

Struvite-(K), $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$, the potassium equivalent of struvite – a new mineral

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Abstract: The new mineral struvite-(K) is the natural potassium equivalent to struvite $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$. It was discovered independently at two different localities: (1) at the famous sulphosalt locality Lengenbach in Binntal, Switzerland, where it occurs in a dolomitic rock of Triassic age, in close association with various Pb-As-sulphosalts (mainly rathite). It forms extremely fine needles reaching up to a maximum length of about 0.3 mm. The needles are elongated along the crystallographic **a**-axis, they are completely colourless and transparent. The acicular crystals are generally well developed, and several forms such as {0 0 1}, {0 1 0}, {1 0 1}, {0 1 2}, {1 1 0}, {1 1 1}, {0 1 2} could be identified by optical goniometry. Single-crystal study showed the mineral to be orthorhombic, with space group $Pmn2_1$ (from analogy to struvite), $a = 6.903(3)$, $b = 6.174(2)$, $c = 11.146(3)$ Å, $V = 475.0(2)$ Å³ (refined from powder data). Qualitative chemical data derived from EDS analyses on an SEM gave major K, Mg, P, and traces of Sb, Fe, and Cu. Attempts to prepare samples for quantitative EMP analyses failed, therefore a structure determination (using a Bruker AXS three-circle diffractometer) and a refinement of K *versus* NH_4 were carried out which prove that the mineral represents the pure K end-member. Optically, the mineral is biaxial positive, with $2V_Z = \text{large}$, $\alpha = 1.490(2)$, $\beta = 1.493(2)$ (for 589 nm), γ could not be measured, the optic axes plane (OAP) is perpendicular to the needle axis, therefore β parallels the crystallographic **a**-axis. At the Lengenbach occurrence, struvite-(K) is a product of the latest stage of hydrothermal activity to supergene alteration.

A second occurrence (2) is Rossblei, Schladminger Tauern, Styria, Austria, an abandoned galena mine. The host rock of the Pb-mineralisation is a sericite-schist belonging to the polymetamorphic basis of the Schladminger Tauern. The mineral occurs as pseudomorphosed aggregates of dirty white colour reaching up to several millimetres. The aggregates represent close intergrowths of fine-grained struvite-(K) and newberyite $\text{Mg}(\text{PO}_3\text{OH}) \cdot 7\text{H}_2\text{O}$. Cell parameters refined from the powder data, after deduction of newberyite lines, are $a = 6.878(1)$, $b = 6.161(1)$, $c = 11.100(1)$ Å, $V = 470.41(9)$ Å³. No additional physical, optical, morphological data could be derived due to the close intergrowth of the two minerals. Struvite-(K) from Schladming obviously represents a recent alteration product.

Key-words: struvite-(K), new mineral species, potassium magnesium phosphate, crystal structure, Lengenbach, Switzerland, Schladming, Austria.

Introduction

The locality Lengenbach in the Valley of Binn, Ct.Valais, Switzerland is well known for its wealth of rare and uncommon sulphosalt minerals since more than 200 years. At least 26 members of this fascinating mineral family have been discovered for the first time in Lengenbach and were described as new mineral species, starting with the mineral

dufrénoysite in 1845 (Damour, 1845) up to the latest new sulphosalt member gabrielite (Graeser *et al.*, 2006). The interest in sulphosalt minerals, mainly of scientific character, has led to the surprising fact that, during the summer months, the locality had been mined for minerals exclusively for scientific research by several syndicates for more than 150 years. Since 1993 it is a new syndicate which, under the name "Forschungsgemeinschaft Lengenbach

(FGL)”, is occupied with the exploitation of minerals from the dolomitic rocks. It is obvious that the main interest concerns the numerous sulphides and sulphosalts, nevertheless there may occur also very uncommon minerals of non-sulphidic character: in 1999, a member of the FGL (Markus Ecker), when looking through material from an earlier (1998) exploitation, discovered a sample with extremely small needle-like crystals of colourless to whitish appearance. A qualitative EDS analysis carried out on an SEM yielded a chemical composition of mainly K, Mg, and P for the unknown crystals. The subsequent study of the material proved that it is the potassium analogue of struvite, hence representing a new mineral species. Description and name (proposed by the chairman of the CNMMN-IMA) have been submitted to the Commission on New Minerals and Mineral names, I.M.A. (proposal number 2003-048) and were approved by the Commission. Type material is deposited (under number S176) in the Natural History Museum of Basel.

