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Kanonerovite, $MnNa_3P_3O_{10} \cdot 12H_2O$, first triphosphate mineral (Kazennitsa pegmatite, Middle Urals, Russia)

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With 3 figures and 2 tables

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Abstract: Kanonerovite, $MnNa_3P_3O_{10} \cdot 12H_2O$ [a = 14.71(1) Å, b = 9.33(1) Å, c = 15.13(2) Å, $\beta = 89.8(1)^0$, V = 2075(3) Å^3, $P2_1/n$, Z = 4], is the first described triphosphate mineral. It has been found in the Kazennitsa pegmatite vein, the Alabashka pegmatite field, Middle Urals, Russia. Associated minerals are quartz, albite, microcline, muscovite, topaz, beryl, cassiterite, milarite. Kanonerovite occurs as tiny, snow-white radial-platy aggregates on cassiterite, topaz, quartz and microcline. It is transparent with a white streak and vitreous lustre and does not fluoresce under long- or short-wave ultraviolet light. In transmitted light kanonerovite is colourless, transparent, non-pleochroic; biaxial (–), nearly parallel extinction ($\alpha \wedge c \sim 0–7°$); α = 1.453(2), γ = 1.459(2), β and 2V not measured because of the lamellar habit; birefringence is 0.005 – 0.006. Kanonerovite is brittle, Mohs hardness of 2.5 – 3; poor {010} cleavage. D_{meas} 1.91(2) g/cm^3, D_{calc} 1.90 g/cm^3. Strongest reflections in the X-ray powder diffraction pattern [d(Å) (I), (hkl)]: 10.50(75)(101), 7.36(100)(200), 6.95(90)(111,–111), 3.316(60)(411,– 411,–123,321,– 321,313), 3.162(50)(214,– 214), 2.889(60)(420,124,032,421). Electron-microprobe analysis gives: Na_2O 14.80, K_2O 0.05, CaO 0.20, MgO 0.14, MnO 11.20, FeO 0.15, P_2O_5 35.23, H_2O(calc.) 36.46, sum 98.23 wt.%. Occurrence of the triphosphate group (P_3O_{10}) in kanonerovite is shown by IR-data and the crystal structure of the synthetic equivalent compound. The mineral is named for Kanonerov Aleksandr Anatol'evich (b. 1955).

Key words: kanonerovite, new mineral, triphosphate, Alabashka, Urals.

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Introduction

Kanonerovite, $MnNa_3P_3O_{10} \cdot 12H_2O$, is a new mineral approved by the Commission on New Minerals and Mineral Names (CNMMN) of IMA (International Mineralogical Association). The mineral is named for Kanonerov Aleksandr Anatol'evich (b. 1955), mining historian (Nizhnii Tagil Museum of Mining Industry of the Middle Urals), who has been collecting minerals all his life and who first collected samples of kanonerovite in 1995. In fact, the new mineral was firstly noted (Popov et al. 1996) during an investigation of samples from Kanonerov's private collection. Type material is deposited at the Mineralogical Museum, Ilmen Natural Reserve, Miass, Russia.

Kanonerovite is the first described example of a triphosphate mineral and, after the pyrophosphates canaphite $CaNa_2P_2O_7 \cdot 4H_2O$ (Peacor et al. 1985, Rouse et al. 1988) and wooldridgeite $Na_2CaCu^{2+}{}_2(P_2O_7)_2(H_2O)_{10}$ (Hawthorne et al. 1999, Cooper & Hawthorne 1999), is the third occurrence of condensed phosphates as minerals.

Occurrence

Kanonerovite is of hydrothermal origin and occurs in the Kazennitsa pegmatite vein, the Alabashka pegmatite field, Middle Urals, Russia (57° 47′ N and 61° 03′ E). Associated minerals are quartz, albite, microcline, muscovite, topaz, beryl, cassiterite and milarite.

The Kazennitsa pegmatite vein is confined to the central part of the Alabashka pegmatite field, Middle Urals, on the right bank of the Alabashka river, a small tributary of the Neiva river (Fig. 1a). On the whole, 44 pegmatite veins are known for the Alabashka pegmatite field. Mining at the Kazennitsa vein was set up at the end of the XVIII century mainly for beryl and aquamarine. Even if not constantly continued, in 1938 the exploration of the vein reached a depth of 10–14 m. In 1991–1993, a new exploration of the vein proceeded to a depth of 30 m. In spite of its more than 200-year history, the mineralogy of the Kazennitsa vein had never been described in well known publications on the Urals mineralogy, e.g. Vertushkov (1954), till recently (Rozhkov et al. 1991, Popov et al. 1996).

