

Katerinopoulosite, $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, a new mineral from the Esperanza mine, Lavrion, Greece

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Abstract: Katerinopoulosite, a new picromerite-group mineral, was discovered in the Esperanza mine, Lavrion District, Attiki Prefecture, Greece. The new mineral occurs in the oxidation zone of a sphalerite-rich orebody in association with chalcantite, nickelbousingaultite, ammoniojarosite, aurichalcite, and goethite. Katerinopoulosite forms white, pale blue or pale green vermiform polycrystalline aggregates, in fact, anthodite crusts with separate anthodites up to 3-cm long and up to 5-mm thick. The lustre is vitreous, and the streak is white. Katerinopoulosite is brittle, has Mohs hardness of 2½ and an uneven fracture. Neither cleavage nor parting is observed. $D_{\text{meas}} = 1.97(2) \text{ g/cm}^3$, $D_{\text{calc}} = 1.986 \text{ g/cm}^3$. The new mineral is optically biaxial (+), with $\alpha = 1.492(2)$, $\beta = 1.496(2)$, $\gamma = 1.502(2)$ (589 nm). $2V(\text{meas.}) = 80(5)^\circ$, $2V(\text{calc.}) = 79^\circ$. The infrared spectrum shows the presence of ammonium cations, sulfate anions, and water molecules. The chemical composition is (EDS-mode electron microprobe for Ni, Cu, and Zn; gas chromatography of ignition products for H, N and S, wt%): SO_3 38.33, $(\text{NH}_4)_2\text{O}$ 11.9, NiO 1.82, CuO 0.37, ZnO 16.83, H_2O 29.4, total 98.65. The empirical formula based on 2 S atoms per formula unit (apfu) is $\text{H}_{0.13}(\text{NH}_4)_{1.91}(\text{Zn}_{0.86}\text{Ni}_{0.10}\text{Cu}_{0.02})(\text{SO}_4)_{2.00} \cdot 6.75\text{H}_2\text{O}$. Katerinopoulosite is monoclinic, $P2_1/a$, $a = 9.230(6)$, $b = 12.476(4)$, $c = 6.249(4) \text{ \AA}$, $\beta = 106.79(5)^\circ$, $V = 688.9(9) \text{ \AA}^3$, and $Z = 2$. The strongest lines of the powder X-ray diffraction pattern [d , Å (I , %) (hkl)] are: 5.400 (37) (011), 4.411 (19) (200), 4.314 (19) (021), 4.229 (24) (12–1), 4.161 (100) (20–1, 210, 111), 3.749 (53) (130), 3.034 (29) (211, 11–2). The new mineral is named in honour of the prominent Greek geologist and mineralogist Prof. Dr. Athanassios Katerinopoulos. The type material is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia.

Key-words: Katerinopoulosite; new mineral; ammonium zinc sulfate; picromerite group; oxidation zone; Lavrion; Greece.

1. Introduction

The picromerite group includes monoclinic sulfates with the general formula $A_2M_6(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in which $A = \text{K}$ or NH_4 and $M = \text{Mg}$, Fe^{2+} , Cu^{2+} , or Ni (Back, 2014). Among five picromerite-group minerals described until recently, three species (namely, bousingaultite, mohrite, and nickelbousingaultite) contain ammonium as a species-defining component. The new mineral katerinopoulosite, $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ described in this paper is the fourth ammonium-dominant and the first zinc-dominant member of this group.

The new mineral is named in honour of the prominent Greek geologist and mineralogist Prof. Dr. Athanassios Katerinopoulos (1950) who works at the Section of Mineralogy and Petrology, Department of Geology and Geoenvironment, National and Kapodistrian University of Athens (NKUA), Greece. He is the director of the Museum of Mineralogy and Petrology, NKUA, and of the Laboratory of Museum Studies, NKUA, since 2010. Prof. Katerinopoulos is a specialist in regional geology of Greece and made significant contribution to the geology and mineralogy of the Lavrion mining district and popularization of geological and mineralogical knowledge

(Katerinopoulos & Zisimopoulou, 1994; Katerinopoulos, 2008a, b). He is also a co-author of several new mineral discoveries from the Lavrion district (agardite-(Nd), hilarionite, nickeltsumcorite) and investigations of old metallurgical slags from this area.

