

The Canadian Mineralogist
Vol. 50, pp. 65-72 (2012)
DOI: 10.3749/canmin.50.1.65

AMMONIOMAGNESIOVOLTAITE, A NEW VOLTAITE-RELATED MINERAL SPECIES FROM PÉCS-VASAS, HUNGARY

SÁNDOR SZAKÁLL[§]

Department of Mineralogy and Petrology, University of Miskolc, H-3515 Miskolc, Egyetemváros, Hungary

ISTVÁN SAJÓ

Institute of Materials and Environmental Chemistry, Research Center for Natural Sciences, Hungarian Academy of Sciences, Pusztaszeri út 59-67, H-1025 Budapest, Hungary

BÉLA FEHÉR

Department of Mineralogy, Herman Ottó Museum, Kossuth u. 13, H-3525 Miskolc, Hungary

SIMONA BIGI

Department of Earth Sciences, University of Modena and Reggio Emilia, Via Santa Eufemia 19, I-41100 Modena, Italy

ABSTRACT

Ammoniomagnesiovoltaite (IMA no. 2009-040) was found on a burning coal dump in an abandoned open coal pit at Pécs-Vasas, Mecsek Mountains, South Hungary. It is closely associated with tschermigite, sabieite, kieserite, pickeringite, and hexahydrite, but other ammonium minerals (salammoniac, mascagnite, clairite, boussingaultite, efremovite, koktaite, mohrite, ammoniojarosite, godovikovite, letovicite) as well as native sulfur, millosevichite, alunogen, metavoltine, voltaite, gypsum, anhydrite, halotrichite, butlerite, jarosite, and copiapite also occur in the surrounding area. Ammoniomagnesiovoltaite was formed by the interaction of organic matter with oxidizing iron sulfides (pyrite and marcasite). It forms crusts consisting of cubo-octahedral and octahedral crystals up to 0.05 mm in size. The mineral is translucent and pale yellow to yellowish brown in color, with white streak and vitreous luster. Its Mohs hardness is about 2-3 and the measured density is 2.55(1) g/cm³. Cleavage was not observed; fracture is uneven. Optically it is isotropic with $n = 1.60(1)$. The chemical composition was found to be: SO₃ 47.56, Al₂O₃ 3.31, Fe₂O₃ 12.28, FeO 5.94, MnO 1.18, MgO 7.02, K₂O 0.05, (NH₄)₂O 3.11, and H₂O (calc.) 17.72; total 98.17 wt.%. The empirical formula is [(NH₄)_{2.18} K_{0.02}]_{Σ=2.20} (Mg_{3.19} Fe²⁺_{1.51} Mn_{0.30})_{Σ=5.00} (Fe³⁺_{2.81} Al_{1.19})_{Σ=4.00} S_{10.87} O_{44.70}•18H₂O, and its simplified formula is (NH₄)₂Mg₃Fe³⁺₃Al(SO₄)₁₂•18H₂O. The strongest six lines in the X-ray powder diffraction pattern are [d_{hkl} in Å (I_{obs} %, hkl): 5.59 (100, 422), 3.420 (72, 800), 3.562 (66, 731), 1.7836 (25, 15.3.1), 1.5582 (25, 16.6.4), and 6.85 (24, 400)]. According to X-ray powder diffraction, ammoniomagnesiovoltaite is structurally analogous to voltaite-group minerals; it is cubic, space group $Fd\bar{3}c$, $a = 27.260(2)$ Å, $V = 20257(2)$ Å³, $Z = 16$. The new mineral is named for the dominant ammonium and magnesium in the composition and its membership in the voltaite group.

INTRODUCTION

Coal beds of Liassic age occur in Jurassic Formations in the Mecsek Mountains, South Hungary, and have been mined since the 18th century (Némedi Varga 1995). Secondary sulfates were reported as efflorescences from near-surface coal beds from the Pécs-Vasas area as early as 1799 (Gombocz 1945). The coal seams are composed of paralic sediments and clastic and

phytogenic rocks: sandstones, mudstones, claystones. The mudstone series contains carbonate rocks, represented mainly by sphaerosiderite. Pyrite and marcasite are the main sulfide minerals in the Pécs-Vasas coalfield.

The new mineral, ammoniomagnesiovoltaite, (NH₄)₂Mg₃Fe³⁺₃Al(SO₄)₁₂•18H₂O, was discovered in an investigation of the burning dumps at Komló and Pécs-Vasas, where a considerable number of ammonium sulfates have been observed in recent years (Szakáll &

[§] E-mail address: askszs@uni-miskolc.hu

Kristály 2008). After the closing of mines, spontaneous combustion and burning of coal seams and the waste dump material has become well-known. In this environment, there is an exceptionally wide range of coal-fire gas minerals, which form from burning coal seams and material of coal-waste dumps. Variegated associations of NH_4 , Al, Fe, Mg, and Ca sulfates, in variable stages of hydration, are the most abundant. Similar associations are known from many other localities of the world, *e.g.*, in the Czech Republic (Žáček & Povondra 1988), Poland (Parafiniuk & Kruszewski 2009), and Russia (Chesnokov *et al.* 2008). The name of the new mineral species recalls the dominance of ammonium and magnesium in the composition and its membership in the voltaite group. Both the mineral and the mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA CNMNC) under No. 2009-040. Type materials are deposited in the collections of the Herman Ottó Museum, Miskolc (part of the holotype, catalogue number: 2008.233) and the Department of Mineralogy and Petrology, Hungarian Natural History Museum, Budapest (part of the holotype, catalogue number: Gyn.1590), both in Hungary.

