

Gravegliaite, $\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$, a new mineral from Val Graveglia (Northern Apennines, Italy)

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Abstract. A crystallographic and crystal chemical study has been performed on a new mineral, an orthorhombic $\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$ occurring in manganese ores at the Gambatesa Mine (Val Graveglia, Italy), associated with tephroite, bementite, braunite, hausmannite and hematite. Gravegliaite, appearing mainly as few radial aggregates of prismatic crystals, elongated parallel to [010] and up to 0.5 mm long, crystallizes in *Pnma* space group with $a = 9.763(1) \text{ \AA}$, $b = 5.635(1) \text{ \AA}$ and $c = 9.558(1) \text{ \AA}$. It is colourless, transparent, optically biaxial and nonpleochroic with $n_\alpha = 1.590$, $n_\beta = 1.596$, $n_\gamma = 1.636$ and $2V_\gamma = 41^\circ$ ($Z = b$). The strongest lines in the powder pattern are ($d \text{ \AA}$) 6.83, 4.33 and 3.43. Microprobe analyses reveal a good compositional homogeneity and a quasi-ideal chemical composition. The crystal structure refinement confirms this mineral to be the natural analogue of synthetic $\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$ described by previous authors. The attempt to localize hydrogen atoms and to assign hydrogen bonds is discussed, since hydrogen bonds seem to play the major role in assuring cohesion to the structure.

Introduction

The mineralizations occurring in the manganeseiferous layers of the radiolarian cherts in the ophiolitic sequences from the Eastern Liguria (Italy) are well known for the abundance of mineral species which originated during various crystallization phases (Cortesogno, Lucchetti, Penco, 1979;

Lucchetti, Cortesogno and Palenzona, 1988). During recent research a significant number of rare minerals were identified, some of them being new species (Gramaccioli, Griffin and Mottana, 1980, 1982; Lucchetti, Penco, Rinaldi, 1981; Basso, 1987). Recently, in a rock sample collected at Gambatesa Mine (near Reppia, Val Graveglia) another new mineral, an orthorhombic manganese sulfite, was found.

Two synthetic compounds with this chemical composition are known: the corresponding orthorhombic phase, the structural study of which has been performed by means of X-ray and infrared analyses (Baggio and Baggio 1976), and a monoclinic modification (Lutz, El-Suradi and Engelev, 1977).

Up to now, the only two natural sulfites found were scotlandite, PbSO_3 (Paar, Braithwaite, Chen and Keller, 1984; Sarp and Burri, 1984; Pertlik and Zemann, 1985; Green, 1989), and hannebachite, $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$ (Hentschel, Tillmanns and Hofmeister, 1985).

The new mineral has been named gravegliaite from the valley so rich of unusual minerals. The mineral and the name have been approved by the IMA Commission on New Minerals and Mineral Names. Type material is deposited in the collection of the Dipartimento di Scienze della Terra, Sezione di Mineralogia, Università di Genova.

Occurrence and physical properties

The gravegliaite mineralization occurs at the surface of cavities along fractures crosscutting tephroite, bementite, braunite, hausmannite and hematite bearing layers in the cherts (Diaspri of Mt Alpe Formation). In the same fractures, but mainly in the siliceous layers, also chalcocite and rarely alabandite are locally found.

This occurrence primarily leads to the question about the origin of the sulfur, which is lacking in the mineral phases of the manganeseiferous layers. Sulfide phases, mainly pyrite, are however common both in the stratigraphically underlying ophiolitic breccias and in the overlying pelitic levels (Calcari a Calpionella and Argille a Palombini Formations).

In the Ligurian ophiolitic sequences remobilization, by hydrous solutions, and redeposition of sulfides (mainly chalcopyrite and pyrite) constitute a very common feature that often gives rise to concentrations even of economic interest (Cortesogno et al., 1979). The wide range circulation of such solutions, at low thermality ($T < 200^\circ\text{C}$) and commonly S^{2-} -enriched, generally occurs along fractures formed during brittle, mainly tensional, deformative phases, which arise after folding and metamorphic re-equilibration in the prehnite-pumpellyite facies.