Struvite-(K) has also been recorded at the abandoned lead-mine Rossblei near Schladming, Styria, Austria, on samples collected in the 1960-ies and preserved at the Landesmuseum Joanneum in Graz under the name “phosphorrösslerite”. A recent study showed that this determination was erroneous, and that the material consisted of a close intergrowth of the two minerals struvite-(K) and newberyite, instead (Postl *et al.*, 2000).

Occurrence

(1) *Lengenbach*: at the moment only one sample containing struvite-(K) is known from this locality. The sample in question is of “thumb-nail” dimension (approx. $2 \times 1 \times 1$ cm) of white dolostone with small cavities which contain mainly dolomite crystals, some quartz, frequent realgar, and various As-sulphosalts like jordanite, dufrénoysite, rathite, tennantite. Struvite-(K) has grown on sulphosalt minerals (rathite), and on dolomite crystals as well. The phosphorous necessary for the formation of struvite-(K) may be derived from several phosphate minerals like goyazite $\text{SrAl}_3[(\text{OH})_6\text{PO}_3\text{OH}|\text{PO}_4]$, gorceixite $\text{BaAl}_3[(\text{OH})_6\text{PO}_3\text{OH}|\text{PO}_4]$, and rarely apatite, that have formed in the dolomitic host-rock under late hydrothermal conditions. It is not clear whether struvite-(K) has to be treated as a product of hydrothermal activity too, or rather of supergene alteration.

(2) *Rossblei*, Schladming: Struvite-(K) occurs as fine-grained intergrowth with newberyite in pseudomorphosed flat tabular crystals (Fig. 3) of an unknown precursor. The crystals of struvite-(K) are xenomorphic and up to 20 μm large, whereas newberyite is hypidiomorphic up to 100 μm . Both form flat tabular dirty-white aggregates. Struvite-(K) was found in small water puddles in the adit of the abundant galena-mine “Rossblei” south of Schladming. The host rock is a sericite schist which is a member of the polymetamorphic crystalline of the Schladminger Tauern. The phosphates are an alteration product of animal bones and circulating fluids (Laskovic & Weninger, 1967).

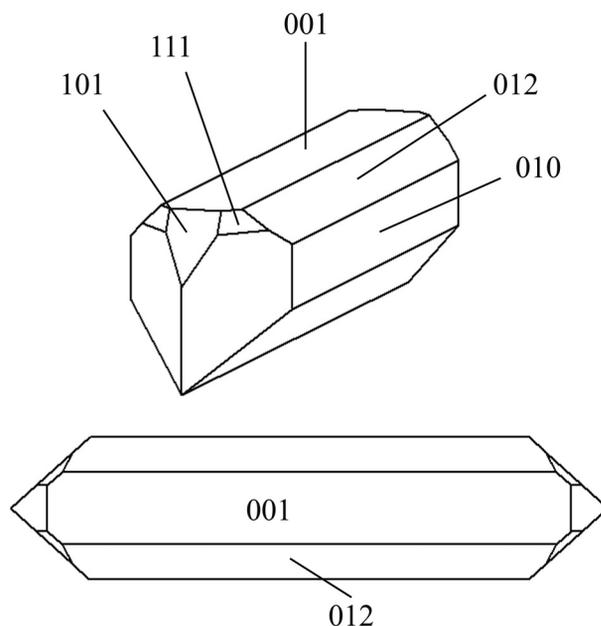


Fig. 1. Morphology of struvite-(K), Lengenbach, Switzerland, based on goniometrical measurement (SHAPE drawing).

Habit and physical properties

(1) *Lengenbach*: the thumb-nail sample contains a large number of acicular crystals which rarely exceed 0.5–0.7 mm in length, and 20–30 μm across. They are completely transparent, with a whitish lustre (because of total reflection effects). The tip of the crystals is always clearly wedge shaped (due to the development of the form $\{101\}$, as proven by optical goniometry), in rare cases visible on both ends. One of the crystals was measured on an optical goniometer, after having adjusted it by X-ray diffraction on a Weissenberg camera. The crystals are elongated along the crystallographic **a**-axis, the habit is determined by the following forms: $\{001\}$, $\{010\}$, $\{101\}$, $\{012\}$, $\{110\}$, $\{111\}$, $\{01\bar{2}\}$ (Fig. 1). Under the polarizing microscope, struvite-(K) is colourless, has low refraction indices and small birefringence. The optic normal lying parallel to the needle axis, the mineral shows (\pm) elongation, depending on the position of the needles. Dispersion of the optic axes is visible (with $r < v$). Due to the small crystal size the determination of physical properties must remain incomplete (Table 1).