OCCURRENCE AND PARAGENESIS

Ammoniomagnesiovoltaite was found in an open coal pit near the Köves Hill (46.16°N 18.32°E), Pécs-Vasas, Mecsek Mountains, Southern Hungary. Many ammonium minerals occur near the surface, especially in the open pit. The common salammoniac, tschermigite, and mascagnite (with native sulfur) are formed directly by condensation from the vapor phase and occur as porous crusts and fibrous or dendritic masses, usually consisting of minute euhedral or subhedral crystals. Exceptionally, salammoniac crystals may reach 1 cm in size. The nitrogen of the ammonium is provided by the decay of the organic matter of coal. Sulfur and sulfur compounds are derived from the alteration of pyrite and marcasite, and from the organic sulfur content of the coal seams. Sulfur oxides are released as gases into the atmosphere during spontaneous coal-seam fires. Sulfur oxides react with different ions in the fluid phase to form sulfur-bearing minerals, mainly sulfates. The ammonium sulfates require a source of metallic compounds to form; these are derived from the waste-rocks accompanying the coal seam.

To date, 16 ammonium sulfate minerals have been identified in the Mecsek coalfield. They occur as very fine admixtures, forming coatings, efflorescences, nodules, and porous masses. Each of the samples was investigated using a combination of approaches. Usually, X-ray powder-diffraction studies in combination with analyses made with a scanning electron microscope allowed us to identify the mineral phases. The most abundant ammonium-bearing sulfate is tschermigite. It mainly forms colorless to white porous,

fibrous, or dendritic masses, and in some cases in mm-size octahedra. Clairite (yellow tabular crystals with a hexagonal outline), mohrite (yellowish tabular crystals), and boussingaultite (white tabular crystals) were identified in close association with tschermigite. Mascagnite commonly occurs in encrustations composed of thick tabular crystals. It is rarely associated with efremovite, sabieite, koktaite, and mohrite. Ammoniojarosite occurs as a crust, in some cases consisting of minute rhombohedra. Godovikovite appears as pale brown crusts, locally associated with tschermigite. Microcrystalline masses of sabieite are found to occur together with mohrite and tschermigite. Millosevichite, koktaite, and letovicite also occur as crusts. Other associated sulfate minerals are: alunogen, hexahydrite, metavoltine, voltaite, gypsum, anhydrite, halotrichite, pickeringite, butlerite, jarosite, and copiapite (Szakáll & Kristály 2008).

Ammoniomagnesiovoltaite is closely associated with tschermigite, pickeringite, and hexahydrite. It forms thin crusts, nodules and, on the surface, minute cubo-octahedral or octahedral crystals. The mineral is formed by the interaction of organic matter with iron sulfides in an oxidizing environment.

APPEARANCE AND PHYSICAL PROPERTIES

Pale yellow to yellow-brown crusts of ammoniomagnesiovoltaite are composed of microscopic isometric crystals. The cubo-octahedral and octahedral crystals attain 0.05 mm in size (Fig. 1). Crystal forms identified by SEM are: {111} octahedron, {100} cube, and minor {110} rhombic dodecahedron. Twinning was not observed. The luster of the crystals is vitreous, translucent. The streak is white. The Mohs hardness is about 2-3. The crystals are quite brittle. Cleavage was not observed, and the fracture is uneven. Ammoniomagnesiovoltaite is soluble in water. No fluorescence was detected in either long- or short-wave ultraviolet radiation. The measured density is 2.55(1) g/cm³ based on the sink-float method (with a pycnometer, in an acetone-bromofom mixture). The density calculated for the empirical formula, using the unit-cell volume of the natural sample, is 2.351 g/cm³. The relatively large difference between the measured and calculated densities is attributed to inaccurate measurement owing to poor perceptibility of the aggregate of the investigated material in the measuring fluid. Therefore, we take the calculated density to be more realistic.

Ammoniomagnesiovoltaite is isotropic, $n = 1.60(1)$. The compatibility index according to Mandarino (1981) is 0.001, *i.e.*, "superior".

X-RAY CRYSTALLOGRAPHY

Single-crystal X-ray studies were not possible owing to the small size of the crystal. Powder X-ray diffraction data were obtained for natural and synthetic ammo-