Sulfites, intermediate phases between the more common sulfides and sulfates, are rarely observed in nature. Concerning gravegliaite, it can be supposed that, at the contact of the circulating S^{2-} -bearing brines with



Fig. 1. Gravegliaite crystal aggregates.

Mn^{2+} -, Mn^{3+} -, Fe^{3+} -mineral phases, takes place a redox reaction leading to a precipitation of $\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$. The sulfates, possibly formed during this reaction, cannot precipitate owing to their higher solubility.

Gravegliaite appears as euhedral prismatic crystals elongated parallel to $[010]$, up to 0.5 mm long, and as sheaf-like or radial aggregates (Fig. 1), up to 0.2 mm in diameter. The mineral morphology is characterized by two forms: a dominant prism $\{h0l\}$ terminated by dipyrmaid. Very few crystals show a pseudo-hexagonal habit possibly related to twinning. Gravegliaite is colourless, with white streak and vitreous lustre, transparent and non-fluorescent. It presents cleavage parallel to $[010]$ and no fracture.

The mineral is insoluble in water and in ethyl alcohol, soluble in strong acids.

It is biaxial, nonpleochroic and shows strong dispersion. The refractive indices, measured by Becke's method using Cargille's liquids (Na light at 25°C), are: $n_x = 1.590(2)$, $n_\beta = 1.596(2)$, $n_\gamma = 1.636(2)$, $Z = b$. The mineral is optically positive and has an optical axial angle, measured by a five axes universal stage, $2V_\gamma = 41 \pm 3^\circ$ ($2V_{\text{calc}} = 43^\circ$).

The density could not be measured, as other physical and chemical properties, because of the small size and paucity of the crystals ($d_{\text{calc}} = 2.39 \text{ g} \cdot \text{cm}^{-3}$).

The internal consistence among the refractive indices, density and chemical composition, based on the Gladstone-Dale relationship, has been tested; the index $(1 - K_p/K_c) = 0.023$ indicates an excellent compatibility (Mandarino, 1981).

Table 1. Chemical composition of gravegliaite.

	Range	Standard deviation	Mean wt%	Atoms numbers on the basis of 6 oxygens
MnO	36.55–38.46	0.5	37.83	1.01
SO ₂	32.94–34.86	0.4	33.51	0.99
Total			71.34	
H ₂ O ^a			28.66	6.02

^a H₂O wt% evaluated as 100 – sum.

Chemical composition

Thirteen chemical analyses of three different crystals, obtained from the holotype specimen, were performed by means of a Philips SEM 515 electron microscope equipped with an EDAX PV9100 in energy dispersive mode, with an accelerating voltage of 15 kV and beam current of about 2 nA. The pure synthetic compound (NH₄)₂Mn(SO₄)₂ · 6 H₂O was used as standard for both Mn and S. No other element was detected, except traces of Ca in a few cases. Spot analyses show neither compositional zoning in individual crystals nor variation of composition among them over 5 σ for both MnO and SO₂. Because of the paucity of the available mineral the water content could not be measured experimentally, hence the value of H₂O weight percent, reported in Table 1, was calculated by difference.

The empirical formula obtained is very close to the ideal MnSO₃ · 3 H₂O, confirmed by the structural analysis.

X-ray powder diffraction pattern

X-ray powder pattern was obtained by a Gandolfi camera using a Mn-filtered FeK_α radiation. Relative intensities were assigned by visual estimate and the reflections were indexed on the basis of the X-ray powder pattern calculated by the LAZY PULVERIX program (Yvon, Jeitschko and Parthé, 1977). Input data of the calculated pattern were the ideal composition and space group, unit cell parameters, structural model and temperature factors according to X-ray single-crystal analysis. Scattering factors for neutral atoms were used and anomalous dispersion correction was applied.

