DETAILED STUDY OF "MONSMEDITE" SPECIMENS FROM THE ORIGINAL (1963) FIND, BAIA SPRIE, BAIA MARE ORE DISTRICT (ROMANIA)

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Abstract: "Monsmedite", originally described as a unique, Tl(III)-rich mineral of $Tl_2O_3 \cdot K_2O \cdot 8SO_3 \cdot 15H_2O$ formula from Baia Sprie, Romania, was reinvestigated using authentic specimens from the original finder of the mineral. "Monsmedite" is discredited as voltaite but the discreditation was based on specimens of unspecified origin, as the type material had been lost. Open questions related to the Tl-content and the limited scope of investigations done prior to the discreditation of "monsmedite" prompted this study. The presented results of the X-ray powder diffraction, thermoanalytical, IR-spectroscopic, Mössbauer spectroscopic, scanning electron microscopic and different kinds of chemical investigations confirmed that our "monsmedite" is Tl(I)-bearing voltaite but revealed a wide variability of Tl-content, reaching up to 7.49 wt% Tl_2O. Empirical formula of "monsmedite" (from full chemical analysis of two samples) is:

$K_{1.52-1.77}Tl^+_{0.23-0.33}Fe^{2+}_{1.79-1.91}Mn^{2+}_{0.84-2.16}Zn^{2+}_{0.51-0.64}Mg^{2+}_{0.06-2.03}Fe^{3+}_{2.63-2.82}Al^{3+}_{1.01-1.50}(SO_4)_{11.92-12.16} \cdot 15.52-17.72H_2O$.

Key words: Monsmedite, Tl-bearing voltaite, Baia Sprie, Romania, XRPD, thermal analysis, IRS, SEM-EDX, Mössbauer spectroscopy, chemical analyses.

1. INTRODUCTION

"Monsmedite" was first mentioned in a monograph of the Baia Sprie ore deposit, Baia Mare district (Romania) written by Manilici et al. (1965) as a new mineral discovered by Götz and his co-workers (1968) in the oxidation zone of the hydrothermal mineralization of the Baia Sprie ore deposit. The name of the species was derived from the Latin name of the locality Baia Sprie: Mons Medius. Manilici et al. (1965) published a brief macroscopic description of the mineral together with some preliminary data (hardness, specific gravity, optical properties), listed the associated minerals and provided the calculated formula of $Tl_2O_3 \cdot K_2O \cdot 8SO_3 \cdot 15H_2O$. In his review of the preliminary description of monsmedite Hey (1968) noted that "the cited composition seems highly improbable and needs confirmation", whereas

Fleischer (1968, 1969) was of the opinion that the data were insufficient to justify a new name, but the composition was unique.

Götz et al. (1968) gave a detailed description including photographs; in addition to the earlier data, they published the results of wet chemical, visual spectroscopic, XRPD (tabulated Debye–Scherrer data), thermoanalytical (DTA curve and numerical TG data) and IR studies (absorption curve). Based on their results, Götz et al. (1968) concluded that monsmedite was a new species with the composition of $K_2O \cdot Tl_2O_3 \cdot 8SO_3 \cdot 15H_2O$ and orthorhombic (pseudocubic) symmetry. This oxide formula can be rewritten as $H_8K_2Tl^{3+}_2(SO_4)_8 \cdot 11H_2O$ (Johan et al. 2009; see Zemann, 1993, for other possible interpretations). The International Mineralogical Association Commission on New Minerals and Mineral Names (1971) approved the mineral as new species.

There were, however, some doubts concerning the validity of the species, especially the trivalent state of Tl was considered strange. Based on theoretical grounds, on the critical analysis of the data of Götz et al. (1968) and on his own single-crystal XRD study of specimens labelled monsmedite from two collections, Zemann (1993) pointed out that "at least part of the material kept in collections as monsmedite from Romania is as a matter of fact (possibly Tl-bearing) voltaite" and urged a new chemical study of type material. Jambor et al. (1995), reviewing the paper of Zemann (1993), concluded that "the results indicate that monsmedite may be voltaite". In 1998 the IMA CNMMN eventually discredited monsmedite as voltaite (Grice & Ferraris 2003). The Commission recommended reserving the name for a possible find of a specimen that corresponds to the description and chemical composition of "monsmedite" (Johan et al. 2009). The "state of the art" of the monsmedite problem was summarized by Johan et al. (2009), who confirmed the identity of their monsmedite samples with voltaite. The experimental part of this paper was confined to single-crystal XRD study and EPMA analyses of four samples from European mineral collections, as the original specimens deposited by Götz and his co-workers in the collection of the local ore mining company (Combinatul Minier Baia Mare) have not been found any more. A specimen from the Mineralogical Institute of the University of Bucharest "which is said to be co-type «monsmedite» from Baia Sprie (no inventory number)" was also found to be voltaite with minor Tl by Johan et al. (2009).