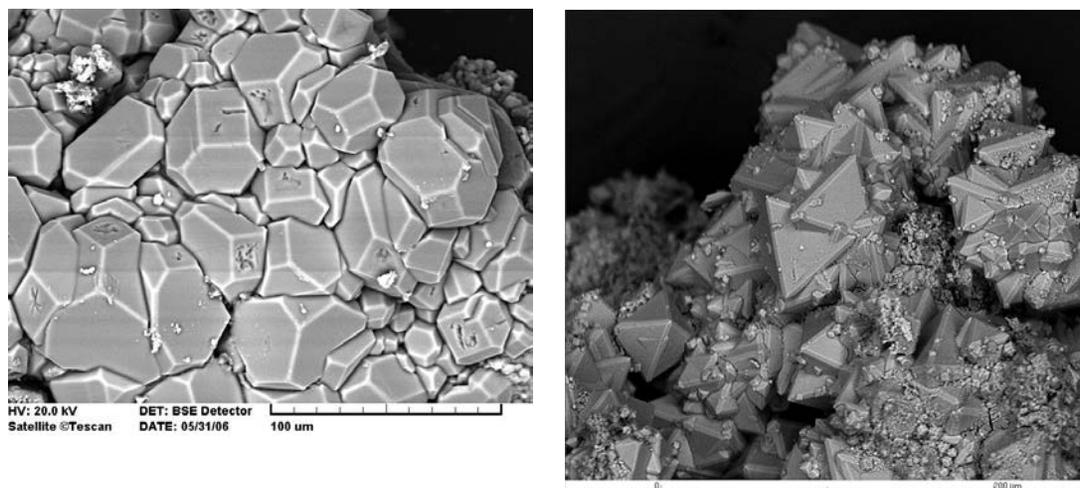


FIG. 1. SEM images of (a) cubo-octahedral and (b) octahedral crystals of ammoniomagnesiovoltaite, Pécs-Vasas.

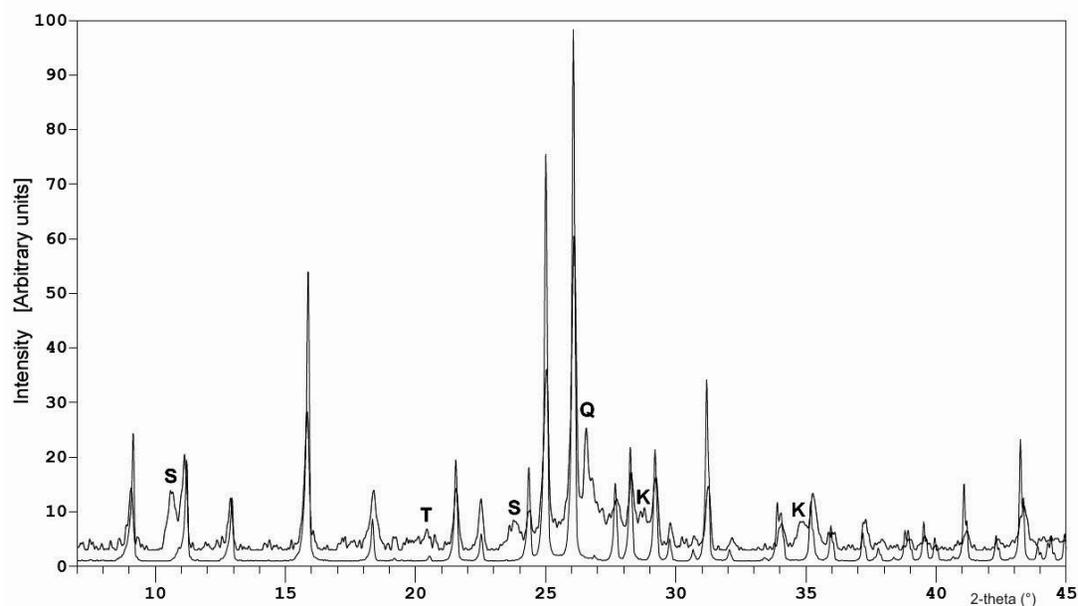


FIG. 2. X-ray powder diffraction patterns of natural (Pécs-Vasas) and synthetic ammoniomagnesiovoltaite. Extra lines in the natural sample originate from intimately intergrown impurities. Abbreviations: K = kieserite, Q = quartz, S = sabeite, and T = tschermigite.

niomagnesiovoltaite with a Philips model PW1050 Bragg-Brentano-type diffractometer using $\text{CuK}\alpha$ radiation (40 kV, 35 mA) and a secondary graphite monochromator. The XRD data were recorded over the 2θ range $4\text{--}80^\circ$ using 0.02° steps and a counting

time of 2 s/step. Synthetic ammoniomagnesiovoltaite was prepared using the method of Mereiter (1972). The traces of natural and synthetic materials are practically identical (Fig. 2). However, owing to the scarcity of the mineral, high-quality powder data (in \AA for $\text{CuK}\alpha$) are

given for the synthetic analogue (Table 1). Synthetic fluorophlogopite (NIST SRM 675) and silicon powder (NIST SRM 640) were used as internal standards.

According to the single-crystal structure determinations, two structural modifications can be distinguished within the voltaite group: (1) cubic, with space group