Unit cell parameters refined from powder data are: $a = 9.762(8)$, $b = 5.639(4)$ and $c = 9.564(9)$ Å. In Table 2 the X-ray powder diffraction data are shown. A few very weak reflections, in the range $1.056 < d < 1.512$ Å, are not reported.

Table 2. X-ray powder diffraction data of gravegliaitc (d in Å).

hkl	Calculated		Measured		hkl	Calculated		Measured	
	d	I	d	I		d	I	d	I
1 0 1	6.380	100	6.83	S	4 2 0	1.845	9	1.851	VW
0 0 2	4.779	38	4.77	W	4 1 3	1.832	13	1.836	VW
2 0 1	4.347	30	4.33	VS	1 3 1	1.811	9	1.812	VW
1 1 1	4.347	98			0 1 5	1.810	7		
1 0 2	4.292	58	3.69	VVW	5 0 2	1.807	4	1.790	VW
2 1 0	3.690	4			1 2 4	1.791	29		
2 1 1	3.442	42	3.43	VS	3 2 3	1.771	6	1.772	VW
2 0 2	3.415	13			2 3 1	1.724	3		
1 1 2	3.415	49	3.024	W	5 1 2	1.721	10	1.726	M
1 0 3	3.029	18			4 2 2	1.721	7		
2 1 2	2.920	11	2.930	VW	1 3 2	1.721	13	1.703	VW
0 2 0	2.817	13	2.818	VVW	2 1 5	1.697	7		
3 1 1	2.703	51	2.704	M	3 1 5	1.582	3	1.586	VVW
2 0 3	2.668	29	2.666	M	6 1 0	1.563	2	1.562	VVW
1 1 3	2.668	5			1 2 5	1.561	6		
1 2 1	2.605	34	2.605	W	2 3 3	1.536	9	1.537	VVW
2 1 3	2.411	51	2.414	M	5 0 4	1.512	8	1.512	VVW
2 2 1	2.364	14	2.362	W	8 2 3	1.056	3	1.056	VW
1 2 2	2.355	15			7 2 5	1.046	3	1.046	VW
4 1 0	2.240	10	2.244	VW	2 5 3	1.038	6	1.039	VW
3 2 1	2.079	6	2.080	VVW	5 4 4	1.031	9	1.030	VW
4 1 2	2.028	8	2.028	VW	4 2 8	1.003	10	1.003	W
3 0 4	1.926	9	1.929	VW	7 4 1	0.986	19	0.987	W
1 0 5	1.876	2	1.877	VVW					

Crystal structure refinement

X-ray data collection was performed on a prismatic crystal with dimensions $0.292 \text{ mm} \times 0.125 \text{ mm} \times 0.063 \text{ mm}$ by means of an Enraf-Nonius CAD-4 automatic single-crystal diffractometer. Cell dimensions were determined and refined from 25 reflections with $19 < \theta < 22$ degrees. The intensity data were collected up to $\theta = 30$ degrees, using graphite monochromatized Mo-radiation and ω - θ scan mode, and corrected for absorption (ψ scan mode: North, Phillips and Scott Mathews, 1968). The crystal structure was refined in $Pnma$ space group starting with the coordinates resulted from the structural analysis of the corresponding synthetic compound (Baggio and Baggio, 1976). Eight cycles of least squares refinement were carried out by a largely modified version of the ORFLS program (Busing, Martin and Levi, 1962), using the scattering factors for neutral atoms from the International Tables for X-ray Crystallography, Vol. IV. Total site occupancy was fixed for Mn and S; scale factor, secondary extinction coefficient, coordinates and temperature factors were simultaneously derived. The anisotropic temperature factors were introduced after the fourth cycle.

Table 3. Crystal and X-ray data for gravegliaite.