According to the English pronunciation rules in the international phonetic alphabet (see <http://www.anti-moon.com/how/pronunc-soundsipa.htm>), the pronunciation of the mineral name is [kʌtəriːnɔːpɒlɔːsɪt]. The Russian Cyrillic name of the new mineral is КАТЕРИНОПУЛОСИТ.

The new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2017-004). The type specimen is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 5014/1.

2. Occurrence, general appearance and physical properties

Esperanza is an abandoned ancient mine located about 2.5 km NE of the town of Lavrion, Lavrion District, Attiki Prefecture, Greece. Mineralization at Esperanza occurs as carbonate-hosted replacement ore bodies at marble–schist contact, consisting mainly of sphalerite, galena, chalcopyrite, pyrite, arsenopyrite and pyrrhotite (Bonsall *et al.*, 2011). Fluorite and calcite are gangue minerals. The mine includes also zones with unusual secondary Cd and Ni mineralization and is the type locality of four new cadmium sulfates: niedermayrite $\text{Cu}_4\text{Cd}(\text{SO}_4)_2(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ (Giester *et al.*, 1998), drobecite $\text{Cd}(\text{SO}_4) \cdot 4\text{H}_2\text{O}$ (Giester & Rieck, 2010), voudourisite $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ (Rieck & Giester, 2012a), and lazarisite $(\text{CdSO}_4)_3 \cdot 8\text{H}_2\text{O}$ (Rieck & Giester, 2012b); see also Rieck (2012).

The new mineral katerinopoulosite was found in the Esperanza mine by one of the authors (V.S.) in July 2016. Associated minerals are chalcantite, nickelboussingaultite, ammoniojarosite, aurichalcite, and goethite. Katerinopoulosite is a supergene mineral formed in the oxidation zone of a sphalerite-rich orebody situated in the contact zone between calcite marble and mica schist.

The new mineral occurs as vermiform polycrystalline aggregates, in fact, anthodite crusts with separate anthodites up to 3-cm long and up to 5-mm thick (Fig. 1). Some anthodites are mixed, formed by both katerinopoulosite and nickelboussingaultite (Fig. 2).

Katerinopoulosite is brittle. It has Mohs hardness of $2\frac{1}{2}$ and an uneven fracture. Neither cleavage nor parting is observed. The new mineral is colourless, pale blue, or pale green and has vitreous lustre. Small fragments are transparent. The streak is white. The density measured by flotation in heavy liquids (diiodomethane–ether mixtures) is $1.97(2) \text{ g/cm}^3$. Densities of the liquids have been measured using a density bottle. Density calculated using the empirical formula is 1.986 g/cm^3 . Katerinopoulosite is non-fluorescent under short- and long-wave UV light.



Fig. 1. Anthodites of katerinopoulosite *in situ*. Field width 10 cm. Only online version in colour.



Fig. 2. Anthodites formed by both katerinopoulosite and nickelboussingaultite *in situ*. Field width 8.5 cm. Only online version in colour.

The new mineral is optically biaxial (+), with $\alpha = 1.492(2)$, $\beta = 1.496(2)$, $\gamma = 1.502(2)$ (589 nm); $2V$ (meas.) = $80(5)^\circ$, $2V$ (calc.) = 79° . Dispersion of optical axes is weak, $r < v$. Under the polarizing microscope, katerinopoulosite is colourless and nonpleochroic.

3. Infrared spectroscopy

In order to obtain infrared (IR) absorption spectra, powdered samples were mixed with dried KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) with a resolution of 4 cm^{-1} and 16 scans (Fig. 3). The IR spectrum of an analogous pellet of pure KBr was used as a reference.