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC AMMONIOMAGNESIOVOLTAITE

<i>I</i> _{rel.} (%)	<i>d</i> _{meas.} (Å)	<i>d</i> _{calc.} (Å)	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i> _{rel.} (%)	<i>d</i> _{meas.} (Å)	<i>d</i> _{calc.} (Å)	<i>h</i>	<i>k</i>	<i>l</i>
2	9.69	9.67	2	2	0	3	1.7804	1.7800	14	6	2
14	7.91	7.90	2	2	2	1	1.7509	1.7510	12	8	6
24	6.85	6.84	4	0	0	2	1.7367	1.7370	14	6	4
100	5.59	5.58	4	2	2	7	1.7263	1.7260	13	9	1
2	4.84	4.83	4	4	0	1	1.7092	1.7090	16	0	0
1	4.63	4.62	5	3	1	3	1.6831	1.6830	14	8	2
1	4.324	4.324	6	2	0	4	1.6706	1.6710	14	6	6
7	4.126	4.123	6	2	2	1	1.6582	1.6580	16	4	0
2	3.949	3.947	4	4	4	1	1.6491	1.6490	13	9	5
14	3.657	3.655	6	4	2	2	1.6346	1.6340	12	10	6
66	3.562	3.560	7	3	1	1	1.6259	1.6260	15	7	3
72	3.420	3.418	8	0	0	22	1.6114	1.6110	12	12	0
12	3.225	3.223	6	6	0	3	1.6004	1.6000	12	12	2
12	3.159	3.158	7	5	1	1	1.5895	1.5900	14	8	6
22	3.059	3.058	8	4	0	5	1.5813	1.5820	17	3	1
1	3.003	3.002	7	5	3	4	1.5790	1.5790	14	10	2
2	2.916	2.915	6	6	4	1	1.5685	1.5690	12	12	4
19	2.868	2.867	9	3	1	25	1.5582	1.5580	16	6	4
4	2.792	2.791	8	4	4	1	1.5481	1.5480	14	10	4
2	2.682	2.682	10	2	0	5	1.5406	1.5410	17	5	1
11	2.644	2.644	9	5	1	1	1.5286	1.5290	16	8	0
8	2.633	2.632	6	6	6	2	1.5191	1.5190	16	8	2
11	2.551	2.550	9	5	3	1	1.5009	1.5010	18	2	2
4	2.497	2.497	10	4	2	1	1.4917	1.4920	16	8	4
8	2.418	2.417	8	8	0	1	1.4848	1.4850	17	7	1
1	2.389	2.389	9	7	1	1	1.4747	1.4750	18	4	2
2	2.381	2.380	10	4	4	2	1.4680	1.4680	17	7	3
6	2.320	2.320	9	7	3	2	1.4573	1.4580	12	12	8
4	2.312	2.311	10	6	2	1	1.4516	1.4510	15	9	7
9	2.279	2.279	12	0	0	2	1.4495	1.4490	16	8	6
2	2.255	2.256	11	5	1	2	1.4412	1.4410	18	6	0
1	2.218	2.218	10	6	4	5	1.4352	1.4350	17	7	5
22	2.197	2.197	9	7	5	1	1.4333	1.4330	18	6	2
4	2.136	2.136	12	4	2	1	1.4198	1.4200	13	11	9
15	2.092	2.091	11	7	1	2	1.4103	1.4100	14	12	6
1	2.086	2.085	10	6	6	1	1.3815	1.3810	18	8	2
3	2.062	2.061	12	4	4	10	1.3758	1.3760	15	13	1
2	2.044	2.044	13	3	1	1	1.3669	1.3670	16	12	0
3	2.039	2.038	10	8	4	1	1.3605	1.3610	16	12	2
6	2.016	2.016	12	6	2	1	1.3487	1.3490	19	7	1
1	1.9731	1.9740	8	8	8	4	1.3407	1.3410	16	12	4
1	1.9586	1.9580	13	5	1	1	1.3278	1.3280	18	10	0
1	1.9530	1.9530	12	6	4	1	1.3159	1.3160	12	12	12
1	1.9341	1.9340	14	2	0	1	1.3036	1.3040	14	12	10
1	1.9187	1.9190	13	5	3	1	1.2862	1.2860	18	8	8
4	1.9149	1.9150	14	2	2	1	1.2805	1.2810	16	10	10
3	1.8964	1.8960	12	8	0	1	1.2762	1.2760	17	13	1
3	1.8784	1.8780	12	8	2	1	1.2694	1.2700	16	12	8
1	1.8609	1.8610	14	4	2	1	1.2548	1.2550	21	5	3
3	1.8274	1.8270	12	8	4	1	1.2325	1.2330	22	2	2
2	1.8153	1.8150	13	7	3	1	1.2240	1.2240	21	7	3
2	1.8114	1.8110	10	8	8	1	1.2233	1.2230	16	12	10
25	1.7836	1.7840	15	3	1						

$Fd\bar{3}c$ (voltaite, see Mereiter 1972), and (2) tetragonal, with space group $I4_1/acd$ (pertlikite, see Ertl *et al.* 2008). In the case of pertlikite, the lowering of symmetry from isometric to tetragonal occurs as a result of cation ordering. This symmetry reduction is indicated by optical anisotropy (see Ertl *et al.* 2008). In the case of ammoniomagnesiovoltaite, such an optical feature has not been observed, therefore X-ray powder-diffraction data were indexed on the basis of a cubic lattice, and the resulting cubic unit-cell (space group $Fd\bar{3}c$) was refined to $a = 27.260(2)$ Å, $V = 20257(2)$ Å³, $Z = 16$ for the synthetic material. It is worth mentioning that the lattice constant of the mineral is slightly larger ($a = 27.275$ Å, $V = 20291$ Å³), probably because of the substitution of Fe²⁺ for Mg.

CHEMICAL COMPOSITION

Initially, a semiquantitative energy-dispersive analysis of the type ammoniomagnesiovoltaite was performed using a JEOL JXA8600 electron microprobe. The result showed that the mineral contains abundant Fe, Mg, Al, S, and some Mn and K, as well. No other elements with atomic number > 10 were detected. X-ray powder diffraction indicated that the mineral has the voltaite structure, however, its potassium content is extremely low for the voltaite composition. Since the paragenesis of the new mineral contains ammonium sulfates, ammonium substitution for potassium was considered likely. It was confirmed by spectrophotometry, which revealed 3.11 wt.% (NH₄)₂O. The presence of ammonium was also confirmed by IR spectroscopy.