(2) *Rossblei*: the mineral occurs here as pseudomorphosed aggregates of dirty white colour reaching up to several millimetres. The aggregates represent close intergrowths of fine-grained struvite-(K) and newberyite, $\text{Mg}(\text{PO}_3\text{OH}) \cdot 7\text{H}_2\text{O}$. Due to the close intergrowth of the two minerals no additional physical, optical, morphological data could be derived.

X-ray diffraction

(1) *Lengenbach*: Several of the needle-shaped crystals were studied by X-ray diffraction with a Gandolfi camera

Table 1. Morphology, physical and optical properties of struvite-(K) (Lengenbach).

Habit	acicular, elongated along the crystallographic a -axis
Forms	{0 0 1}, {0 1 0}, {1 0 1}, {0 1 2}, {1 1 0}, {1 1 1}, {0 1 $\bar{2}$ }
Twins	frequent, presumably contact twins along (1 0 1)
$a : 1 : c$	1.15 : 1 : 1.87 (from optical goniometry) 1.118: 1 : 1.805 (from unit-cell parameters)
Colour	colourless transparent
Lustre	vitreous, whitish
Streak	white
Cleavage	not visible, presumably absent
Fracture	conchoidal
Hardness	not determined
Density _{calc}	1.864 g/cm ³
<u>Optical data (589 nm)</u>	
n_α	1.490 (3)
n_β	1.493 (2)
n_γ	not determined
$2V_\gamma$ (+)	large ($> 70^\circ$)
Pleochroism	no pleochroism was detected
Dispersion	weak ($r < v$)
Orientation	β // cryst. a -axis, Optic Axes Plane (OAP) perpendicular to needle axis

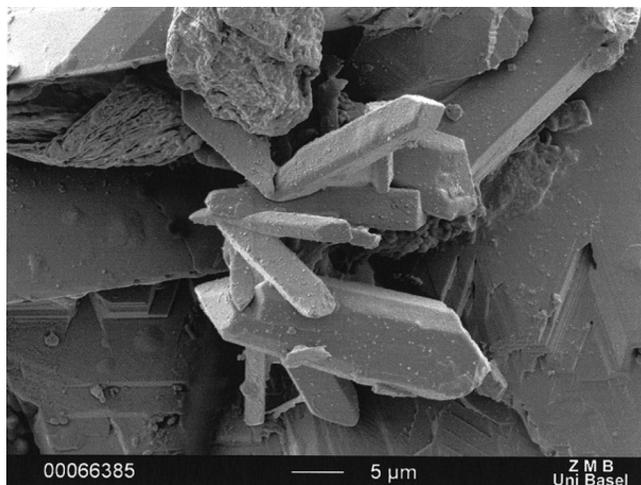


Fig. 2. SEM picture of struvite-(K) from Lengenbach, Switzerland.

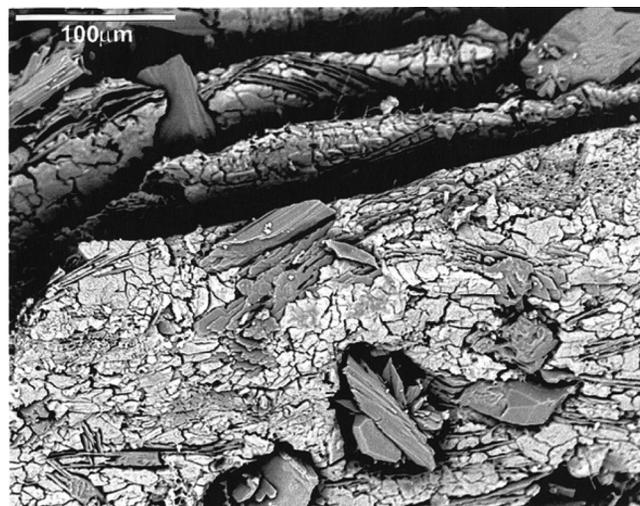


Fig. 3. Struvite-(K) (light-grey) beside newberyite (dark-grey) from Witterschacht, Rossblei, Schladminger Tauern, BSE image.