Idealized formula	MnSO ₃ · 3 H ₂ O
<i>Z</i>	4
Space group	<i>Pnma</i>
a (Å)	9.763(1)
b (Å)	5.635(1)
c (Å)	9.558(1)
μ (MoK α , mm ⁻¹)	2.95
Measured reflections	1641
Independent reflections	829
Observed reflections $I > 3\sigma(I)$	594
<i>R</i> (observed)	0.036
<i>R</i> (all)	0.058
Extinction parameter	$6.5(9) \times 10^{-4}$

Table 4. Atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) for gravegliaite.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B_H</i> (Å ²)
Mn	0.2236(1)	0.25	0.0622(1)	1.17
S	0.9344(2)	0.25	0.9099(2)	1.01
O1	0.0892(4)	0.25	0.8824(5)	2.03
O2	0.1185(3)	0.5348(6)	0.1716(3)	1.85
O3	0.3686(5)	0.25	0.2367(5)	2.28
O4	0.3638(3)	0.5056(6)	0.9507(3)	1.41

Tables 3, 4 and 5 summarize experimental details and results of the crystal structure refinement.¹

Discussion

The crystal structure refinement confirms gravegliaite to be the natural analogue of the orthorhombic MnSO₃ · 3 H₂O studied by Baggio and Baggio (1976).

According to the description of the structure of these authors, the atomic framework of gravegliaite may be outlined as consisting of slabs running indefinitely along [010]. Each slab is made by a pair of infinite linear sequences, linked together by bridging sulphur atoms, of isolated Mn octahedra. Projecting the structure down *b* axis, each slab may be

¹ Additional material to this paper can be ordered referring to the no. CSD 55015, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik GmbH, W-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 5. Selected interatomic distances (Å) and angles (°) in gravegliaite.

Mn—O1	2.162(4)	S—O1	1.535(4)
2 Mn—O2	2.173(3)	2 S—O2	1.531(3)
Mn—O3	2.187(4)	Average	1.532
2 Mn—O4	2.255(3)		
Average	2.201	2 O1—O2	2.419(4)
		O2—O2''	2.425(6)
		Average	2.421
2 O1—O2	3.209(5)		
2 O1—O4	3.113(4)	2 O1—S—O2	104.18(16)
O2—O2'	3.210(7)	O2—S—O2''	104.75(25)
2 O2—O3	2.987(4)	Average	104.37
2 O2—O4	3.197(4)		
2 O3—O4	3.090(5)		
O4—O4'	2.881(6)		
Average	3.107		
2 O1—Mn—O2	95.50(10)		
2 —O4	89.58(11)		
O2—Mn—O2'	95.24(17)		
2 O2—Mn—O3	86.49(11)		
2 —O4	92.42(11)		
2 O3—Mn—O4	88.14(12)		
O4—Mn—O4'	79.40(15)		
Average	89.91		

Symmetry code: (') = $x, 1/2-y, z$; (") = $x, 3/2-y, z$.

schematically depicted by a parallelogram representing the contour line of the section orthogonal to [010]. The short sides of parallelograms are nearly parallel to [001], the long ones are alternately quasi-parallel to [401] or [40 $\bar{1}$] (Fig. 2). Since only hydrogen bonds seem to play the role of linking neighbouring slabs, in agreement with observed cleavage parallel to [010], an attempt to localize the hydrogen atoms has been made. Some difficulties arose for distinguishing noise from true H peaks using a conventional difference synthesis. Therefore difference maps, calculated removing high-angle reflections, and Fourier maps were also used to improve the chances of finding H atoms (Teller, Bau and Gutlich, 1981).

H3A at 0.445, 0.25, 0.294 and H3B at 0.284, 0.25, 0.305 can be reasonably assumed as the hydrogen atoms forming with O3 oxygen atom one of the water molecules of gravegliaite. The values of O3—H3A (0.93 Å), O3—H3B (1.05 Å), H3A—H3B (1.58 Å) distances and of H3A—O3—H3B angle (105.4°) agree with the common geometry of water molecule in crystalline hydrates.