Quantitative chemical analyses were performed using an ARL-SEMQ electron microprobe operated in wavelength-dispersive mode. Operating conditions were as follows: excitation voltage 15 kV, probe current

10 nA, a final beam diameter of 25 μm, peak count-times 10 s, and background count-times 5 s. Raw intensity data were corrected using a $\varphi(\rho Z)$ matrix correction.

Average results and ranges of electron microprobe analyses (five points on the same crystal), standard deviations, as well as the probe standards used, are shown in Table 2. The Table also contains the ammonium oxide content based on spectrophotometric analysis and the calculated H₂O content. From the total iron content (given as FeO), the Fe²⁺/Fe³⁺ ratio was calculated on the basis of the equation $(Mg + Fe^{2+} + Mn^{2+}) / (Fe^{3+} + Al) = 5/4$. The mean composition of ammoniomagnesiovoltaite corresponds to the empirical formula, calculated on the basis of $(Mg + Mn + Fe + Al) = 9$ cations, is $[(NH_4)_{2.18}K_{0.02}]_{\Sigma 2.20}(Mg_{3.19}Fe_{2+1.51}Mn_{0.30})_{\Sigma 5.00}(Fe^{3+}_{2.81}Al_{1.19})_{\Sigma 4.00}S_{10.87}O_{44.70} \cdot 18H_2O$. The simplified formula $(NH_4)_2Mg_5Fe^{3+}_3Al(SO_4)_{12} \cdot 18H_2O$, contains (in wt.%): SO₃ 52.52, Al₂O₃ 2.79, Fe₂O₃ 13.09, MgO 11.02, (NH₄)₂O 2.85, and H₂O 17.73, for a total of 100.

THERMOGRAVIMETRY

The TG, DTG, and DTA curves for natural ammoniomagnesiovoltaite were performed at the Earth Sciences Department of the University of Modena and Reggio Emilia with a SEIKO SSC/5200 instrument operating in air at a heating rate of 5 °C/min over the range of 25 °C (room temperature) to 1012 °C, using a 9.30 mg sample in a Pt crucible. A Pt pan was used as reference material for the DTA analysis.

In order to interpret the thermogravimetric curves of the mineral, synthetic NH₄-doped voltaite was also analyzed at the University of Debrecen, where the evolved gases were measured with an ATOMKI QGA-D quadrupole mass spectrometer. During the analysis, the sample was kept at a high vacuum (10⁻⁵-10⁻⁶ mbar) and was measured at a heating rate of 10 °C/min over the range of 25 °C (room temperature) to 700 °C, using a 5.60 mg sample in stainless steel crucibles.

Unfortunately, pure material could not be prepared from the new mineral owing to its close association with other ammonium sulfates. Therefore, the thermogravimetric curves obtained are quite complex (Fig. 3). On the DTG curve, nine thermal decomposition steps can be distinguished. The first three mass losses are 1.88, 0.54, and 3.24 wt.% observed at 78, 137, and 235 °C, respectively. These peaks are attributed to the loss of H₂O, from which, at least in part, only the third reaction can be assigned to ammoniomagnesiovoltaite. The first two evolutions of H₂O probably pertain to a tschermigite impurity (López-Beceiro *et al.* 2011). The next two mass losses are 10.13 and 3.23 wt.%, at 306 and 405 °C. They correspond to the simultaneous liberation of H₂O and ammonium. The last four thermal decomposition steps are attributed to the decomposition of sulfates. They are assigned to Fe sulfate (642 and 685 °C), Al sulfate (877 °C), and Mg sulfate (especially >1000 °C).

TABLE 2. THE COMPOSITION OF AMMONIOMAGNESIOVOLTAITE

Constituent	Mean (wt.%)	Range (wt.%)	Stand. Dev.	Probe Standard
SO ₃	47.56	46.59-48.75	1.01	barite
Al ₂ O ₃	3.31	3.25-3.36	0.05	microcline AB
[FeO(total)]	[16.99]	15.99-18.11	0.18	ilmenite A128
Fe ₂ O ₃ *	12.28			
FeO*	5.94			
MnO	1.18	1.11-1.25	0.07	Mn-rich fayalite
MgO	7.02	6.87-7.27	0.16	olivine P140
K ₂ O	0.05	0.05-0.06	0.01	microcline AB
(NH ₄) ₂ O**	3.11			
H ₂ O***	17.72			
Total	98.17			

* Calculated from the equation $(Mg + Fe^{2+} + Mn^{2+}) / (Fe^{3+} + Al) = 5/4$.

** From spectrophotometry (1 analysis)

*** Calculated from the stoichiometry.

From the TG curve, the total sulfate content cannot be determined because the last desulfuration reaction did not terminate until 1012 °C. Thermogravimetric data are summarized in Table 3.