(114.6 mm, $\text{FeK}\alpha$ radiation). Powder data of struvite-(K) in comparison with the synthetic compound are presented in Table 2. The patterns were always identical and indicated a close relationship to the mineral struvite. Yet, as it was obvious from SEM studies that the mineral contains K instead of NH_4 , the true nature as a K-equivalent of struvite could clearly be predicted. From additional Weissenberg and precession single-crystal diagrams the crystallographic orientation of the needles could be derived, and further proofs for the isotopy of the two minerals were gained.

(2) *Rossblei*: Due to the intimate intergrowth of struvite-(K) with newberyite always both phases appear in the powder-pattern (diffractometer Siemens D5000, $\text{CuK}\alpha$). The data for struvite-(K) are in good agreement with the

pattern of synthetic $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ (ICDD 75-1076) (Table 2).

Chemistry and structure refinement

(1) *Lengenbach*: the original material found by M. Ecker among Lengenbach samples was primarily tested by qualitative EDS analyses on an SEM, yielding K, Mg, and P as major components, with traces of Sb, Fe, and Cu. With the result of the single-crystal study as a presumably new K-Mg-P-mineral with struvite structure, quantitative EMP analyses were indispensable for a further study. Unfortunately, any attempts to produce proper preparations

Table 2. X-ray powder data of struvite-(K).

<i>h k l</i>	1			2			3	
	d_{obs} (Å)	$\dagger d_{calc}$ (Å)	I/I_o	d_{obs} (Å)	d_{calc} (Å)	I/I_o	d (Å)	I/I_o
*1 0 1	5.830	5.869	40	5.849	5.847	13	5.842	11
0 0 2	5.573	5.573	30	5.552	5.550	45	5.543	28
0 1 1	5.400	5.401	10	5.387	5.387	26	5.385	16
1 1 0	4.604	4.602	20				4.587	15
1 1 1	4.255	4.254	100	4.241	4.241	100	4.239	100
0 1 2	4.136	4.137	80	4.125	4.124	75	4.121	48
1 1 2	3.547	3.548	10	3.537	3.537	6	3.534	4
2 0 0				3.439	3.439	25	3.436	16
1 0 3	3.271	3.272	90	3.258	3.259	37	3.255	38
0 2 1				2.969	2.968	19	2.968	12
2 1 1	2.905	2.908	50	2.899	2.899	52	2.897	57
0 0 4	2.787	2.787	40	2.775	2.775	47	2.772	29
0 2 2	2.699	2.700	50	2.694	2.693	64	2.692	39
2 1 2	2.650	2.650	70	2.641	2.641	33	2.639	41
1 2 2	2.513	2.515	30	2.507	2.508	17	2.507	11
1 1 4	2.387	2.384	30				2.372	7
2 1 3	2.341	2.340	40				2.330	13
2 2 1	2.256	2.253	10				2.246	5
2 1 4	2.045	2.046	10				2.036	5
1 1 5	2.007	2.006	40				1.9964	11
2 2 3	1.9541	1.9561	50	1.9499	1.9500	14	1.9488	17
2 1 5	1.7928	1.7920	40				1.7834	9
2 3 0	1.7691	1.7676	40				1.7626	9

Notes:

1 = Lengenbach, Binntal, Switzerland (Gandolfi camera, 114.6 mm, FeK α , this work)

* not used for refinement

 $\dagger d_{calc}$ for $a = 6.903(3)$, $b = 6.174(2)$, $c = 11.146(3)$ Å I/I_o = intensities visually estimated

2 = Rossblei, Schladminger Tauern, Styria, Austria

(Diffractometer, Siemens D5000, CuK α , this work)3 = synthetic KMgPO $_4$ ·6H $_2$ O (ICDD 75-1076)Table 3. Unit-cell parameters of struvite-(K) (calculated from X-ray powder data), synthetic KMgPO $_4$ ·6H $_2$ O, and struvite.

