII. — Molecular ratios

Locality (analysis number of Table VII)	{Na, K} ₂ O	MgO	Fe ₂ O ₃ (+ Al ₂ O ₃)	SO ₃	H ₂ O
1. Troja ¹³	—	1,64	3,00 (1)	8,0	39,23
3. Valachov ¹²	{ 1 0,61	—	5,17 (1)	13,08	66,38
4. Valachov ³⁷		—	3,16 (1)	8,0	40,60
5. Luka ²⁸ (2) (3)	—	1,95	2,99 (1)	8,0	—
6. Jarov ²⁸ (2) (3)	—	2,05	2,76 (1)	8,0	37,93
7. Jarov ²⁸ (2) (3)	—	2,31	2,76 (1)	8,0	39,93
9. Pöham (2)	—	2,23	2,67 (1)	8,0	40,84
10. Argentina ⁹	—	2,1	2,6 (4)	8,0	—
11. Argentina ³⁷	—	2,02	2,77 (4)	8,0	38,23
12. Franquénies ³⁶	—	2,2	3,2 (4)	8,0	42,7
13. Mandát ³⁷	—	2,31 (5)	2,86 (1)	8,0	44,01
14. Stavelot ³⁸ (6)	—	2,23	2,89 (1)	8,0	—
15. Kaymar ¹⁶ (2)	—	1,4	3,1 (1)	8,0	42,3
16. Medzev ¹⁹ (2)	—	1,86	2,46 (4)	8,0	38,74
17. Medzev ¹⁹ (2)	—	1,98	3,13 (4)	8,0	40,04
18. Yukon (2)	—	1,86	2,72 (4)	8,0	40,67
19. St Peter, Rennweg (2)	—	1,93	2,82 (4)	8,0	—
20. Aigen (2)	—	2,2	2,9 (4)	8,0	—
	—	1,97	2,5 (4)	8,0	—

(1) Al₂O₃ included. (2) CaO deducted as gypsum. (3) FeO deducted as halotrichite, and {Na, K}₂O as jarosite. (4) Al₂O₃ not determined or not included. (5) FeO included. (6) impure; ? fibroferrite admixed.

Crystal structure

X-ray powder diffraction data were obtained in 1949³⁷ on fine grained slavíkite from the type locality Valachov, from Mandát, from Troja (Klvaňa's material), from Franquénies, from Argentina and in later years on material from Val-Dieu³⁸, Stavelot³⁸, Smolnik³, Medzev¹⁹ and Kaymar^{16,7)} Single crystal observations³⁷ were made on good crystals from Argentina and indicated rhombohedral symmetry with parameters **a** = 12,22 Å and **c** = 34,86 Å in the hexagonal cell and **a**_{rh} = 13,6 Å and α = 53°24' in the rhombohedral cell.

⁶⁾ Analysis due to Dr. J. Pelsmaekers, Metallurgy Dept, SCK-CEN (Nuclear Science Centre, Mol).

⁷⁾ The A. S. T. M. diffraction data file provides the card 20—679 with values after Makovický and Strěško (1967).

Four single crystal photographs taken on slavíkite from Argentina are shown in figures 1 to 4. Figure 1 is a rotation photograph with **c** as rotation axis; figure 2 a rotation photograph with **a** as rotation axis; figure 3 is a precession photograph with **c** as rotation axis and figure 4 is a drawing after a Laue photograph with the X-ray beam perpendicular to the pinacoid.⁸⁾

The Laue pattern indicates trigonal symmetry as observed for symmetry classes 3 or $\bar{3}$. The precession photograph shows the reflections for the **hko**, **hk1** and **hk2** levels recorded successively on the same film sheet. The pattern confirms the above mentioned symmetry and parameter.

The axial ratio **c** : **a** found³⁷ by X-rays is 2,85, which is twice the ratio 1,421 obtained from optical goniometer measurements (not 1,389 as given by Gordon⁹⁾).

