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MITRYAEVAITE, $Al_{10}[(PO_4)_{8.7}(SO_3OH)_{1.3}]_{\Sigma 10}AlF_3 \cdot 30H_2O$, A NEW MINERAL SPECIES FROM A CAMBRIAN CARBONACEOUS CHERT FORMATION, KARATAU RANGE AND ZHABAGLY MOUNTAINS, SOUTHERN KAZAKHSTAN

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ABSTRACT

Mitryaevaite, ideally $Al_{10}[(PO_4)_{8.7}(SO_3OH)_{1.3}]_{\Sigma 10}AlF_3 \cdot 30H_2O$, is a new mineral species discovered in northwestern Karatau Range and Zhabagly Mountains, in the southern part of Kazakhstan. It triclinic, $P1$ or $P\bar{1}$, with unit-cell parameters refined from powder data: *a* 6.92(1), *b* 10.09(1), *c* 22.46(6) Å, α 92.42(4)°, β 96.43(7)°, γ 104.3(2)°, *V* 1507(2) Å^3, *Z* = 1. It occurs as white powder-like masses of crystals 0.01 to 0.04 mm in length. The streak is white, and the microcrystals are prismatic and transparent, and have a dull luster. The (001) cleavage is perfect, and the (010) and (100) cleavages are good. D_m 2.02, D_x 2.033 g/cm^3. The indices of refraction γ and α are 1.515(1) and 1.504(1), respectively, $\gamma \wedge b = 14°$, with positive elongation. Mitryaevaite dissolves slowly in cold acids. The chemical analysis gave CaO 0.90, Al_2O_3 30.00, Fe_2O_3 0.30, P_2O_5 32.40, SO_3 5.50, H_2O^- 1.90, H_2O^+ 27.80, F 3.00, –O = F 1.27, total 100.53 wt.%. The infrared-absorption spectrum includes bands at 500, 560, 615, 650, 1020, 1040, ~1100, 1150, 1630, 1660, 3400 and 3575 cm^{-1}. The thermal curve of mitryaevaite shows two dehydration maxima, at 100 and 165°C. The strongest nine reflections in the X-ray powder pattern [*d* in Å(*I*)(*hkl*)] are: 9.75(10)(010), 9.24(2)$(01\bar{1})$, 6.35(3)$(\bar{1}10)$, 3.763(1)$(02\bar{4})$, 3.333(2)(200), 3.222(2)(201), 3.131(1)(115), 2.923(2)(210), and 2.761(1)$(02\bar{7})$. Mitryaevaite occurs in the weathered zone of vanadium-bearing black shale, in carbonaceous concretions containing clay and fluorapatite. Minyullite, crandallite, gorceixite, wavellite, variscite, evansite, aluminite, meta-aluminite, kaolinite, gypsum and hewettite are the associated minerals. The name honors Dr. Nonna Mikhailovna Mitryaeva for her contributions to mineralogy in Kazakhstan.

Keywords: mitryaevaite, new mineral species, hydrated Al fluorosulfate–phosphate, vanadium-bearing black shales, northwestern Karatau Range, southern Kazakhstan.

SOMMAIRE

Nous décrivons la mitryaévaïte, idéalement $Al_{10}[(PO_4)_{8.7}(SO_3OH)_{1.3}]_{\Sigma 10}AlF_3 \cdot 30H_2O$, nouvelle espèce minérale découverte dans le secteur nord-ouest de la chaîne de Karatau, dans le sud du Kazakhstan. Il s'agit d'un minéral triclinique, $P1$ ou $P\bar{1}$, dont les paramètres réticulaires ont été affinés à partir du spectre de poudre: *a* 6.92(1), *b* 10.09(1), *c* 22.46(6) Å, α 92.42(4), β 96.43(7), γ 104.3(2)°, *V* 1507(2) Å^3, *Z* = 1. Elle se présente en masses pulvérulentes blanches de cristaux de 0.01 à 0.04 mm en longueur, ayant un éclat terne. La rayure est blanche, et les microcristaux sont prismatiques et transparents. Le clivage (001) est parfait, et les clivages (010) et (100) sont bons. La densité mesurée est 2.02, et la densité calculée, 2.033. Les indices of refraction γ et α sont 1.515(1) et 1.504(1), respectivement, $\gamma \wedge b = 14°$, avec allongement positif. La mitryaévaïte se dissout lentement dans les acides à froid. Une analyse chimique a donné CaO 0.90, Al_2O_3 30.00, Fe_2O_3 0.30, P_2O_5 32.40, SO_3 5.50, H_2O^- 1.90, H_2O^+ 27.80, F 3.00, –O = F 1.27, pour un total de 100.53% par poids. Le spectre d'absorption infra-rouge montre des bandes à 500, 560, 615, 650, 1020, 1040, ~1100, 1150, 1630, 1660, 3400 et 3575 cm^{-1}. La courbe thermique montre deux