From O3 two shorter inter-slab O—O distances, O3—O2 (3.050 Å) and O3—O4 (3.351 Å), both repeated by mirror plane, were considered for possible weak and bifurcated hydrogen bonds involving H3A and H3B, respectively. The O2 atom, whose position relative to the O3(donor)—H3A

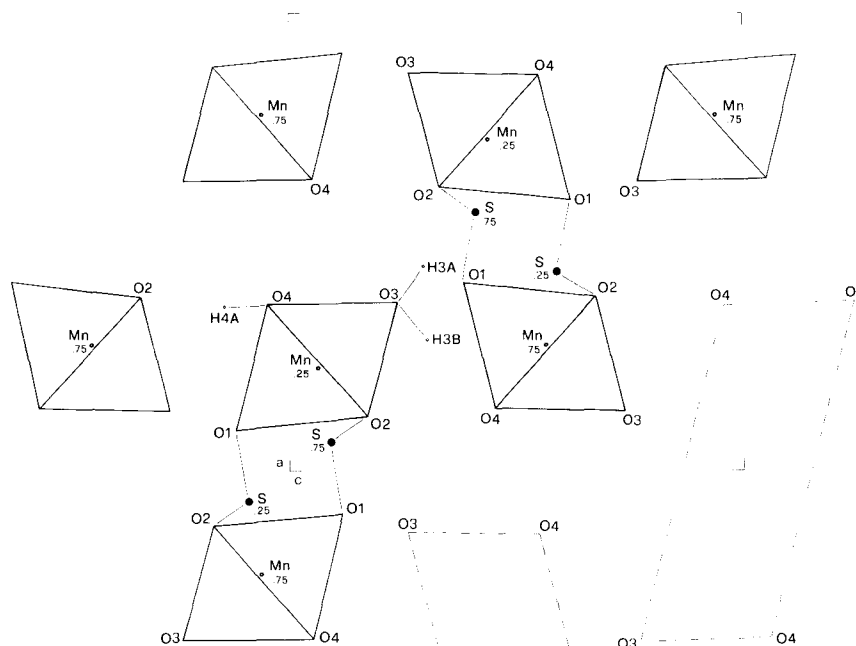


Fig. 2. Schematic picture of gravgliite structure, view along [010].

bond leads to the H3A...O2 distance of 2.36 Å and to the O3–H3A...O2 angle of 131.5°, is expected to act as an acceptor oxygen according to Brown (1976). On the contrary it is hard to establish whether interaction, to be considered a hydrogen bond, takes place between O3 and O4, on account of the very long distances O3–O4 and H3B...O4 (2.43 Å) and the large angular value O3–H3B...O4 = 145.1° (Brown, 1976).

Regarding the other water molecules, H4A at 0.358, 0.505, 0.859 gives a slightly short O4–H4A distance (0.88 Å).

The shortest inter-slab O4–O2 distance (2.683 Å), the H4A...O2 (acceptor) distance (1.82 Å) and the nearly linear bond O4–H4A...O2 angle (167.1°) delineate a good geometry for a strong hydrogen bond (Brown, 1976).

Great difficulties were encountered to determine a reasonably certain position of the second hydrogen atom (H4B) bonded to O4 and consequently to ascertain whether the two short O4–O4 distances, an intra-slab one of 2.754 Å (not octahedral edge) and another inter-slab of 2.822 Å, indicate interactions between pairs of equivalent O4 oxygens to assign to hydrogen bonds. In such a case O4 would act as donor and acceptor oxygen at the same time.

On the basis of the available data a suggestive hypothesis could be to suppose a hydrogen atom delocalized between at least two positions near

Table 6. Empirical bond valences for gravegliaite.