The indexed powder data, up to 2 Å in Table IX, are based on data either for reflections with measured intensity (Lenfant 1964) or for mean reflections obtained, with internal standards, either with goniometer counter or with a Guinier camera (Makovický and Streško 1967). These data confirm the powder data obtained since 1949³⁷. The indexing is made on the basis of the **a** and **c** parameters of the hexagonal cell³⁷. All the reflections satisfy the equation $-\mathbf{h} + \mathbf{k} + \mathbf{l} = 3\mathbf{n}$, characterizing a rhombohedral cell as pointed out in 1949³⁷.

Admitting the formula $\text{MgFeSO}_4 \cdot 18\text{H}_2\text{O}$ of S. G. Gordon (1941), the molecular weight is 951,4. From this, using the density 1,99 of the purest slavíkite (Argentina), the number of molecules entering the rhombohedral unit cell is found³⁷ to be $Z = 1,89$, which means $Z = 2$. Starting from $Z = 2$, the calculated density is 2,10. For the hexagonal cell Z observed is 5,67, which means $Z = 6$.

The crystal structure of slavíkite has not yet further been examined.⁹⁾

Alteration

The thermal behaviour of slavíkite was examined in 1944³⁶, 1949³⁷, 1964¹⁶ and 1967¹⁹. The substance is easily decomposed by heat. Dehydration proceeds already at low temperature and at 200 °C nearly the total amount of water is expelled. The loss of water is accompanied by a gradual change in colour from yellowish green to brown, the residue being already of brown colour at 110 °C with destroyed crystal structure. Thermogravimetric and differential thermal analysis data have been provided in 1964¹⁶ and 1967¹⁹, showing dehydration completed below 520 °C.

The gradual loss of water is illustrated in figure 5 for slavíkites from several localities. This behaviour stresses the aberrant data (3,10 % at 110 °C) in the original description of 1926¹².

The action of water on slavíkite is slow, produces corroded crystals and leaves an iron hydroxide precipitate by hydrolysis.

⁸⁾ Precession photograph kindly taken by Prof. P. Piret, University of Louvain.

⁹⁾ It is hoped that Dr. P. Süsse, Göttingen, who already studied the crystal structure of many natural iron sulfates, will find suitable material among the slavíkite crystals from Argentina put at his disposal.

Table IX. — X-ray powder diffraction data

hkl a = 12,22 Å c = 36,86 Å	Kaymar ¹⁶ (1)		Medzev ¹⁹ (2)		d calculated
	d	I	d	I	
003	11,62 Å	53	11,68 Å	vs	11,63 Å
101	10,04	26	10,12	s	10,15
012	9,02	100	9,04	vs	9,04
110	—	—	6,20	vw	6,10
006	5,82	82	5,84	vs	5,81
113	5,37	47	5,42	s	5,41
202	5,03	21	5,06	mw	5,06
024	4,53	16	4,55	m	4,52
205	4,21	68	4,21	s	4,22
211	3,97	24	3,97	mw	3,97
009	3,88	21	3,89	mw	3,88
214	3,63	26	3,64	mw	3,635
030	3,52	26	3,52	w	3,529
125	3,48	47	3,47	s	3,471
303	3,36	13	3,37	w	3,376
208	—	—	3,34	w	3,364
119	—	—	3,25	w	3,272
217	3,11	18	3,12	w	3,119
223	2,95	45	2,95	s	2,955
0.0.12	2,91	26	2,92	mw	2,906
312	2,89	26	2,89	mw	2,894
134	—	—	2,78	mw	2,781
315	—	—	2,70	ms	2,706
042	—	—	2,606	w	2,616
137	—	—	2,526	w	2,529
229	—	—	2,400	w	2,400
327	—	—	2,184	vw	2,183
146	—	—	2,145	vw	2,146
238	—	—	2,118	vw	2,121
4.0.10	—	—	2,106	vw	2,108

(1) CuK α radiation, (2) mean values of data with powder goniometer, NaCl internal standard, FeK α radiation and with Guinier camera (diam. 114,6 mm), Al internal standard, CuK α radiation.