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maxima de déshydratation, à 100 et à 165°C. Les neuf raies les plus intenses du spectre de diffraction X [*d* en Å(*I*)(*hkl*)] sont: 9.75(10)($01\underline{0}$), 9.24(2)($01\bar{1}$), 6.35(3)($\bar{1}10$), 3.763(1)($02\bar{4}$), 3.333(2)(200), 3.222(2)(201), 3.131(1)(115), 2.923(2)(210), et 2.761(1)($02\bar{7}$). On trouve la mitryaévaïte dans la zone météorisée de shales carbonacés vanadifères, dans des concrétions carbonacées contenant des argiles et fluorapatite. Lui sont associés minyullite, crandallite, gorceixite, wavellite, variscite, evansite, aluminite, méta-aluminite, kaolinite, gypse et hewettite. Le nom signale les contributions à la minéralogie au Kazakhstan de Nonna Mikhailovna Mitryaeva.

(Traduit par la Rédaction)

Mots-clés: mitryaévaïte, nouvelle espèce minérale, fluorosulfate–phosphate hydraté de Al, shales carbonacées vanadifères, secteur nord-ouest de la chaîne de Karatau, Kazakhstan du sud.

INTRODUCTION

Mitryaevaite, a new hydrated Al fluorosulfate–phosphate mineral, has been found in outcrops of black shales of the Cambrian vanadium-bearing Kurumsak Formation of the Ulytau – Karatau – Naryn Belt, which runs from its northwestern boundary in the Karatau Range, Taldyk ore field to the northern spurs of Tien-Shan, in the Zhabagly Mountains, in southern Kazakhstan. The geological setting has been discussed in previous publications (Ankinovich 1955, 1961). The Kurumsak Formation consists of alternating intercalations of pelitic, carbonaceous, clayey and siliceous vanadium-bearing shales and phthanites (siliceous shale), with rare lenses of dolomite, dolomitic limestone and carbonaceous to cherty mudstone.

The shales, where unweathered, contain vanadium-bearing mica, iron sulfides (rarely vanadium, zinc and copper sulfides), dispersed apatite, concretions of collophane and phosphatic nodules. All rocks, with the exception of phthanites in the zone of weathering, are intensely altered, with the formation of a wide range of secondary minerals; mitryaevaite is one of these. We have named the mineral in honor of the distinguished mineralogist Dr. Nonna Mikhailovna Mitryaeva (b. 1920), for her contributions to the mineralogy of Kazakhstan. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA. The type specimen is deposited in the Geological Museum of the Satpaev Institute of Geological Sciences MS–AS RK, Almaty, Kazakhstan, under catalog number GM IGS 24/1270.

OCCURRENCE AND ASSOCIATED MINERALS

Mitryaevaite is developed in carbonaceous, vanadium-bearing shale subjected to incomplete oxidation during weathering. It forms either as a very fine powdery coating on walls of fractures in the rocks or as fine subparallel and complex dendritic veins. Rarely, the mineral is observed in nodule form 0.3 to 0.4 mm across. Occasionally there are sharply defined globular nodules 0.5 to 0.8 cm across that possess a bulbous surface; these are found in the loose products of disintegrated shale. Mineral aggregates are reminiscent of powdery gypsum. Associated minerals are minyullite, crandallite, gorceixite, wavellite, variscite, evansite, aluminite, meta-aluminite, kaolinite, fibrous gypsum and hewettite.