Other papers that gave a shorter or longer description of monsmedite, e.g. that of Bologa (1970, 1977), Rösler (1981), Mureşan et al. (1990),

Udubaşa et al. (1992), Nicolescu (1998), and others dealt with monsmedite as a characteristic mineral for the Baia Mare ore district and have not provided new data except for a new occurrence, the upper part of the Săsar ore deposit (Bologa 1970). Research history of monsmedite was summarized by Papp (2004) in his book on the minerals first described from the Carpathian region.

New data on monsmedite are scarce and, in lack of the original material, they were obtained from museum specimens of unspecified origin. These circumstances prompted us to perform a detailed study of authentic monsmedite specimens received from the private collection of József Muske (Nürnberg, Germany), original finder of the mineral in 1963. This paper presents the results of our X-ray powder diffraction, thermoanalytical, IR-spectroscopic, Mössbauer spectroscopic, scanning electron microscopic and different kinds of chemical investigations, following a summary of earlier data on monsmedite. The first results of this study were published by Kovács-Pálffy et al. (2009).

2. GEOLOGICAL SETTING, PARAGENESIS, FORMATION OF MONSMEDITE

The Baia Mare mining district, located in the north-western part of Romania, is one of the major metallogenetic provinces of the Neogene volcanic chain of the Eastern Carpathians. The ore deposits are hosted by Miocene calc-alkaline volcanic rocks.

The Baia Mare area (Gutâi Mountains; Fig. 1.) includes several important epithermal gold-polymetallic ore deposits (Ilba, Nistru, Săsar, Herja, Baia Sprie, Şuior, Cavnic) and has a long history of mining, beginning in the antiquity.
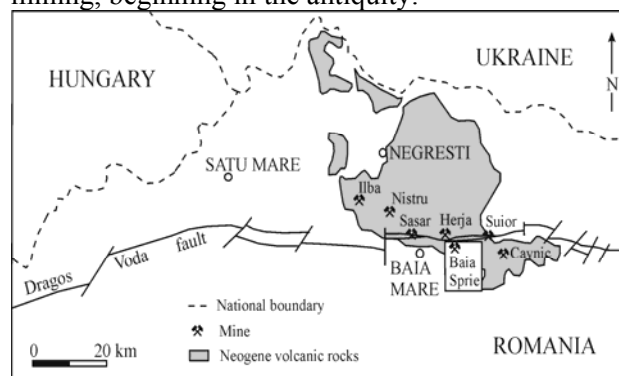

Figure 1. Simplified geological map of the Baia Mare district (Romania) showing the major Dragoş-Vodă fault and the location of the main mines

One of the most important ore deposits is at Baia Sprie. The ore deposit, located in the Mine Hill (Dealul Minei), have two main veins, Principal

("Main vein") and Nou ("New vein"), which are collinear (~E–W) with a regional lineament (Dragoş Vodă fault). Between them lies the NE–SW-trending Diagonal vein. These veins have many branches.

Monsmedite was discovered by one of us (József Muske) in 1963 as a second-year student of the technical school of geology in Baia Mare, during sampling and mapping of the pilot tunnels of the Screper gallery (516 m level), in the oxidation zone of the Rothmundy vein (branch of the Principal vein) on the SE part of the Mine Hill (Fig. 2).
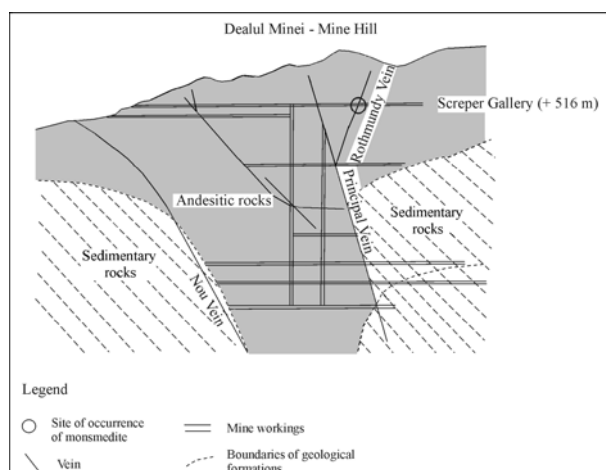

Figure 2. Geological cross section through the Baia Sprie ore deposit at the Mine Hill (after Manilici et al. 1965)

The gallery intercepted the Rothmundy vein at 489 m from the entry of the gallery and traversed it in 17-m length (Götz et al., 1968). Monsmedite was also reported from the upper part of the Săsar ore deposit, Sofia-XXV vein, from the oxidation zone of the mineralization (Bologa 1970). Microprobe data of a sample from this occurrence were published by Johan et al. (2009).

The main ore minerals of the vein are pyrite, sphalerite, galena with accessory amounts of pyragyrite, stephanite, chalcopyrite and stibnite. Dominant gangue minerals are calcite and quartz; dominant secondary minerals are kaolin-group minerals, iron hydroxides and (mainly iron) sulfates. Monsmedite crystals of the 1963 find were found by József Muske in vugs arranged in the middle of the vein in 1-2 m length. According to Götz et al. (1968) the vugs (that they call geodes) contained barite and marcasite and were filled by a white mass of iron sulfate(s) resembling cotton wool. Smaller monsmedite crystals were found grown on marcasite, intergrown with barite and (the larger and better-formed crystals and crystal groups) were embedded in the iron sulfate mass.