INFRARED SPECTROSCOPY

Synthetic ammoniomagnesiovoltaite was prepared using the method of Mereiter (1972). The FTIR spectra of natural and synthetic ammoniomagnesiovoltaite as well as voltaite from Smolník, Slovakia were recorded in the 4000 to 400 cm^{-1} range with a Thermo Nicolet Avatar 320 FT-IR spectrometer using KBr discs (Fig. 4). The spectrum of the natural ammoniomagnesiovoltaite sample shows a broad band due to O–H stretching from 3735–2615 cm^{-1} with a peak at 3423 cm^{-1} and a shoulder at 3263 cm^{-1} . The absorption band at 1641 cm^{-1} is due to H–O–H bending, indicating the presence of molecular water. The diagnostic band at 1431 cm^{-1} indicates the presence of ammonium. A strong split band at 1122 and 1065 cm^{-1} is attributable to the $(\text{SO}_4)^{2-}$ asymmetric stretch ν_3 , a weak band at 1014 cm^{-1} is attributable to the $(\text{SO}_4)^{2-}$ symmetric stretch ν_1 , and a band at 594 cm^{-1} is attributable to the $(\text{SO}_4)^{2-}$ asymmetric bend ν_4 . Finally, a band at 474 cm^{-1} is due to $(\text{SO}_4)^{2-}$ symmetric bend ν_2 (*cf.* Lane 2007). Bands between 3000 and 2000 cm^{-1} are spectral artefacts.

The spectra of natural and synthetic ammoniomagnesiovoltaite are practically identical. The spectrum of ammoniomagnesiovoltaite is very similar to that of voltaite, with the only difference being that ammoniomagnesiovoltaite exhibits a strong absorption band at *ca.* 1430 cm^{-1} owing to the presence of $(\text{NH}_4)^+$.

RELATED MINERALS

The chemical formula of the voltaite-group minerals can be expressed as $\text{R}^+_2\text{R}^{2+}_5\text{R}^{3+}_4(\text{SO}_4)_{12}\cdot 18\text{H}_2\text{O}$. Although the voltaite structure can accommodate a wide variety of cations, as studies of synthetic materials show (*e.g.*, Gossner & Fell 1932), only two additional members besides voltaite had been added to the group until now: zincvoltaite (Li *et al.* 1987), $\text{K}_2\text{Zn}_5\text{Fe}^{3+}_3\text{Al}(\text{SO}_4)_{12}\cdot 18\text{H}_2\text{O}$, and pertlikite (Ertl *et al.* 2008), $\text{K}_2(\text{Fe}^{2+}, \text{Mg})_2(\text{Mg}, \text{Fe}^{3+})_4\text{Fe}^{3+}_2\text{Al}(\text{SO}_4)_{12}\cdot 18\text{H}_2\text{O}$. The thallium-bearing end-member, “monsmedite” (Götz *et al.* 1968), $\text{Tl}_2\text{O}_3\cdot \text{K}_2\text{O}\cdot 8\text{SO}_3\cdot 15\text{H}_2\text{O}$, was discredited (Johan *et al.* 2009, Kovács-Pálffy *et al.* 2011).

TABLE 3. THERMOGRAVIMETRIC DATA OF CONTAMINATED AMMONIOMAGNESIOVOLTAITE

Peak temperature on the DTG curve (°C)	Mass lost (%)	Released component(s)	Phase*
78	1.88	H ₂ O	T
137	0.54	H ₂ O	T
235	3.24	H ₂ O	AMV, T
306	10.13	H ₂ O + NH ₃	AMV
405	3.23	H ₂ O + NH ₃ + (SO ₃)	AMV, T
642	22.11	SO ₃	AMV
685	4.14	SO ₃	AMV
877	15.36	SO ₃	AMV, T
987	> 0.96 (not terminated)	SO ₃	AMV

* AMV = ammoniomagnesiovoltaite, T = tschermigite

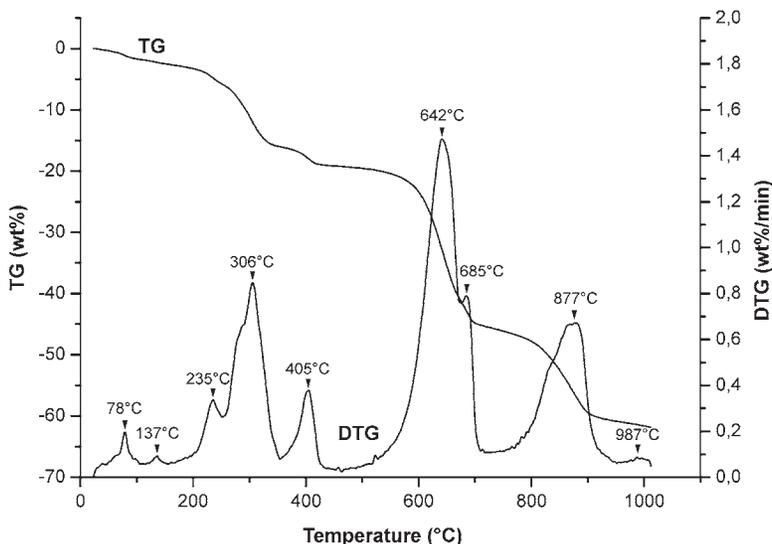


FIG. 3. TG and DTG curves of natural contaminated ammoniomagnesiovoltaite.