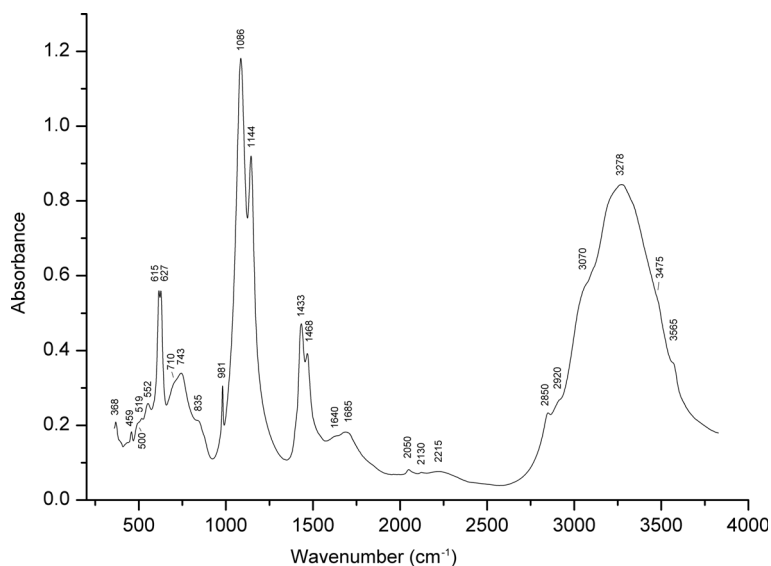


Fig. 3. Powder IR spectrum of katerinopoulosite.

The IR spectrum of katerinopoulosite is similar to those of other ammonium members of the picromerite group. Absorption bands and their assignments are (cm^{-1} ; s – strong band, w – weak band, sh – shoulder): 3565sh, 3475sh (O–H-stretching vibrations of H_2O molecules), 3278s (overlapping bands of O–H-stretching vibrations of H_2O molecules and N–H-stretching vibrations of NH_4^+ cations), 3070sh, 2920sh, 2850 (N–H-stretching vibrations of NH_4^+ cations), 2215w (stretching vibrations of acid OH groups), 2130w, 2050w (overtone and combination mode corresponding to S–O stretching vibrations), 1685, 1640sh (bending vibrations of H_2O molecules), 1468, 1433 (bending vibrations of NH_4^+ cations), 1144s, 1086s [$\nu_3(F_2)$ asymmetric stretching vibrations of SO_4^{2-} ions], 981 [$\nu_1(A_1)$ symmetric stretching vibrations of SO_4^{2-} ions], 835sh, 743, 710sh (NH_4^+ librational modes), 627, 615 [$\nu_4(F_2)$ – asymmetric bending vibrations of SO_4^{2-} ions], 552w, 519w, 500sh, 459w, 368w [lattice modes involving Zn–O stretching vibrations, librational vibrations of H_2O molecules and $\nu_2(E)$ symmetric bending vibrations of SO_4^{2-} ions].

The weak and broad band at 2215 cm^{-1} may be assigned to trace amounts of acid groups, H_3O^+ or HSO_4^- .

4. Chemical data

Five chemical analyses were obtained with a Tescan VEGA-II XMU INCA Energy 450 digital electronic microscope (energy-dispersive mode, 20 kV, 600 pA, beam diameter 0.16–0.18 μm (for Ni, Cu and Zn). The beam was rastered on an area $8\ \mu\text{m} \times 8\ \mu\text{m}$. Attempts to use wavelength-dispersive spectroscopy, with higher beam current, were unsuccessful because of the instability of the mineral. Gas chromatography of products of ignition in oxygen stream at 1200°C was used for quantitative determination of H, N and S. CO_2 was not measured because chemical tests show the absence of

Table 1. Chemical composition of katerinopoulosite.

Constituent	wt%	Range	Standard deviation	Probe standard
SO_3^*	38.33 ± 0.15	–	–	–
$(\text{NH}_4)_2\text{O}^*$	11.9 ± 0.5	–	–	–
H_2O^{**}	29.4 ± 2.5	–	–	–
NiO	1.82	bdl – 4.54	1.87	Ni
CuO	0.37	bdl – 0.96	0.45	Cu
ZnO	16.83	13.03–18.95	2.05	Zn
Total	98.65	–	–	–

* $38.33\text{ wt}\%$ SO_3 and $11.9\text{ wt}\%$ $(\text{NH}_4)_2\text{O}$ are calculated from $15.35\text{ wt}\%$ S and $6.4\text{ wt}\%$ N, respectively, determined by gas chromatography.

** Rest of hydrogen after subtraction of H in NH_4^+ cations. Total H content determined by gas chromatography is $5.1\text{ wt}\%$.

carbonate anions in katerinopoulosite. Contents of other elements with atomic numbers >6 are below detection limits. Analytical data are given in Table 1.