Synthesis

Makovický and Streško (1967) reported the synthesis of slavíkite by evaporation of appropriate solutions, slightly acidified with nitric acid. The reproductibility of the experiments appeared sensible to operation conditions and were not further studied. The crystals obtained showed the same optical and crystallographic data as the natural substance, but unfortunately no further chemical proof for the composition was given. The present author was rather unsuccessful in synthesizing slavíkite by spontaneous evaporation or by slight heating of stoichiometric prepared solutions, slightly acidified with HNO₃, HCl or H₂SO₄, or not acidified. The only substances identified by X-rays along the numerous runs of experiments were copiapite, hexahydrate, hydroniumjarosite and some doubtful slavíkite. Although a supergene mineral, slavíkite does not seem to be easily synthesized.

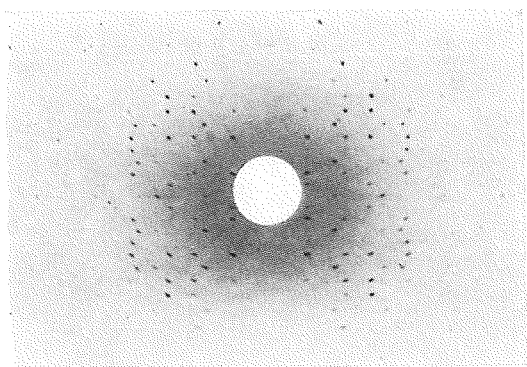


Fig. 1.

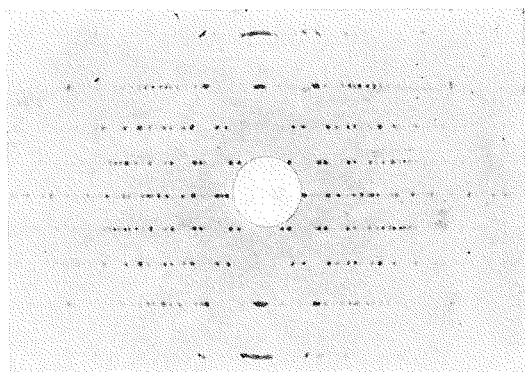


Fig. 2.

Fig. 3.

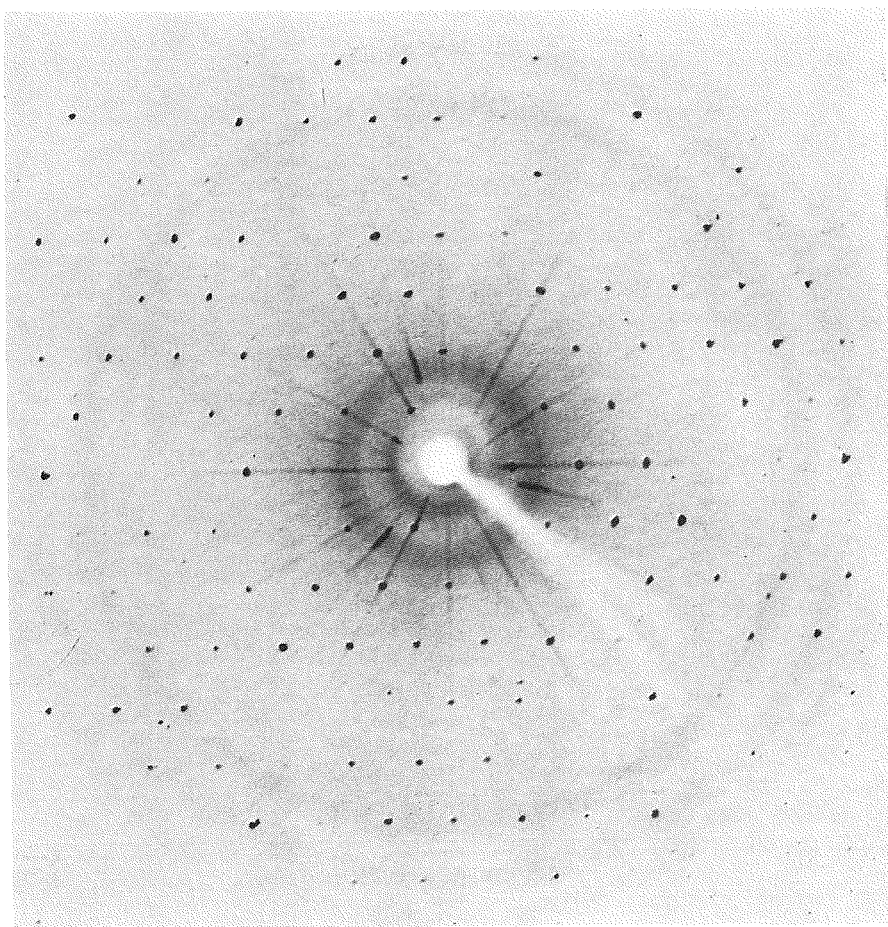


Fig. 4.