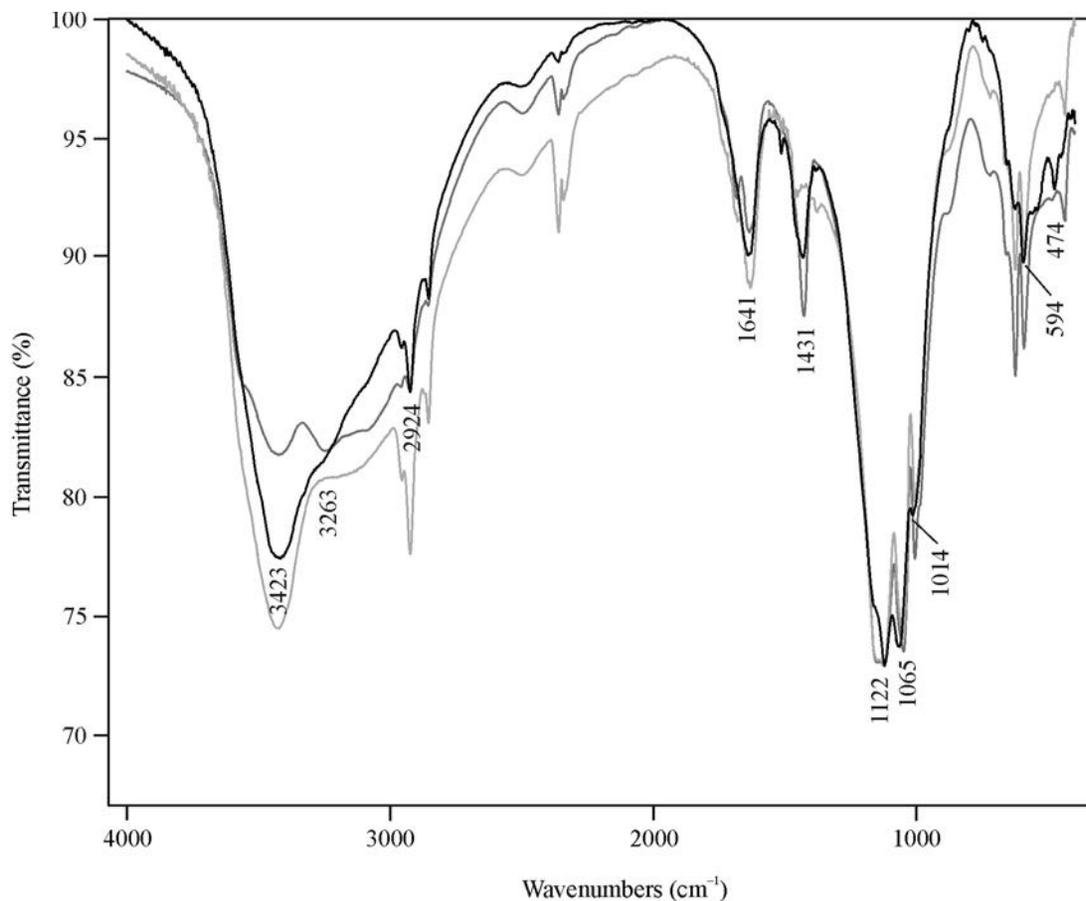


FIG. 4. FTIR spectra of natural (black) and synthetic (medium grey) ammoniomagnesiovoltaite, as well as a natural voltaite from Smolník, Slovakia (light grey). Wavenumbers of IR absorption bands are indicated only for natural ammoniomagnesiovoltaite.

We have described the fourth member of the voltaite group, ammoniomagnesiovoltaite, in which ammonium is the dominant monovalent cation. As a synthetic phase, “ammonium-magnesium-voltaite” was investigated by Gossner & Fell (1932). This synthetic material is rather different than the mineral we have described here. It forms pale greenish hexahedral crystals with narrow faces of rhombic dodecahedron. Its unit cell is much larger ($a = 27.42 \text{ \AA}$) and its density is lower (2.375 g/cm^3) than ammoniomagnesiovoltaite.

All the members of the voltaite group are listed in Table 4.

ACKNOWLEDGMENTS

The first samples were collected by Csaba Papp (Pécs). We are indebted to Ferenc Mádai (University of Miskolc) for his help with the optical studies, Norbert

Zajzon (University of Miskolc) for the measurement of density, Mária Földvári (Hungarian Geological Institute, Budapest) for interpretation of thermal data, and László Kótai (Institute of Materials and Environmental Chemistry, Research Center for Natural Sciences, Hungarian Academy of Sciences) for preparing of the synthetic material. Both referees, Andreas Ertl (Institut für Mineralogie und Kristallographie, Universität Wien, Austria) and Joel D. Grice (Canadian Museum of Nature, Ottawa, Canada), as well as Associate Editor Olga Yakubovich, and Editor Robert F. Martin, are highly acknowledged for comments and suggestions that helped to improve the manuscript. The work described was carried out as part of the project TÁMOP-4.2.1.B-10/2/KONV-2010-0001 in the framework of the New Hungarian Development Plan. The realization of this project is supported by the European Union, co-financed by the European Social Fund.