	1	1a	2	3	4
Sp-Gr.	$Pmn2_1$	$Pmn2_1$	$Pmn2_1$	$Pmn2_1$	$Pmn2_1$
a (Å)	6.892 (2)	6.903(3)	6.878 (1)	6.873	6.95
b (Å)	6.166 (2)	6.174(2)	6.161(1)	6.160	6.14
c (Å)	11.139 (4)	11.146(3)	11.100 (1)	11.087	11.22
V (Å 3)	473.4 (3)	475.0(2)	470.41 (9)	469.40	478.8
Z	2	2	2	2	2

Notes:

1 = Lengenbach, Binntal, Switzerland (from structure determination, this work).

1a = Lengenbach, Binntal, Switzerland (refined from X-ray powder data, this work).

2 = Rossblei, Schladminger Tauern, Styria, Austria (from X-ray powder data, this work).

3 = synthetic KMgPO $_4$ ·6H $_2$ O (ICDD 75-1076).4 = Struvite NH $_4$ MgPO $_4$ ·6H $_2$ O (Strunz & Nickel, 2001).complete structure determination, including a refinement of K versus NH $_4$.

A prismatic, colourless, and transparent crystal of struvite-(K) from Lengenbach (Switzerland), about 0.20 × 0.04 × 0.04 mm in size, was measured on a Bruker AXS three-circle diffractometer (equipped with a CCD 1000 K area detector and a flat graphite monochromator) using Mo K α X-radiation from a fine focus sealed tube. A SMART system of programs was used for crystal-lattice determination and X-ray data collection, and SAINT+ for the data reduction including intensity integration, background and Lorentz-polarization corrections. The program XPREP was used for empirical absorption correction based on pseudo ψ -scans. The structure was solved in the space group $Pmn2_1$ by direct methods (program SHELXS) and refined with the program SHELXL. The refinement converged at $R_1 = 6.35\%$ for 758 reflections with $I > 2$ sigma(I); $R_1 = 7.01\%$ for all 818 reflections; $wR_2 = 12.92\%$; $R_{int} = 4.90\%$; $R_{sigma} = 4.19\%$. The refinement of K versus NH $_4$ yielded the pure K end-member (Fig. 4).

(2) Rossblei: Electron-microprobe analyses were done on a SEM JEOL JSM-6310 with energy- and wavelength dispersive spectrometers. No quantitative data were achieved, due to instability of these phosphates under the micro-beam

for EMP analyses from the completely transparent minute crystals failed. The only solution to this problem was the

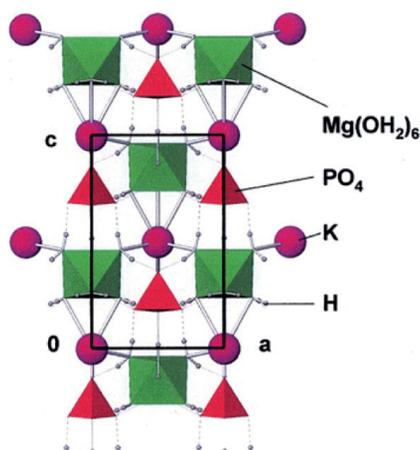


Fig. 4. Crystal structure of struvite-(K), projected along [010], and displaying H \cdots O hydrogen bonds.

and at vacuum condition (fractures as seen in Fig. 3). Only the main elements Mg, K and P were detected.

Discussion

The Lengenbach sample, with a more complete data collection, has to be designated as the holotype sample for the new species struvite-(K), $\text{KMgPO}_4 \cdot \text{H}_2\text{O}$. Moreover, its formation is undoubtedly the result of a natural process. According to the definitions given by Dunn & Mandarino (1987) for type mineral specimens, the Rossblei occurrence represents a cotype for the species.

Struvite-(K) is a member of the schertelite-struvite group and belongs to the Strunz class 8.CH.25 according to Strunz & Nickel (2001).

Acknowledgements: Markus Ecker (member of the Lengenbach syndicate FGL) kindly put all material in his

possession at our disposal for the study. Samples from Rossblei were provided by Prof. J.G. Haditsch (Graz). The help and advice of Ernst A.J. Burke (chairman of the Commission on New Minerals and Mineral Names, I.M.A.) is greatly acknowledged. The comments of the two reviewers, Th. Witzke and I.V. Pekov, helped to improve the quality of the publication.

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Received 4 June 2007

Modified version received 7 January 2008

Accepted 10 March 2008