Götz et al. (1968) concluded that monsmedite formed as a result of hypergene alteration of Tl-containing hydrothermal sulfide ores and K-containing gangue minerals. The presence of Tl is characteristic in the gold-silver ore deposits from Baia Mare district, as trace elements in galena, sphalerite and pyrite (Giuşcă et al. 1973). The accompanying minerals of monsmedite also have some Tl content: barite 100 ppm, kaolinite 300 ppm, marcasite 100 ppm (Götz et al. 1968). Galena from Baia Sprie may contain 100–500 ppm Tl (Manilici et al. 1965). According to Borcoş et al. (1973) the presence of Tl is characteristic for the Nou Vein in the Baia Sprie deposit.

Giuşcă et al. (1973), Borcoş et al. (1973, 1974a, 1974b), and Bologa (1977) also cited the presence of Tl in pyrite-marcasite from Ramură-III vein at Herja (210 ppm), in pyrite from vein VI at Nistru (30 ppm) and from Ţigher vein (>300 ppm), Diagonal (3-100 ppm), Sofia- XXV (3-50 ppm) and Alexandru-III (3-16 ppm) in different minerals at Săsar ore deposit.

3. MACROSCOPIC DESCRIPTION, MORPHOLOGICAL, OPTICAL AND SIMPLE PHYSICAL PROPERTIES OF MONSMEDITE

The colour is dark green to black, nearly opaque, pitchy, orthorhombic bipyramidal (pseudocubic octahedral) crystals up to 1 cm, but usually only 0.25–0.50 cm in size. The crystal forms observed on the frequently well-formed crystals (Fig. 3) were {001}, {111} and {110}.

In transmitted light, monsmedite is dark green, non-pleochroic. Cleavage is parallel with (100), rarely (111). Biaxial negative, –2V variable, about 52°. The dispersion of the axes is bisymmetric, $\rho > \nu$. Refractive index $n_{average} = 1.608$, birefringence $n_g–n_p = 0.011$, zoning is frequently observable between crossed polarizers. Density 3.0 g/cm^3, Mohs' hardness 2. Soluble in water. The main physical properties of monsmedite and voltaite are presented in the table 1.

Figure 3. Monsmedite crystals (J. Muske collection) (width of the crystal aggregate is 10 mm)

Table 1. Comparison of the physical properties of monsmedite and voltaite

	Monsmedite (Götz et al. 1968)	Voltaite (Anthony et al., 2003 and other handbooks)
Cleavage	parallel with (100), (111)	none
Colour, lustre	dark green to black, pitchy	green to black, resinous
Density	3.00 g/cm^3	2.645 (D_{calc} = 2.663)
Hardness	2	3
Refractive index	$n_{average}$ = 1.608	n = 1.593–1.608
Other optical properties	–2V ≈ 52°, ρ > ν, n_g–n_p = 0.011, zoned	Isotropic, typically sectored with anomalously biaxial parts
Water solubility	Soluble in water, leaves a red-brown residue.	Soluble in water, leaves a lemon residue

4. MATERIALS AND METHODS USED IN THIS STUDY

A few crystals from the private collection of József Muske (Nürnberg, Germany), finder of the mineral, have been used for the reinvestigation of monsmedite. Samples were studied by X-ray powder diffraction, thermal analysis, scanning electron microscopy, IR spectroscopy, Mössbauer spectroscopy and chemical analyses.

X-ray diffraction analysis was done by a Philips PW 1730 diffractometer under the following conditions: Cu K$_\alpha$ radiation, 40 kV acceleration voltage, 30 mA tube current, graphite monochromator, goniometer speed 2° 2θ/min.

Thermoanalytical investigation was executed using a MOM Derivatograph-PC, a computer-controlled simultaneous TG, DTG, DTA apparatus. The tests were carried out in ceramic (corundum) crucible, heated up to 1000 °C. The temperature of the furnace was regulated by a linear heating program at a rate of 10 °C/min. Analytical conditions: air atmosphere, sample mass ~100 mg, and reference material Al$_2$O$_3$.

Infrared spectroscopic analysis was carried out on a Perkin-Elmer 1600 FT-IR spectrometer in the interval 400–4000 cm^{-1}, using a KBr disc.

SEM investigations were made on a JEOL JSM 35 scanning electron microscope equipped with an EDAX unit.

Mössbauer spectroscopic studies were made with a Ranger spectrometer in constant acceleration mode. A standard Ritverc ^{57}Co (Rh) source of about 700 MBq activities was used. Calibration was done against a standard α-Fe foil, which is the reference of the isomer shifts quoted in this paper.