The empirical formula of katerinopoulosite based on 2 S atoms per formula unit (apfu) is $\text{H}_{0.13}(\text{NH}_4)_{1.91}(\text{Zn}_{0.86}\text{Ni}_{0.10}\text{Cu}_{0.02})(\text{SO}_4)_{2.00} \cdot 6.75\text{H}_2\text{O}$. Excess of H_2O relative to the idealized formula may be due to water adsorbed by the hygroscopic mineral.

Taking into account the presence of trace amounts of acid groups showing weak IR band at 2215 cm^{-1} , the empirical formula could be written as follows:

$(\text{H}_3\text{O})_{0.13}(\text{NH}_4)_{1.91}(\text{Zn}_{0.86}\text{Ni}_{0.10}\text{Cu}_{0.02})(\text{SO}_4)_{2.00} \cdot 6.62\text{H}_2\text{O}$,
or $(\text{NH}_4)_{1.91}(\text{Zn}_{0.86}\text{Ni}_{0.10}\text{Cu}_{0.02})(\text{H}_{0.065}\text{SO}_4)_{2.00} \cdot 6.75\text{H}_2\text{O}$.

The end-member formula is $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, which requires $(\text{NH}_4)_2\text{O}$ 12.97, ZnO 20.26, SO_3 39.85, H_2O 26.92, total 100.00 wt%. The Gladstone–Dale compatibility index is: $1 - (K_p/K_c) = 0.035$ (excellent). Katerinopoulosite readily dissolves in water at room temperature. No gas evolution is observed in 20% HCl, showing the absence of admixed carbonates.

Table 2. Powder X-ray diffraction data for katerinopoulosite and its synthetic analogue.