TABLE 4. COMPARATIVE DATA FOR THE MINERALS OF THE VOLTAITE GROUP

Name	Voltaite	Zincovoltaite	Pertlikite	Ammonio- magnesiovoltaite
Formula	$K_2Fe^{2+}_5Fe^{3+}_3Al(SO_4)_{12} \cdot 18H_2O$	$K_2Zn_5Fe^{3+}_3Al(SO_4)_{12} \cdot 18H_2O$	$K_2(Fe^{2+},Mg)_2(Mg,Fe^{3+})_4Fe^{3+}_2Al(SO_4)_{12} \cdot 18H_2O$	$(NH_4)_2Mg_5Fe^{3+}_3Al(SO_4)_{12} \cdot 18H_2O$
Crystal system	Cubic	Cubic	Tetragonal	Cubic
Space group	$Fd\bar{3}c$	$Fd\bar{3}c$	$I4_1/acd$	$Fd\bar{3}c$
a (Å)	27.254(8)	27.180(1)	19.2080(3)	27.260(2)
c (Å)			27.2158(7)	
V (Å ³)	20244	20079(2)	10041.2(6)	20257(2)
D _{calc.} (g/cm ³)	2.663	2.767	2.56	2.351
Reference	Mereiter (1972)	Li <i>et al.</i> (1987)	Ertl <i>et al.</i> (2008)	This study

REFERENCES

- CHESNOKOV, B.V., SHCHERBAKOVA, E.P., & NISHANBAEV, T.P. (2008) *Minerals of burned dumps of Chelyabinsk coal basin*. Institute of Mineralogy, Ural Division, Russian Academy of Sciences, Miass (in Russian).
- ERTL, A., DYAR, M.D., HUGHES, J.M., BRANDSTÄTTER, F., GUNTER, M.E., PREM, M., & PETERSON, R.C. (2008) Pertlikite, a new tetragonal Mg-rich member of the voltaite group from Madeni Zakh, Iran. *Canadian Mineralogist* **46**, 661-669.
- GOMBOCZ, E. (1945) *Diaria Itinerum Pauli Kitaibelii 1*. Mitteilungen der Ungarischen Naturwissenschaftlichen Museums, Budapest.
- GOSSNER, B. & FELL, E. (1932) Beitrag zur Kenntnis voltaitartiger Sulfate. *Berichte der Deutschen Chemischen Gesellschaft* **65**, 393-395.
- GÓTZ, A., MIHÁLKA, S., IONIȚĂ, I., & TÓTH, Z. (1968) Monsmeditul – un nou mineral de taliu de la Baia Sprie [Monsmedite – a new thallium mineral from Baia Sprie]. *Revista Minelor* **19(4)**, 154-159 (in Romanian).
- JOHAN, Z., UDUBAŞA, G., & ZEMANN, J. (2009) “Monsmedite”, a discredited potassium thallium sulphate mineral from Baia Sprie and its identity with voltaite: The state of the art. *Neues Jahrbuch für Mineralogie - Abhandlungen* **186**, 63-66.
- KOVÁCS-PÁLFFY, P., MUSKE, J., FÖLDVÁRI, M., KÓNYA, P., HOMONNAY, Z., NTAFLÓS, T., PAPP, G., KIRÁLY, E., SAJÓ, I., SZILÁGYI, V., & BOZSÓ, G. (2011) Detailed study of “monsmedite” specimens from the original (1963) find, Baia Sprie, Baia Mare ore district (Romania). *Carpathian Journal of Earth and Environmental Sciences* **6**, 321-330.
- LANE, M.D. (2007) Mid-infrared emission spectroscopy of sulfate and sulfate-bearing minerals. *American Mineralogist* **92**, 1-18.
- LI, W., CHEN, G., & SUN, S. (1987) Zincovoltaite – a new sulfate mineral. *Acta Mineralogica Sinica* **7**, 307-312 (in Chinese with English abstract).
- LÓPEZ-BECEIRO, J., PASCUAL-COSP, J., ARTIAGA, R., TARRÍO-SAAVEDRA, J., & NAYA, S. (2011) Thermal characterization of ammonium alum. *Journal of Thermal Analysis and Calorimetry* **104**, 127-130.
- MANDARINO, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Canadian Mineralogist* **19**, 441-450.
- MEREITER, K. (1972) Die Kristallstruktur des Voltaits, $K_2Fe^{2+}_5Fe^{3+}_3Al[SO_4]_{12} \cdot 18H_2O$. *Tschermaks Mineralogische Petrographische Mitteilungen* **18**, 185-202.
- NÉMEDI VARGA, Z. (ed.) (1995) A mecseki feketeköszén kutatása és bányaföldtana [Exploration and mining geology of the black coal in the Mecsek Mts.]. In Zsámboki, L. (series ed.). *Közlemények a magyarországi ásványi nyersanyagok történetéből*, Vol. 7. Miskolci Egyetem, Miskolc (in Hungarian).
- PARAFINIUK, J. & KRUSZEWSKI, L. (2009) Ammonium minerals from burning coal-dumps of the Upper Silesian Coal Basin (Poland). *Geological Quarterly* **53**, 341-356.
- SZAKÁLL, S. & KRISTÁLY, F. (2008) Ammonium sulphates from burning coal dumps at Komló and Pécs-Vasas, Mecsek Mts., South Hungary. *Mineralogia. Special Papers* **32**, 155.
- ŽÁČEK, V. & POVONDRA, P. (1988) New mineralogical data of rostit from Libušín, Central Bohemia, Czechoslovakia. *Neues Jahrbuch für Mineralogie – Monatshefte*, 476-480.

Received October 24, 2011, revised manuscript accepted March 5, 2012.