The chemical composition of the samples was determined by:

− Prompt-gamma activation analysis (PGAA) at the Budapest Research Reactor of the KFKI Atomic Energy Research Institute by the Department of Nuclear Research, HAS Institute of Isotopes. The instrument is located at the end of a cold neutron beam, which is extracted from the cold neutron source of the 10-MW research reactor.

− ICP-MS at Geological Institute of Hungary and Chemical Research Centre of Hungarian Academy of Sciences.

− The LA-ICP-MS work (Geological Institute of Hungary) was carried out with a New Wave UP213 laser ablation system coupled to a quadrupole Elan DRC II ICP-MS by Perkin Elmer.

− Electron Microprobe Analysis (EMPA) at University of Vienna, Department of Lithospheric Research.

− HORIBA Jobin Yvone XGT-5000 micro-XRF Analyser at University of Szeged, X-ray Tube: 15 kV and 0,700 mA tube current, Rh target High-Purity Si Detector.

4.1. X-ray powder diffraction

Götz et al. (1968) published tabulated data of their X-ray powder data (Debye–Scherrer pattern, Ni filtered Cu radiation). Of the 15 lines given (see the data of the discredited monsmedite card ICDD 41-1448 in Table 2), the strongest ones were 3.560 (s), 3.403 (vs), 2.860 (s), 2.320 (s), 2.081 (s) and 1.569 Å (s). Zemann (1993) already noted that the XRPD data of monsmedite published by Götz et al. (1963) corresponded "fairly well" to those of voltaite. The comparison of the first X-ray powder diffractogram of monsmedite with the data of the ICDD 20-1388 card of voltaite and with the diffractogram of a reference voltaite sample from Smolník (Slovakia) (obtained from Dr. Gábor Papp – collection of the Hungarian Natural History Museum, Budapest) confirmed this correspondence both in d spacing and intensity values (Table 2, Fig. 4).

The unit-cell parameter of our monsmedite sample, refined by the Rietveld method (LeBail fitting) is a = 27.2587 Å, space group Fd3c. Previous data published for monsmedite are a = 25.29(2) Å (Zemann 1993) and a = 27.235(8) Å (Johann et al. 2009, from Săsar). Cell value and space group corresponds to the data given by the ICDD card 20-1388 for voltaite (a = 27.178 Å) or by those published

by Mereiter (1972) for synthetic voltaite (a = 27.254(8) Å), and a=27.254(8) (Anthony et al. 2003).
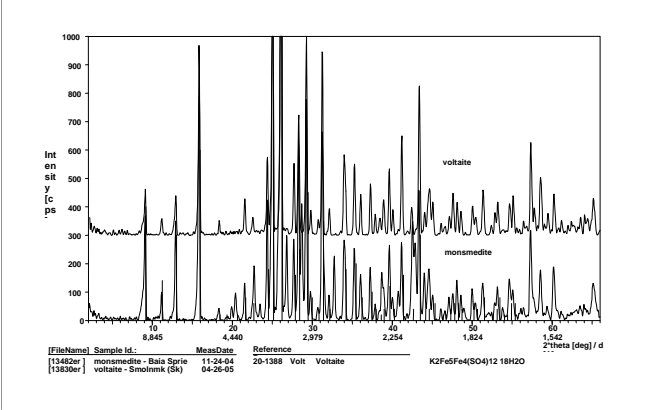

Figure 4. X-ray diffractograms of monsmedite (Baia Sprie) and voltaite (Smolník, SK) with reference values taken from the ICDD 20-1388 card of voltaite

Table 2. X-ray diffraction data of monsmedite (Baia Sprie) and voltaite

Monsmedite This study		Monsmedite Götz et al. (1968) ICDD 41-1448 (NR)		Voltaite Smolník (SK)		Voltaite ICDD 20-1388	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
9.571	16			9.612	11	9.630	40
7.844	4			7.844	4	7.860	14
6.791	15			6.806	9	6.800	30
5.553	41	5.485	10	5.558	31	5.550	60
4.101	6			4.105	8	4.100	8
3.636	15			3.638	18	3.630	18
3.545	58	3.560	40	3.545	83	3.540	80
3.399	100	3.403	100	3.405	100	3.400	100
3.208	12	3.181	5	3.209	16	3.200	16
3.141	26			3.144	27	3.140	25
3.042	33	3.063	10	3.043	45	3.030	45
(2.988	4			2.988	6	2.980	8
2.852	28	2.860	40	2.855	41	2.850	35
2.627	12	2.647	10	2.630	18	2.620	18
2.537	11	2.526	5	2.539	16	2.530	20
2.481	7	2.474	10	2.485	9	2.480	8
2.406	8			2.407	12	2.400	10
2.321	7	2.320	40	2.309	8	2.330	2
2.267	11			2.270	15	2.270	12
2.078	4	2.214	10	2.082	34	2.080	30
2.186	12	2.167	10	2.187	22	2.180	16
2.082	19	2.081	40	2.082	34	2.080	30
1.887	6	1.877	10	1.888	7	1.885	6
1.719	5			1.719	7	1.714	8
1.605	13			1.605	21	1.601	20
1.573	8	1.569	40	1.574	12	1.570	12