PHYSICAL AND OPTICAL PROPERTIES

Mitryaevaite is white to colorless in dense aggregates. The streak is white, and the microcrystals (0.01 – 0.04 mm in diameter) are prismatic and transparent. The luster is dull and vitreous in concretions. The (001) cleavage is perfect, and (010), (100) are good. Because the mineral is a powder, the hardness is indeterminate. The indices of refraction are γ 1.515(1), α 1.504(1), positive elongation, $\gamma \wedge b = 14°$. The density, measured in a study of an aggregate of the mineral in alcohol, is 2.02 g/cm³, and the calculated density is 2.033 g/cm³. Using the observed density of 2.02, the Gladstone–Dale compatibility index, $1 - (K_P/K_C)$, is –0.035, which indicates excellent compatibility. Mitryaevaite slowly dissolves in cold acids; when heated in a closed tube, it gives off copious amounts of H_2O with an acidic reaction.

CHEMICAL COMPOSITION

The chemical composition of mitryaevaite has been determined by both wet-chemical and electron-microprobe analyses. Results are presented in Table 1. The wet chemistry was carried out on 0.733 grams of pure material. The empirical formula is $Al_{10.08}(PO_4)_{8.71}(SO_3OH)_{1.29}Al(F_{2.97}OH_{0.03})_{\Sigma 3}{\bullet}29.63H_2O$, derived from wet-chemical analysis. The idealized formula is $Al_{10}[(PO_4)_{8.7}(SO_3OH)_{1.3}]_{\Sigma 10}AlF_3{\bullet}30H_2O$ for $Z = 1$. Calculation of the results of the chemical analyses leads to a nonintegral ratio of $(PO_4)^{3-}$ to $(SO_3OH)^{3-}$. Research on minerals of the crandallite group and other sulfate–phosphates of aluminum indicates that $(PO_4)^{3-}$ may be replaced according to the scheme: $(PO_4)^{3-} \rightarrow (PO_3OH)^{2-}, (SO_4)^{2-}, (SO_3OH)^{3-}$ (Gevorkyan *et al.* 1976, Kashkai 1969, Somina & Bulakh 1966). Accordingly, the chemical formula of mitryaevaite could also be written as $Al_{10}\,[(PO_4)_{10-x}(SO_3OH)_x]_{\Sigma 10}Al\,F_3{\bullet}30H_2O$. The characteristic feature of mitryaevaite and other sulfate–phosphates of aluminum is the abundance of H_2O in the structure; contents of H_2O may vary from 22.94 (peisleyite: Pilkington *et al.* 1982) to 40.15–49.5 wt.%

TABLE 1. CHEMICAL COMPOSITION OF MITRYAEVAITE

	Results of wet-chemical analysis	Average result of four electron-microprobe analyses*	
MgO wt.%	trace		
CaO	0.90	0.74	(0.67 – 0.80)
Al_2O_3	30.00	29.47	(28.93 – 29.88)
Fe_2O_3	0.30	2.40**	(0.15 – 4.75)
P_2O_5	32.40	32.50	(32.18 – 33.02)
SO_3	5.50	5.49	(5.35 – 5.68)
SO_2	trace		
F	3.00		
H_2O^-	1.90	29.40 (difference)	
H_2O^+	27.80		
–O=F	–1.27		
Total	100.53	100.00	

* Cameca electron-microprobe MS-46 using an operating voltage of 15 kV, a beam current of 10 mA. *Kα* analytical lines were measured for all elements. Pyrope (Fe, Ca, Si, Al), chromite (Fe), spinel (Al, Fe), diopside (Ca, Si), celestine (S), apatite (P), and orthoclase (Al, K) were used as standards. A ZAF correction procedure was applied using the CORREX program on a PDP 11/04. Values in brackets are the ranges.

** The high content of Fe is explained by associated films of secondary goethite on the surface of mitryaevaite.

(sanjuanite, sasaite) (Martini 1978). This fact explains their low density and indices of refraction.

The infrared-absorption spectrum of mitryaevaite was obtained with a Specord-75JR spectrophotometer and recorded over the range 400–4000 cm^{-1} (Fig. 1). The broad bands in the range 1000–1200 cm^{-1}, with maxima at 1020, 1040, ~1100 and 1150 cm^{-1}, are generated by vibrations υ_3 of the tetrahedral anionic complexes $(SO_4)^{2-}$ and $(PO_4)^{3-}$. Absorption bands in the range 500–700 cm^{-1} can be related to vibrations υ_4 of these same ions (615 and 650 cm^{-1} for $(SO_4)^{2-}$, and 500 and 560 cm^{-1} for $(PO_4)^{3-}$). Broad bands with maxima at 3400 and 1630 cm^{-1} belong to H_2O molecules; bands at 3575 and 1660 cm^{-1} belong to $(OH)^-$ ions. The association of cations with $(OH)^-$ manifests itself in the 500 cm^{-1} region and tends to increase the intensity of the $(PO_4)^{3-}$ absorption bands.