The Kazennitsa vein is about 150 m in length with thickness from 0.5 to 3 m (Fig. 1b). It is a granite pegmatite of muscovite–albite–microcline type and is localised in biotite granite–gneisses and porphyry granites. The vein

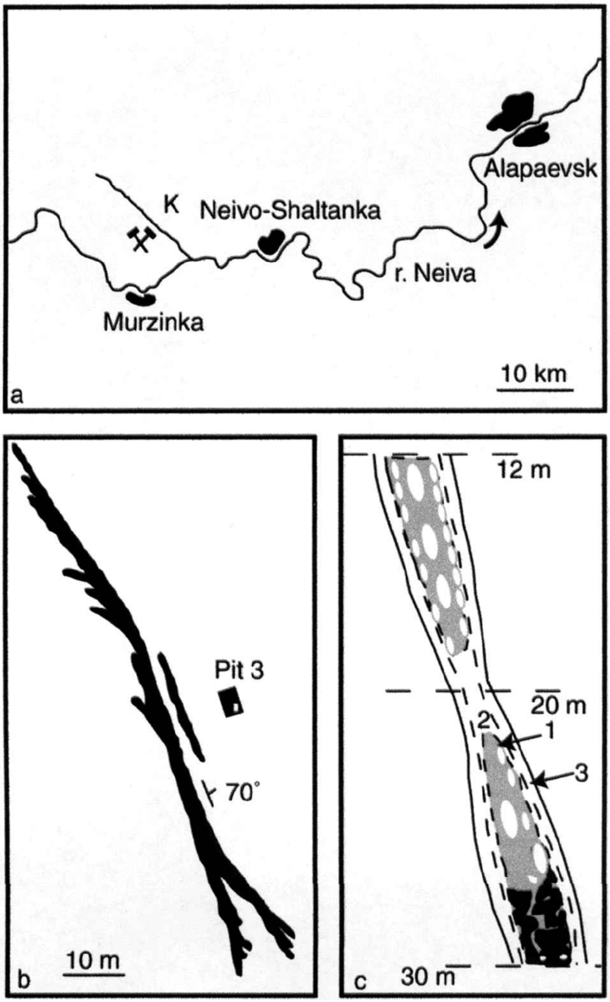

Fig. 1. The Kazennitsa vein (K): geographic position (a); schematic plan at a depth of 20 m (b); cross-section of the southern part (c) showing the pegmatite zones 1, 2 and 3 (see text).

has three main zones (Fig. 1 c): an outer zone 0.3–0.6 m thick contains a two-feldspar pegmatite with potassic feldspar, biotite and oligoclase; an intermediate zone 0.2–0.7 m thick is built by a two-feldspar pegmatite with microline, albite–oligoclase and biotite; a central pegmatoid blocky zone with big crystals of microcline, albite–oligoclase, quartz and muscovite. The central zone of the vein contains more than 200 cavities ranging from few centimetres up to 2–3 meters. In these cavities the following minerals have been reported: muscovite, quartz, elbaite, topaz, milarite, calcite, chabazite, stilbite–stellerite, rutile, fluorite, pyrrhotite, sphalerite, pyrite, and kanonerovite, the only P-bearing mineral.

Appearance and physical properties

Kanonerovite occurs as thin white crust on quartz, topaz, and cassiterite crystals. The crust consists of radial-lamellar cotton-like aggregates (0.1–1.2 mm) composed by apparent individual monoclinic prismatic crystals which are [001] elongated and {100} platy with dimensions of few tenths of mm. Somewhere kanonerovite is covered by secondary fine-flake yellowish-white muscovite and rare crystals of stellerite. Kanonerovite is transparent, colourless with a white streak and vitreous lustre, brittle; it shows Mohs hardness 2.5–3; poor {010} cleavage, no parting, uneven fracture; fluoresce absent under long- or short-wave ultraviolet light. D_{meas} 1.91(2) g/cm^3 was determined by floatation in Clerici liquid, D_{calc} 1.90 g/cm^3. It has been possible to determine the morphology on a unique crystal (Fig. 2) which later went lost: {100}, {001}, {010}, {023}, {423} and {210} forms were observed.