4.2. Thermal analysis

The thermoanalytical (DTA) curve (Fig. 5a) published by Götz et al. (1968) showed two very large endothermic peak, according to the text the two

reactions took place between 260–340 °C with maximum temperature at ~310 °C and between 660–780 °C with maximum temperature at ~730 °C, respectively. The measured mass losses are presented in table 3. For comparison, the same samples were used (Figs. 5b–c) as in the XRPD study.
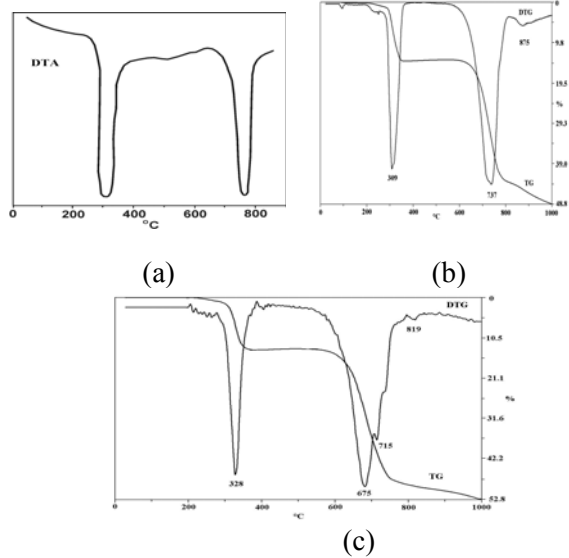

(a)   (b)

(c)

Figure 5. Thermoanalytical curves of (a–b) monsmedite from Baia Sprie: a) Götz et al. (1968), b) this study and (c) of voltaite from Smolník, Slovakia, this study.

Table 3. Thermoanalytical parameters of monsmedite (Baia Sprie) and voltaite (Smolník, SK)

	Monsmedite			Voltaite	
	Götz et al. (1968)	this study		this study	
Sample weight (mg)	no data	98.2		24.5	
Peak temperature/mass loss	°C	°C	%	°C	%
		94	0.11		
	310 15.7	309	14.00	328	13.72
	730 49.8	737	29.92	675 (715)	35.42
		875	5.04	>890	2.35
sum	65.5	49.07		51.49	

The data can be interpreted as follows: the first reaction around 300 °C corresponds to the loss of water, the second main reaction (taken place in several steps) between 700–900 °C corresponds to the liberation of sulphate dominantly bound to iron, subordinately to Al and other substituted elements. The SO_3 bound to potassium does no show thermal reaction below 1000°C.

The rather vague and incomplete thermoanalytical curve published by Götz et al. (1968) is apparently similar to those obtained during this study; however, the mass losses are remarkably different. (This problem can be resolved if we

assume that the value of 49.8 was mistakenly given by Götz et al. (1968) as the mass loss of the second reaction and in fact refers to the whole mass loss.)

4.3. Infrared spectroscopy

Götz et al. (1968) published rather poorly resolved IR absorption spectra for the 400–700, 950–1650 and 2700–3700 cm⁻¹ intervals without tabulated data but with a rough assignment of sulphate and OH bands in the text. The characteristic bands of the IR spectra published by Götz et al. (1968) and those observable in the better resolved spectrum taken during this study (Fig. 6) are practically correspond each other, and these data are in accordance with those published by van der Marel & Beutelspacher (1976) for voltaite (Table 4).
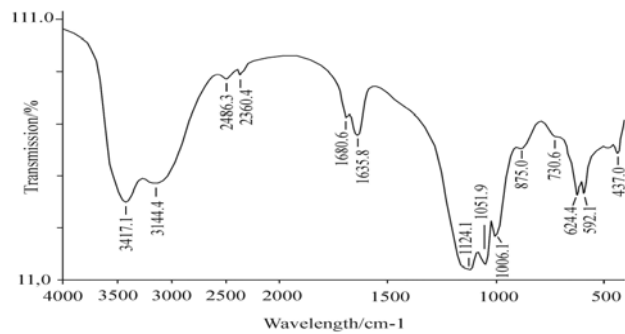

Figure 6. IR spectrum of monsmedite from Baia Sprie (this study).

4.4. SEM morphology and qualitative SEM-EDX data

The morphology of the crystals suggests cubic symmetry, with the cube as dominant form. On the surface of monsmedite, small crystals of barite can be observed (Fig. 7).
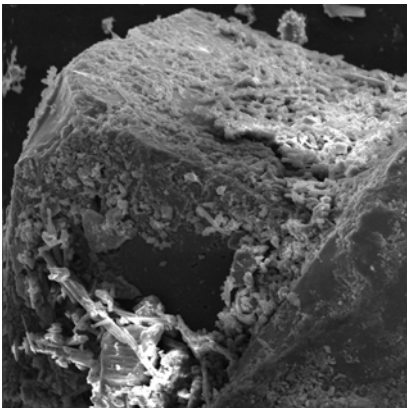

Figure 7. Barite on monsmedite. SEM micrograph by Kákay, Sz. O., 220x

Table 4. Characteristic IR adsorption bands of monsmedite (Baia Sprie) and voltaite.