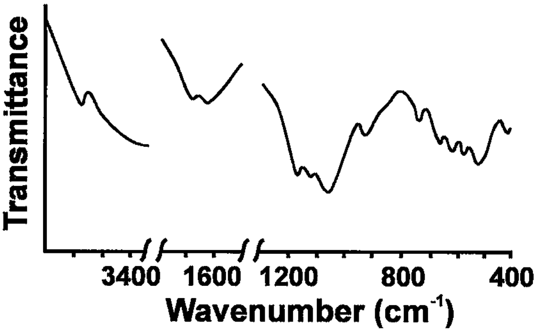

FIG. 1. Infrared-absorption spectrum for mitryaevaite.

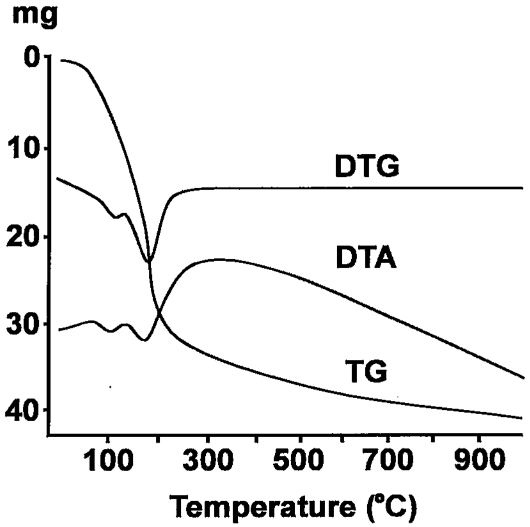

FIG. 2. Results of thermal analysis of mitryaevaite (Q-1000D derivatograph, m = 38.8 mg, DTA = 1/5, DTG = 1/15, rate of heating: 10°C/min).

THERMAL DATA

The role of H_2O in the mineral was analyzed by means of thermal analysis. Most of the H_2O was released in the temperature range from 60 to 350°C, at which point the material became amorphous. A loss of weight accompanies two endothermic effects (Fig. 2); the first (3.4 wt.%) gives a weak peak with a maximum at 100°C, the second (14.5 wt%) gives a strong peak with a maximum at 165°C. If the peak of the endothermic curve is considered completely from the beginning of the process to 250°C, at which point the curve levels off, the total loss of H_2O amounts to 24.8 wt.%. At higher temperatures (up to 1000°C), the additional loss of approximately 3.3 wt.% is related to the emission of water of hydration and the volatility of fluorine.

CRYSTALLOGRAPHY

Because mitryaevaite is a powder, a single-crystal study of the new mineral was not possible. Electron microscopy indicates that the crystals have the shape of a well-defined parallellogram lying on (001). Because mitryaevaite is highly hydrated, crystals tend to swell during continuous examination under the electron beam of the electron microscope. The unstable structure of mitryaevaite is rendered amorphous as H_2O is driven off. It is possible that an appreciable amount of H_2O may be of an interlayer type, or be zeolitic in nature, as in mcauslanite (Richardson *et al.* 1988).

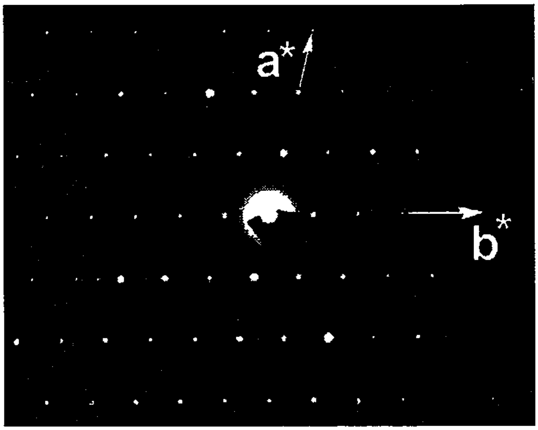

FIG. 3. Selected-area electron-diffraction pattern of mitryaevaite. Axes *a**, *b** of the reciprocal lattice are shown. (JEM-100CX electron microscope, operating voltage of 100 kV).