In transmitted light kanonerovite is colourless, transparent, non-pleochroic. It is biaxial negative with nearly parallel extinction ($\alpha \wedge c \sim 0$–$7°$); $\alpha = 1.453(2)$, $\gamma = 1.459(2)$; β and 2V were not measured because of the very thin lamellar habit; birefringence is 0.005–0.006; dispersion not observed.

Chemical data

Chemical analysis of kanonerovite was done by EMPA (JXA-733 electron microprobe; Table 1). Eighteen points, six on each of three different grains, were analysed. Standards were as follows: scapolite (Ca, Na, Mg), osumilite (K), ilmenite (Mn, Fe), apatite (P). Kanonerovite is not soluble in water; after dissolution in HNO_3 it reacts with $(NH_4)_2MoO_4$ giving evidence of phosphorus. H_2O has been detected by infrared spectroscopy (see ranges 3300–3600 cm^{-1} and 1590–1700 cm^{-1} in Fig. 3); the scarcity of material did not allow a direct measurement of the water content and its amount was taken as 36.46 wt.% on comparison with the synthetic analogue (RAKOTOMAHANINA et al. 1972, LIGHTFOOT & CHEETHAM 1987). On the basis of 22

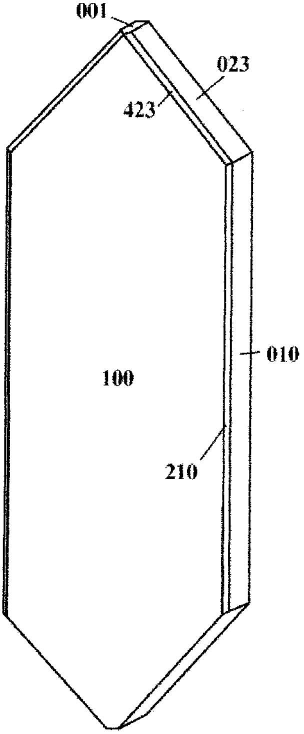

Fig. 2. Morphology of kanonerovite.

oxygen atoms per formula units (apfu) the following empirical chemical formula for kanonerovite was obtained: $(Mn_{0.95}Mg_{0.02}Fe_{0.01})_{\Sigma\ 0.98}(Na_{2.86}Ca_{0.02}K_{0.01})_{\Sigma\ 2.89}P_{2.98}O_{9.87} \cdot 12.13H_2O$. The ideal formula $MnNa_3P_3O_{10} \cdot 12H_2O$ requires Na_2O 15.68, MnO 11.96, P_2O_5 35.90 and H_2O 36.46. The low analysed content of Na can be due to the volatility of this element but also to the instability of the sample under the electron beam because of an easy loosing of water.

Infrared data

The infrared (IR) spectrum (Fig. 3) for kanonerovite was obtained by a Perkin Elmer Fourier spectrometer on a KBr pellet containing about 0.001 mg of kanonerovite. The positions (cm^{-1}) of the main absorption bands are as

Table 1. Chemical composition of kanonerovite.

Oxide	Wt.%	Range	Atom	Apfu
Na_2O	14.80	11.49 – 16.33	Na	2.86
K_2O	0.05	0.04 – 0.08	K	0.01
CaO	0.20	0.02 – 0.34	Ca	0.02
MgO	0.14	0.08 – 0.23	Mg	0.02
MnO	11.20	10.09 – 11.60	Mn^{2+}	0.95
FeO	0.15	0.00 – 0.32	Fe^{2+}	0.01
P_2O_5	35.23	33.23 – 36.37	P	2.98
$H_2O_{calc.}$*	36.46		H	24.26
Total	98.23	96.72 – 99.74		

* H_2O calculated by comparison with the synthetic phosphate $MnNa_3P_3O_{10}\cdot 12H_2O$ (Rakotomahanina et al. 1972, Lightfoot & Cheetham 1987).

follows: 447.9, 519.7, 558.5, 668.0, 875.6, 908.5, 992.3, 1034.2, 1117.9, 1153.8, 1327.3, 1590.6, 1650.4, 3311.1, 3394.9, 3586.3.