Monsmedite		Voltaite	Band assignment
Götz et al. (1968)	this study	van der Marel, Beutelspacher (1976)	
cm⁻¹	cm⁻¹	cm⁻¹	
		3560	
2800–3700 (broad band)	3417	3385	ν OH of water
	3144	3220	
	2486	2450	
	2360	2290	
	1680	1665	δ OH of water
~1600	1636	1625	
~1480			
~1150	1124	1118	v_3SO_4
~1050	1052	1048	
~1000	1006	1000	
	875	840	
	731	786	
		695	
		676	
		666	
~650	624	630	v_4SO_4
~600	592	598	
		465	
~450			
	437		v_2SO_4

Several qualitative EDX point analyses were made on the monsmedite crystal faces. The main elements found were S, Al, K, Mg, and Tl.
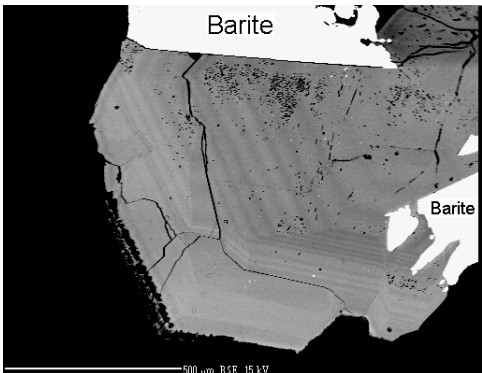

Figure 8. Zoned monsmedite crystal with barite inclusions. BSE (image by Ntaflos, Th.)

The BSE image (Fig. 8) of the sample shows zonality. The main different between the composition of the lighter and darker zones based on the EMP analysis reflected in the Tl₂O and K₂O

content (dark: $Tl_2O=2.33$, $K_2O=4.1$ and light: $Tl_2O=4.04$, $K_2O=3.7$ %).

4.5. Mössbauer spectroscopy

Two and three doublet evaluations resulted in significant misfits and anomalously high line width. A four-doublet evaluation proved to be satisfactory (rel. $\chi^2 = 1.07$). The analysis revealed two Fe^{III} and two Fe^{II} components. On the basis of the isomer shifts, all the four components can be assigned to sixfold coordination. The Fe^{II} as well as the Fe^{III} components differ in their quadrupole splittings, indicating difference in the symmetry of their ligand environment (Table 5.).

Table 5. Mössbauer parameters of monsmedite from Baia Sprie and voltaite from Smolník (Slovakia), registered at room temperature. Isomer shifts are given relative to α-Fe.

Species	Isomer shift (δ) mm/s	Quadrupole splitting (Δ) mm/s	Line width (FWHM), mm/s	Spectral area ratio % (± 1)
Monsmedite 2010/1				
Fe^{II}(1)	1.35(3)	1.87(6)		15.9
Fe^{II}(2)	1.35(2)	1.41(5)	0.45(2)	22.0
Fe^{III}(1)	0.41(1)	0.75(7)		19.9
Fe^{III}(2)	0.40(2)	0.24(3)		42.2
Voltaite				
Fe^{II}(1)	1.270(2)	1.758(8)		35.7
Fe^{II}(2)	1.308(5)	1.33(1)	0.357(4)	21.1
Fe^{III}(1)	0.448(5)	0.72(2)		10.2
Fe^{III}(2)	0.410(5)	0.23(1)		33.0

On the basis of the expected Fe environments in the crystal structure of monsmedite, it is assumed that Fe^{III}(1) represents FeO_6 octahedra, while Fe^{III}(2) belongs to $FeO_4(H_2O)_2$ octahedra. For the Fe^{II} components, a similar assignment can be suggested, but it is not straightforward to find out which doublet belongs to which ligand environment. In principle, in such a structure, altogether six different octahedral environment can be expected: $Fe^{II}O_6$, $Fe^{III}O_6$, cis-$Fe^{II}O_4(H_2O)_2$, trans-$Fe^{II}O_4(H_2O)_2$, cis-$Fe^{III}O_4(H_2O)_2$, and trans-$Fe^{III}O_4(H_2O)_2$. However, even if all these environments were present, overlapping of the doublets would make it impossible to evaluate the spectra with a six-doublet model reliably. The spectral area contributions are considered as molar ratios (possible differences in the Mössbauer–Lamb factors are neglected). One has to note here that while the ratio of Fe^{II} and Fe^{III} can be measured very accurately because of the significant separation of the doublets in the Mössbauer spectrum, the ratio of the different