Katerinopoulosite			Synthetic $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}^*$		<i>hkl</i>
I_{meas}	$d_{\text{meas}}, \text{\AA}$	$d_{\text{calc}}, \text{\AA}$	I_{calc}	$d_{\text{calc}}, \text{\AA}$	
6	7.19	7.211	12	7.220	110
17	6.21	6.238	36	6.257	020
18	6.00	5.983	32	5.978	001
37	5.400	5.394	57	5.394	011
9	5.238	5.253	16	5.256	111
17	5.076	5.096	25	5.107	120
19	4.411	4.418	30	4.420	200
19	4.314	4.318	30	4.322	021
24	4.229	4.244	36	4.250	121
100	4.161	4.177, 4.165, 4.149	90, 87, 77	4.180, 4.168, 4.148	20 $\bar{1}$, 210, 111
6	3.947	3.961	8	3.964	211
53	3.749	3.763	100	3.772	130
13	3.599	3.605, 3.595	12, 16	3.610, 3.597	220, 121
2	3.454	3.471	5	3.476	22 $\bar{1}$
8	3.406	3.415	13	3.421	031
12	3.368	3.378	24	3.385	13 $\bar{1}$
6	3.104	3.119	12	3.128	040
29	3.034	3.051, 3.027	18, 56	3.050, 3.026	211, 11 $\bar{2}$
3	2.931	2.947, 2.926	4, 2	2.952, 2.928	231, 31 $\bar{1}$
3	2.896	2.909, 2.896	4, 5	2.907, 2.896	012, 20 $\bar{2}$
5	2.865	2.867	8	2.868	310
15	2.817	2.809	23	2.810	221
17	2.744	2.791, 2.746	23, 2	2.791, 2.753	12 $\bar{2}$, 14 $\bar{1}$
7	2.703	2.710	8	2.713	321
1	2.662	2.664	1	2.666	320
2	2.624	2.626	3	2.628	22 $\bar{2}$
8	2.542	2.558, 2.544	9, 9	2.553, 2.549	112, 141
5	2.512	2.509, 2.499	8, 4	2.511, 2.505	231, 24 $\bar{1}$
17	2.431	2.441	29	2.442	312
3	2.401	2.404, 2.401	4, 4	2.407, 2.407	330, 150
1	2.373	2.376	2	2.379	23 $\bar{2}$
2	2.296	2.299, 2.292	1, 1	2.301, 2.297	40 $\bar{1}$, 15 $\bar{1}$
10	2.216	2.215, 2.213	16, 11	2.218, 2.213	241, 132
8	2.162	2.166, 2.159	4, 13	2.169, 2.161	34 $\bar{1}$, 042
5	2.137	2.142, 2.136	7, 5	2.145, 2.138	251, 33 $\bar{2}$
4	2.120	2.122	7	2.125	24 $\bar{2}$
7	2.082	2.079	10	2.084	060
1	2.058	2.054	2	2.053	20 $\bar{3}$
1	2.029	2.026	3	2.026	21 $\bar{3}$
2	2.010	2.012	1	2.015	43 $\bar{1}$
1	1.993	1.994	6	1.993	003
1	1.976	1.980, 1.969, 1.964	3, 4, 4	1.982, 1.969, 1.969	42 $\bar{2}$, 013, 061
3	1.955	1.957, 1.955, 1.951, 1.949	3, 2, 2, 2	1.962, 1.958, 1.951, 1.951	161, 251, 22 $\bar{3}$, 15 $\bar{2}$
7	1.908	1.908	15	1.908	31 $\bar{3}$
2	1.863	1.862, 1.859	5, 6	1.866, 1.860	261, 13 $\bar{3}$
4	1.846	1.851, 1.841	4, 6	1.854, 1.842	44 $\bar{1}$, 23 $\bar{3}$
3	1.825	1.829, 1.819	4, 3	1.827, 1.819	312, 421
4	1.803	1.805, 1.798	6, 8	1.805, 1.799	152, 24 $\bar{2}$
3	1.752	1.760, 1.751, 1.750	2, 5, 5	1.759, 1.751, 1.751	123, 33 $\bar{3}$, 510
3	1.724	1.724	5	1.726	351
3	1.717	1.715	5	1.716	24 $\bar{3}$
4	1.687	1.691, 1.688, 1.687	4, 6, 6	1.692, 1.689, 1.689	45 $\bar{1}$, 42 $\bar{3}$, 53 $\bar{1}$
2	1.651	1.654, 1.652, 1.650, 1.648	3, 3, 2, 1	1.656, 1.656, 1.652, 1.647	450, 171, 252, 203
2	1.627	1.624	3	1.625	441
2	1.623	1.621	3	1.623	53 $\bar{2}$
2	1.619	1.616	1	1.617	43 $\bar{3}$
1	1.560	1.560, 1.560, 1.558	2, 3, 3	1.563, 1.560, 1.560	080, 20 $\bar{4}$, 053
1	1.551	1.548	3	1.551	17 $\bar{2}$
1	1.543	1.542	3	1.545	461
1	1.527	1.528, 1.525	3, 2	1.530, 1.525	44 $\bar{3}$, 61 $\bar{1}$
2	1.471	1.473, 1.471, 1.470	5, 5, 3	1.475, 1.475, 1.471	172, 280, 16 $\bar{3}$
1	1.462	1.461, 1.461	1, 1	1.465, 1.461	28 $\bar{1}$, 23 $\bar{4}$
1	1.453	1.453	4	1.452	13 $\bar{4}$
2	1.433	1.438, 1.433	1, 1	1.436, 1.434	41 $\bar{4}$, 620
2	1.428	1.430, 1.427	4, 2	1.430, 1.427	33 $\bar{4}$, 323
1	1.412	1.410	1	1.411	42 $\bar{4}$

* Calculated from the structure data reported by Maslen *et al.* (1988); only reflections with $I_{\text{calc}} \geq 1$ are given.

Table 3. Comparative data for katerinopouloisite and related ammonium picromerite-group minerals.