The band corresponding to the P–O asymmetrical stretching vibrations has its maximum at 1117.9 cm^{-1} and indicates condensation of P-tetrahedra (Mel'nikova et al. 1985); for orthophosphates this maximum is usually localised in the 1020–1080 cm^{-1} range. The large splitting of the band corresponding to the bending O–P–O-vibrations (558.5 – 668.0 cm^{-1}) is also characteristic for condensed (but not ortho-) phosphates. Furthermore, the 908 cm^{-1} band of symmetric stretching vibrations of PO_4-tetrahedra is characteristic for the condensed phosphates, while in orthophosphates this band is shifted towards higher frequencies (~940 – 960 cm^{-1}).

X-ray crystallography

No single crystals of kanonerovite suitable for X-ray diffraction were available from the described cotton-like aggregates of very brittle material; as mentioned above, a presumably unique crystal used for morphology determination went lost. An X-ray diffraction powder pattern (Table 2) has been obtained by a 114.6 mm Debye-Scherrer camera (FeKα, λ 1.9374 Å). Indexing was done by taking into account the diffraction intensities calculated (SHELXL, Sheldrick 1981) by using the structural data of Lightfoot &

Table 2. X-ray diffraction powder pattern of kanonerovite [*a* 14.71(1), *b* 9.33(1), *c* 15.13(2)Å, β 89.8(1)°] (I) and of synthetic phosphate $MnNa_3P_3O_{10} \cdot 12H_2O$ (JCPDS 27-0753) (II); calculated data (III) are from the structure published by Lightfoot & Cheetham (1987) [*a* 14.763(2), *b* 9.325(4), *c* 15.140(4)Å, β 89.87(2)°].

I			II		III		
$I_{meas.}$	$d_{meas.}$	$d_{calc.}$	$I_{meas.}$	$D_{meas.}$	$I_{calc.}$	$d_{calc.}$	h k l
75	10.50*	10.56	100	10.6	78	10.58	1 0 1
		10.53			61	10.56	−1 0 1
35	7.88*	7.94	5	7.93	29	7.94	0 1 1
100	7.36	7.35	45	7.37	79	7.38	2 0 0
90	6.95*	6.99	35	6.98	100	6.99	1 1 1
		6.98					−1 1 1
20	5.87	5.88	16	5.87	46	5.88	0 1 2
			5	5.46	13	5.46	1 1 2
15	5.40	5.39	5	5.39	11	5.40	−2 1 1
35	4.80*	4.78	20	4.77	10	4.78	1 0 3
		4.77			17	4.77	−1 0 3
10	4.65	4.66	7	4.67	13	4.66	0 2 0
			6	4.59	9	4.60	2 1 2
					9	4.59	−2 1 2
10	4.44	4.44	11	4.43	27	4.45	1 2 0
		4.44			9	4.44	0 1 3
			4	4.17	9	4.18	−3 1 1
25	3.97	3.97	11	3.97	41	3.97	0 2 2
			3	3.81	6	3.83	−1 2 2
					5	3.82	2 2 1
20	3.76	3.77	10	3.77	16	3.78	3 1 2
					6	3.77	−3 1 2
45	3.50	3.52	50	3.52	13	3.53	−3 0 3
		3.51			29	3.52	−3 0 3
		3.50			11	3.50	2 2 2
20	3.42	3.42			20	3.43	0 2 3
		3.41			11	3.42	1 1 4
60	3.316	3.338	25	3.34	11	3.348	4 1 1
		3.334			47	3.345	−4 1 1
		3.333			20	3.335	−1 2 3
		3.299	20	3.30	17	3.304	3 2 1
		3.296			10	3.302	−3 2 1
		3.294			12	3.299	3 1 3

Table 2. Continued.