ligand environments within either Fe^{II} or Fe^{III} is strongly affected by parameter correlations (Fig. 9).
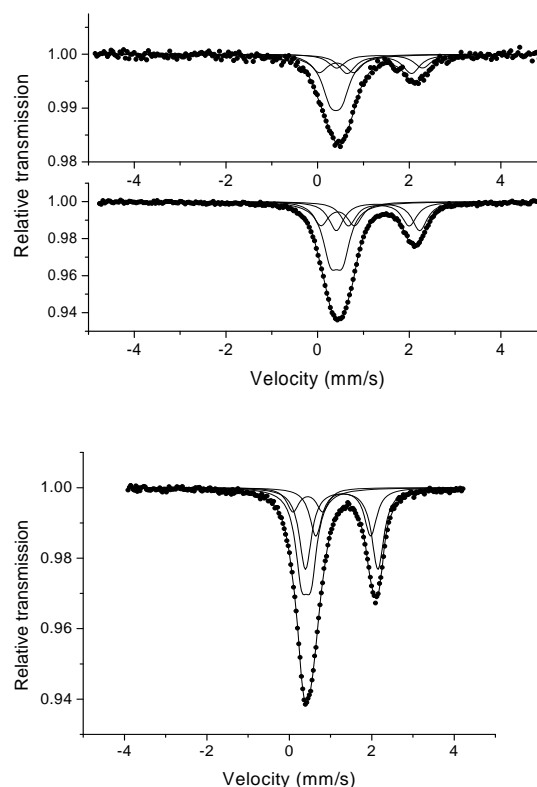

Figure 9. Mössbauer spectra of monsmedite from Baia Sprie (over) and voltaite from Smolník (Slovakia) (down) registered at room temperature. The velocity scale refers to α-Fe.

It can thus be safely concluded that this monsmedite sample contains both iron(II) and iron(III) in a molar ratio of 37.9:62.1, respectively. Both iron forms includes at least two different octahedral ligand environments with 'O' and 'H₂O' ligands as discussed above.

5. CHEMICAL ANALYSES

According to Götz et al. (1968), wet chemical analysis on 0.1 g monsmedite sample gave (in wt%) Tl_2O_3 28.70 (misprint for 28.80, see Johan et al. 2009), K_2O 5.45, Fe_2O_3 1.16, SO_3 47.54, H_2O 16,17, and $MnO + ZnO + CaO + BaO + Al_2O_3$ *0.50 (*by spectroscopic analysis), total 99.52. Trace elements (0.001–0.01%, by spectroscopic analysis): Pb, Cd, Mg, Sb, Cu, As, Si. From these data Götz et al. (1968) calculated the oxide formula of $K_2O \cdot Tl_2O_3 \cdot 8SO_3 \cdot 15H_2O$ for monsmedite. The formula was rewritten to $H_8K_2Tl^{3+}_2(SO_4)_8 \cdot 11H_2O$ by Johan et al. (2009), which corresponds to $Tl_2O_3 = 31.25\%$. Zemann (1993) and Johan et al. (2009) pointed out, that the sums of FeO and Fe_2O_3 in their monsmedite analyses are strikingly close to the amount of Tl_2O_3 in

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the original analysis, although this value was explicitly given by Götz et al. (1968) as an average of two values obtained by two independent analytical methods for Tl. Zemann (1993) and Johan et al. (2009) also gave reasons that Tl in monsmedite should obviously be in monovalent state.

Table 7. Chemical composition and atomic numbers for formula unit of monsmedite from Baia Sprie (calculated to 48 O atoms)

	Monsmedite from Baia Sprie		Monsmedite from Săsar	Voltaite theoretical
	(1)	(2)	(3)	Anthony et al. (2003)
Al_2O_3	3.92	2.38	2.46	–
Fe_2O_3*	10.75	7.75	10.64	15.52
FeO*	6.56	10.05	14.91	17.46
MgO	4.18		0.76	–
MnO	3.03	7.11		–
ZnO	2.11	2.40	1.04	–
K_2O	3.67	3.87	4.54	4.64
Tl_2O	2.49	3.27	0.09	–
SO_3	48.70	45.10	46.06	46.68
H_2O	14.59**	18.07***	19.34***	15.76
Total	100.00	100.00	99.84	99.99
Al	1.5	1.01	1.01	–
Fe^{3+}	2.63	2.82	2.80	4
$\Sigma_{Al+Fe^{3+}}$	4.13	3.83	3.81	4
Fe^{2+}	1.79	1.91	4.36	5
Mg	2.03		0.40	–
Mn	0.84	2.16		–
Zn	0.51	0.64	0.27	–
$\Sigma_{Fe^{2+}+Mg+Mn+Zn}$	5.17	4.71	5.03	5
K	1.52	1.77	2.02	2
Tl	0.23	0.33	0.01	–
Σ_{K+Tl}	1.75	2.10	2.03	2
SO_3	11.92	12.16	12.08	12
H_2O	15.52	17.72	21.20	18

(1) MicroXRF (sample 2010/3), this study; (2) EMPA, average of 20 point analyses, this study; (3) EMPA, average of 10 point analyses, column "D" in Table 1 in Johan et al. (2009).
* Total measured Fe split into Fe^{2+} and Fe^{3+} according to Mössbauer measurements.
** Determined by thermal analysis
*** Difference to 100%

As Tl-content is a basic issue in the monsmedite problem, several monsmedite crystals were investigated during this study with different methods in different institutes to determine the Tl-content. Based on the new chemical analyses, Tl_2O content of monsmedite varies between 1.05–7.49% (Table 6). Based on this variability, we don't exclude the possibility of an even higher Tl-content for monsmedite. Considerable Mg, Mn^{2+} and Zn^{2+} content of monsmedite is in accordance with the substitutions reported for Fe^{2+} in voltaite.