Mineral	Katerinopouloisite	Boussingaultite	Mohrite	Nickelboussingaultite
Formula	$(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{Fe}^{2+}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a^*$	$P2_1/a$	$P2_1/a$	$P2_1/a$
a , Å	9.230	9.324	9.32	9.241
b , Å	12.476	12.597	12.65	12.544
c , Å	6.249	6.211	6.24	6.243
β , °	106.79	107.14	106.8	106.58
V , Å ³	688.9	697.1	704.3	693.6
Z	2	2	2	2
	5.400 (37)	7.20 (70)	5.40 (18)	11.7 (70)
	4.411 (19)	5.11 (85)	4.200 (65)	4.153 (100)
Strongest reflections of the powder X-ray diffraction pattern:	4.314 (19)	4.22 (100)	3.801 (100)	3.759 (80)
d , Å (I , %)	4.229 (24)	3.79 (70)	3.153 (25)	3.022 (60)
	4.161 (100)	2.189 (55)	3.025 (20)	2.793 (60)
	3.749 (53)	2.085 (95)	2.823 (20)	2.119 (70)
	3.034 (29)	1.818 (65)	2.460 (28)	1.806 (60)
Density g cm ⁻³	1.97 (meas.) 1.986 (calc.)	1.722 (meas.) 1.718 (calc.)	1.800–1.862 (meas.) 1.805–1.870 (calc.)	1.85 (calc.)
<i>Optical data</i>				
α	1.492	1.470	1.480–1.486	1.490
β	1.496	1.472	n. d.	1.494
γ	1.502	1.479	1.486–1.493	1.501
$2V$, °	80	51	65–75	n. d.
Optical sign	+	+	+	+
	3278	3290	3190	3267
	1685	1670	1615	1650
	1468	1474	1460	1451
Strong and characteristic bands in the IR spectrum, cm ⁻¹	1433	1434	1401	1419
	1144	1142	1144	1126
	1086	1082	1099	1073
	981	981	984	973
	743	724	770	712
	627	627	631	679
	615	617	615	620
		Larsen & Shannon, 1920	Garavelli, 1964	Yakhontova <i>et al.</i> , 1976
		Margulis & Templeton, 1962	Montgomery <i>et al.</i> , 1967	Montgomery & Lingafelter, 1964
References	This work	Montgomery & Lingafelter, 1964 Chukanov, 2014	Chukanov, 2014	Chukanov & Chervonnyi, 2016

* By analogy with all other picromerite-group minerals and their synthetic analogues, Tutton's salts.

5. X-ray diffraction data

Powder X-ray diffraction data for katerinopouloisite (Table 2) were collected using a Rigaku R-AXIS Rapid II diffractometer (curved image plate, $d=127.4$ mm, $\text{CoK}\alpha$, 40 kV, 15 mA). The sample was rotated around two axes and the XRD data were collected with the Debye-Scherrer geometry using a cylindrical IP detector. The monoclinic unit-cell parameters calculated from the powder data are: $a=9.230(6)$, $b=12.476(4)$, $c=6.249(4)$ Å, $\beta=106.79(5)^\circ$, $V=688.9(9)$ Å³, and $Z=2$. They are close to those of other picromerite-group minerals. By analogy with them and their synthetic analogues, Tutton's salts, the most probable space group of katerinopouloisite is $P2_1/a$.

6. Discussion

Tutton's salts, both synthetic and natural (picromerite-group minerals) form a large group of compounds with the general formula $A^+{}_2M^{2+}(X\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ where A are large univalent cations like NH_4 , K, Cs, Rb, Tl; M are smaller bivalent cations having octahedral coordination, such as Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd; X are penta- or hexavalent cations like S(VI), Se(VI), Cr(VI), or P(V) having tetrahedral coordination; $\text{O}=\text{O}$, OH, F (Tutton, 1901; Margulis & Templeton, 1962; Montgomery & Lingafelter, 1964; Montgomery *et al.*, 1967; Maslen *et al.*, 1988; Bosi *et al.*, 2009; Ettoumi *et al.*, 2015). Recently, a paper on a new mineral of the picromerite group, nickelpicromerite, with full crystal-structure determina-

tion was published (Belogub *et al.*, 2015). All these compounds are isostructural and crystallize in the monoclinic system, space group $P2_1/a$.

Although the crystal structure of katerinopoulosite could not be studied directly because of the absence of suitable single crystals, its stoichiometry, powder X-ray diffraction pattern and IR spectrum undoubtedly indicate that this mineral is isostructural with other members of the picromerite group and synthetic Tutton's salts (Tables 2 and 3).

Sphalerite was the source of zinc and sulfur for the new mineral, and overlying soil saturated by vegetal remains was the most probable source of ammonium for katerinopoulosite and the associated minerals nickel-boussingaultite and ammoniojarosite.

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