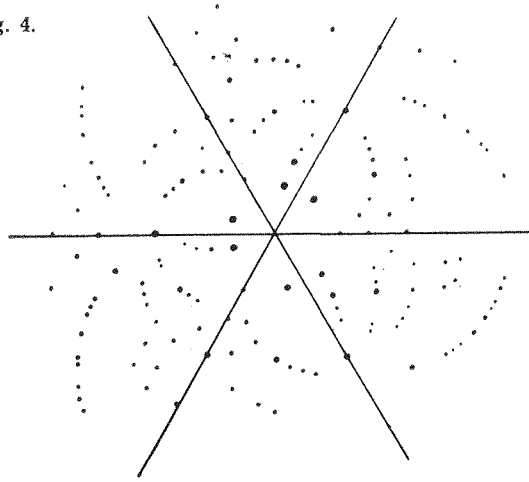
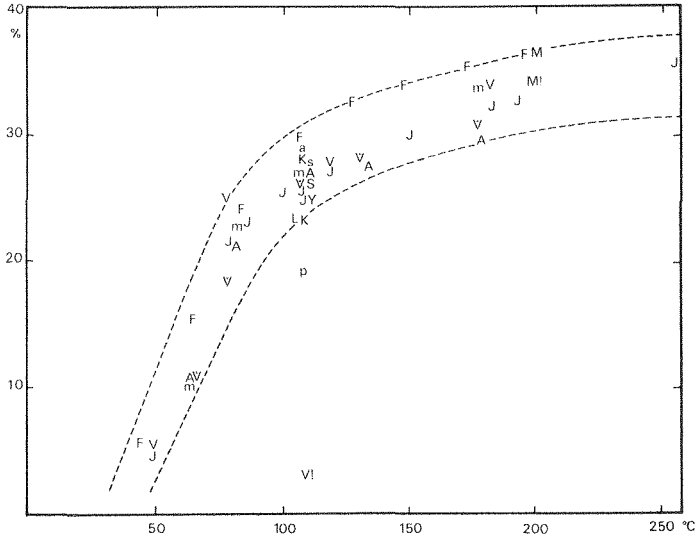


Fig. 5.



Figures 1 and 2. — X-ray rotation photographs (natural size, camera diameter 5,7 cm, $\text{CoK}\alpha$ radiation). 1. Rotationsaxis **c**. 2. Rotationsaxis **a**.

Figure 3. — Precession photograph (natural size). Superposition of **hko**, **hk1** and **hk2** levels. $\text{CuK}\alpha$ radiation; distance crystal-film 6 cm. (Photograph due to P. Piret).

Figure 4. — Laue pattern [drawing after photograph natural size] obtained in cylindrical camera (diam. 5,7 cm) with W radiation.

Figure 5. — Dehydration diagram of slavikite. (A: Argentina, F: Franquénies, J: Jarov, K: Kaymar, L: Luka, M and Ml: Medzev, S: Stavelot, VI: Valachov 1926, V: Valachov 1940, V with point: Valachov 1949, Y: Yukon 1970, a: Aigen 1972, s: St Peter, Rennweg 1972, p: Pöham 1972, contaminating jarosite observed).

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Note added in proof: G. Scaini (Natura, 62, 1971) reported slavikite from Saint Marcel, Aosta, Italy, and P. Süsse (N. Jb. Miner. Mh, 1973) observed, on Argentine slavikite, density 1,90, space group $R\bar{3}$, $a = 12,20 \pm 0,01$, $c = 35,13 \pm 0,05$ Å, and found, according to structural analysis, the new formula $\text{NaMg}_2\text{Fe}_5(\text{SO}_4)_7(\text{OH})_6 \cdot 33\text{H}_2\text{O}$.