Table 6. Tl-content (wt%) of monsmedite from Baia Sprie

	(1)	(2)		(3)	(4)	(5)	(6)
Method	Wet	ICP-MS	LA-ICP-MS	ICP-MS	PGAA	Micro XRF	EMPA
n	2	1	3	1	3	4	20
Tl_2O_3	28.7	–	–	–	–	–	–
Tl_2O		2.23	2.64–3.28	2.90	1.72–7.49	1.69–2.83	1.05–5.08

(1) Götz et al. (1968); (2–6) this study: 2) Geological Institute of Hungary; 3) Chemical Research Centre of the Hungarian Academy of Sciences, 4) Department of Nuclear Research Institute of Isotopes of the Hungarian Academy of Sciences, 5) Department of Mineralogy, Geochemistry and Petrology, University of Szeged, 6) Department of Lithospheric Research, University of Vienna
n – Number of the analyses

Based on the chemical analyses, the empirical formula of monsmedite is about

1. $K^+_{1.52}Tl^+_{0.23}Fe^{2+}_{1.79}Mn^{2+}_{0.84}Zn^{2+}_{0.51}Mg^{2+}_{2.03}Al^{3+}_{1.50}Fe^{3+}_{2.63}(SO_4)_{11.92} \cdot 15.52H_2O$
2. $K^+_{1.77}Tl^+_{0.33}Fe^{2+}_{1.91}Mn^{2+}_{2.16}Zn^{2+}_{0.64}Al^{3+}_{1.01}Fe^{3+}_{2.82}(SO_4)_{12.16} \cdot 17.72H_2O$
3. $K^+_{2.02}Tl^+_{0.01}Fe^{2+}_{4.36}Zn^{2+}_{0.27}Mg^{2+}_{0.4}Al^{3+}_{1.01}Fe^{3+}_{2.80}(SO_4)_{12.08} \cdot 21.2H_2O$

Calculated densities based on the above formulas are 2.72, 2.75, and 2.72 g/cm³. Our determinations give 2.789 g/cm³ by sink-float method.

6. CONCLUSIONS

Our study confirmed the conclusion of Zemann (1992, 1993) that was also supported by Kovács-Pálffy et al. (2009) and Johan et al. (2009), i.e. monsmedite is a Tl-bearing voltaite and supplied further details for the complete characterisation of the mineral, most importantly, revealed that the Tl-content of monsmedite may reach up to 7.49 wt% Tl_2O. Further results of the recent investigations are as follows:

1) The new X-ray diffraction, thermoanalytical and infrared spectroscopy data are very close to those of voltaite and to the published
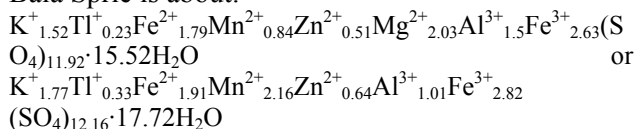
original data of monsmedite.

2) According to the Mössbauer study, the Fe(II): Fe(III) ratio is ~38:62 in the analysed sample.

3) Based on the PGAA, XRMF, EMPA, LA-ICP-MS and ICP-MS data, the Tl_2O content of the mineral varies between 1.05–7.49 wt% (much less than the Tl_2O_3 = 28.7 wt% reported by Götz et al., 1968). There is a considerable Mn^{2+}, Zn^{2+} and Mg for Fe^{2+} replacement in monsmedite.

4) The empirical formula of the two chemically fully analysed monsmedite samples from Baia Sprie is about:

$K^+_{1.52}Tl^+_{0.23}Fe^{2+}_{1.79}Mn^{2+}_{0.84}Zn^{2+}_{0.51}Mg^{2+}_{2.03}Al^{3+}_{1.5}Fe^{3+}_{2.63}(SO_4)_{11.92} \cdot 15.52H_2O$ or $K^+_{1.77}Tl^+_{0.33}Fe^{2+}_{1.91}Mn^{2+}_{2.16}Zn^{2+}_{0.64}Al^{3+}_{1.01}Fe^{3+}_{2.82}(SO_4)_{12.16} \cdot 17.72H_2O$

5) Based on the different analytical results the Tl-content in the voltaite from Baia Sprie something higher as in the samples from Săsar.

Acknowledgement

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