A crystallographic study of mitryaevaite was conducted using electron and X-ray diffraction patterns. Selected-area diffraction (SAD) patterns with spacing d_{100}, d_{010} and angle γ were obtained (Fig. 3). They are confirmed by the texture electron-diffraction pattern of the mineral. Values of d_{001} and angles α, β were obtained from an oblique texture electron-diffraction pattern and were derived from the geometry of the location of space arcs (reflections). The unit-cell parameters refined by least-squares analysis based on the X-ray powder-diffraction data (Table 2) are: *a* 6.92(1), *b* 10.09(1), *c* 22.46(6) Å, α 92.42(4)°, β 96.43(7)°, γ 104.3(2)°, *V* 1507(2) Å^3, *a*:*b*:*c* 0.6858 : 1:2.2260. The space-group choices are $P1$ or $P\bar{1}$.

CONDITIONS OF FORMATION

The formation of a series of rare secondary phosphates and sulfate–phosphates in which aluminum is of primary importance as a cation is the result of disintegration of the hydromica component of clay minerals in shale when previously metamorphosed carbonaceous matter and sulfides decompose. CO_2 and $(SO_4)^{2-}$ generated by this process cause the solution of phosphate minerals, mainly of apatite. The field of stability of the mineral phases is controlled by pH in the environment and the proportion of the elements Ca, Al, and Si. Secondary carbonate-apatite is the most commonly formed phosphate in an alkaline environment with decreasing Ca^{2+} activity. In a weakly acidic medium with a high concentration of $(PO_4)^{3-}$, $(HPO_4)^{2-}$ and $(SO_4)^{2-}$, the minerals formed are variscite, wavellite, crandallite, gorceixite, minyullite, evansite, aluminite, meta-aluminite, kaolinite and columnar gypsum. Mitryaevaite is yet another member of this paragenesis.

The geochemical conditions of the weathering zone allow us to suggest a mode of origin of the mitryaevaite. We contend that it formed by the crystallization of carbonic acid solutions enriched in phosphorus, fluorine and sulfuric acid solutions, which mobilized aluminum.

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TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR MITRYAEVAITE

I	d_{meas}	d_{calc}	*hkl*	I	d_{meas}	d_{calc}	*hkl*
10	9.75*	9.752	010	<1	2.443*	2.443	$04\bar{1}$
2	9.24*	9.180	$01\bar{1}$	<1	2.430	2.425	133
1	7.54	7.614	$01\bar{2}$	<1	2.268*	2.268	043
1	6.53	6.607	$10\bar{1}$	<1	2.235*	2.234	$30\bar{1}$
3	6.35*	6.287	$\bar{1}10$	<1	2.117	2.117	$20\bar{9}$
<1	4.90*	4.876	020	<1	2.069*	2.069	$31\bar{1}$
<1	4.62*	4.590	$02\bar{2}$	<1	2.013*	2.013	208
<1	4.55*	4.562	$10\bar{4}$	<1	1.993		
<1	4.44*	4.452	005	<1	1.971		
<1	4.28*	4.313	112	1	1.932		
<1	4.08	4.025	104	<1	1.906		
1	3.763	3.807	$02\bar{4}$	<1	1.848		
<1	3.645	3.710	006	<1	1.828		
1	3.573	3.529	120	<1	1.779		
2	3.333*	3.326	200	<1	1.763		
2	3.222*	3.230	201	<1	1.752		
1	3.131	3.112	115	<1	1.704		
2	2.923*	2.929	210	<1	1.675		
<1	2.866	2.857	$21\bar{3}$	<1	1.658		
1	2.761*	2.757	$02\bar{7}$	<1	1.614		
<1	2.691	2.691	$10\bar{8}$	<1	1.547		
<1	2.653	2.648	$20\bar{6}$	<1	1.545		
<1	2.624*	2.626	018	<1	1.527		
1	2.550	2.539	035	<1	1.455		
<1	2.501	2.496	$02\bar{8}$	<1	1.437		
<1	2.474	2.473	009	<1	1.417		

DRON-2,0 diffractometer; 35 kV, 20 mA, Cu*K*α radiation (λ = 1.54051 Å). Values of *d* in Å. The pattern is indexed with *a* 6.92(1), *b* 10.09(1), *c* 22.46(6) Å, α 92.42(4)°, β 96.43(7)°, γ 104.3(2)°. Diffraction lines with an asterisk were used for the unit-cell refinement.

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