I			II		III		
$I_{meas.}$	$d_{meas.}$	$d_{calc.}$	$I_{meas.}$	$D_{meas.}$	$I_{calc.}$	$d_{calc.}$	h k l
50	3.162	3.168	15	3.17	20	3.170	2 1 4
		3.161			14	3.165	−2 1 4
10	3.124	3.120	11	3.12	13	3.128	4 1 2
		3.114			13	3.123	−4 1 2
60	2.889	2.887			24	2.894	4 2 0
		2.882			7	2.883	1 2 4
		2.875			14	2.875	0 3 2
					18	2.843	4 2 1
20	2.679	2.695			10	2.702	−4 2 2
		2.683			10	2.685	2 1 5
		2,679			12	2.681	−2 1 5
15	2.581	2.586			17	2.589	−3 3 1
10	2.532	2.541			8	2.545	4 1 4
		2.534			6	2.540	−4 1 4
		2.522			3	2.525	3 2 4
					5	2.523	0 0 6
15	2.479	2.479			12	2.483	−3 1 5
					4	2.461	6 0 0
48	2.391	2.398			5	2.400	−2 2 5
		2.388			16	2.389	2 0 6
		2.383			11	2.386	−2 0 6
10	2.150	2.149			5	2.152	4 3 3
		2.146			7	2.150	−4 3 3
20	1.845	1.838			13	1.845	8 0 0
10	1.736	1.732			5	1.733	3 5 1
		1.730					6 1 6
10	1.647	1.647			5	1.650	6 2 6
		1.647			2	1.648	−3 5 3
		1.643			3	1.646	−6 2 6
10	1.515	1.514			3	1.514	−1 6 2
		1.514			3	1.514	0. 0. 10
		1.513			2	1.513	2 6 1

* Reflections not included in the refinement of cell parameters

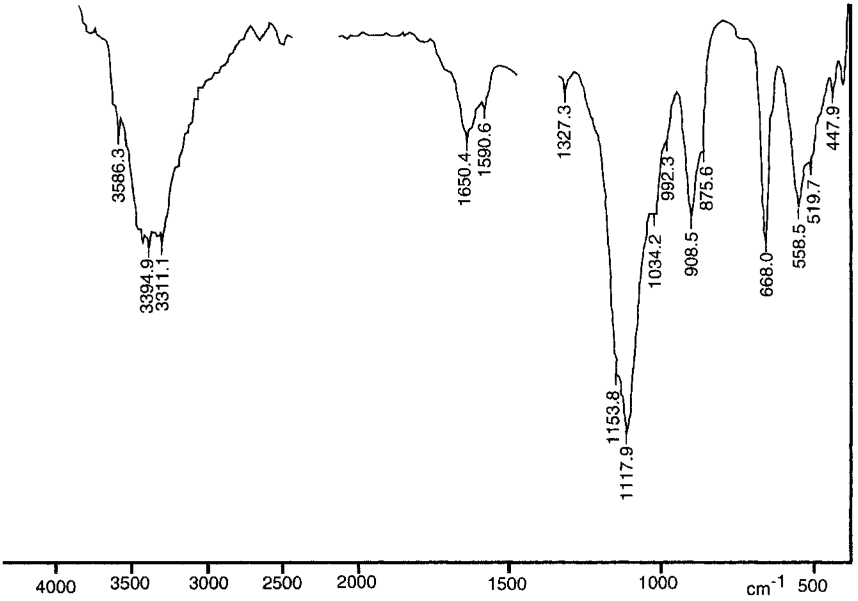

Fig. 3. IR-spectrum of kanonerovite; ordinate and abscissa show transmittance and wavenumbers (cm^{-1}) respectively.

Cheetham (1987). The results presented in Table 2 clearly show that kanonerovite is the natural equivalent of synthetic $MnNa_3P_3O_{10} \cdot 12H_2O$. The refined cell parameters are a 14.71(1) Å, b 9.33(1) Å, c 15.13(2) Å, β 89.8(1)^0, V 2075(3) Å^3; $a : b : c = 1.5766 : 1 : 1.6217$ to be compared with $1.571 : 1 : 1.620$ obtained from morphological data; space group $P2_1/n$, Z 4. These values well agree with those published by Rakotomahanina et al. (1972) (a and c interchanged).

Conclusions

Availability of structural data published for synthetic $MnNa_3P_3O_{10} \cdot 12H_2O$ contributed to identify the first natural triphosphate approved by the CNMMN with the name kanonerovite. The presence of condensed phosphate anions in kanonerovite is proved also by the IR spectrum. Rakotomahanina et al. (1972) obtained several triphospates $M^{2+}Na_3P_3O_{10} \cdot 12H_2O$

(M = Ni, Co, Mn, Mg, Zn, Cd), at room temperature, by addition of a salt of the cation M^{2+} to a solution of sodium triphosphate. This could indicate that kanonerovite formed in the Kazennitsa vein under favourable chemical conditions without particular pressure and temperature requirements.

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