	Mn	S	H3A	H3B	H4A	H4B	Σ
O1	0.37	1.34					1.71
O2	0.36	1.36	0.08		0.21		2.01
O3	0.34	(0.01)	0.84	1.00			2.18
O4	0.28				0.79	1.00	2.07

to a pair of weak peaks in the difference Fourier map (0.358, 0.644, 0.950 and 0.428, 0.515, 0.982). These positions are 0.78 Å and 0.70 Å from the O4 donor oxygen, respectively. Such hypothesis accounts for two facts: both O4–O4 distances, above reported, are well within the range for hydrogen bonds; a hydrogen atom totally assigned to the position suitable to bond the two equivalent O4, pertaining to different slabs (inter-slab bond), infers a too short H–H distance because of the presence of the inversion center. On the other hand this interaction yields an appreciable contribution to the cohesion of the structure.

Unfortunately the bond valence table for gravegliaite, that clearly shows O3 and O4 to be oxygen atoms of water molecules, is not helpful to remove the uncertainties about the doubtful hydrogen bonds and the possible interaction between S and O3 ($\text{S–O3} = 4.438 \text{ \AA}$) suggested by Baggio and Baggio (1976), because the bond valence contributions involved are negligible owing to the empirical procedure of the estimate.

The bond-valence calculation (Table 6) was carried out using the curves of Brown and Altermatt (1985) for manganese, sulphur and oxygen atoms. According to these authors the H...O (acceptor) bond valence has been estimated as a function of the O–O distance and consequently the (donor) O–H valence by subtracting the sum of the H..O (acceptor) valences from 1.0. In agreement with the previous considerations H3B was not considered as involved in hydrogen bond.

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References

- Baggio, R. F., Baggio, S.: Crystal structure and chemical bonding of manganese(II) sulphite trihydrate. *Acta Crystallogr.* **B32** (1976) 1959–1962.
- Basso, R.: The crystal structure of palenzonaite, a new vanadate garnet from Val Graveglia (Northern Apennines, Italy). *Neues Jahrb. Mineral. Monatsh.* (1987) 136–144.
- Brown, I. D.: On the geometry of O–H...O hydrogen bond. *Acta Crystallogr.* **A32** (1976) 24–31.
- Brown, I. D., Altermatt, D.: Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41** (1985) 244–247.

- Busing, W. R., Martin, K. O., Levi, H. A.: ORFLS, a FORTRAN crystallographic least-squares refinement program. U.S. Natl. Tech. Inform. Serv. ORNL-TM-305 (1962).
- Cortesogno, L., Lucchetti, G., Penco, A. M.: Le mineralizzazioni a manganese nei diaspri delle ofioliti liguri: mineralogia e genesi. *Rend. Soc. It. Mineral. Petrol.* **35** (1979) 151–197.
- Gramaccioli, C. M., Griffin, W. L., Mottana, A.: Tiragalloite, $Mn_4[AsSi_3O_{12}(OH)]$, a new mineral and the first example of arsenatotrisilicate. *Am. Mineral.* **65** (1980) 947–952.
- Gramaccioli, C. M., Griffin, W. L., Mottana, A.: Medaite, $Mn_6[VS_i_5O_{18}(OH)]$, a new mineral and the first example of vanadopentasilicate ion. *Am. Mineral.* **67** (1982) 85–89.
- Green, D. I.: Scotlandite from Higher Roughton Gill, Caldbeck Fells, Cumbria. *Mineral. Mag.* **53** (1989) 653.
- Hamilton, W. C.: On the isotropic temperature factor equivalent to a given anisotropic temperature factor. *Acta Crystallogr.* **12** (1959) 609–610.
- Hentschel, G., Tillmanns, E., Hofmeister, W.: Hannebachite, natural calciumsulfite hemihydrate, $CaSO_3 \cdot 1/2 H_2O$. *Neues Jahrb. Mineral. Monatsh.* (1985) 241–250.
- Lucchetti, G., Cortesogno, L., Palenzona, A.: Low-temperature metamorphic mineral assemblages in Mn–Fe ores from Cerchiara Mine (Northern Apennine, Italy). *Neues Jahrb. Mineral. Monatsh.* (1988) 367–383.
- Lucchetti, G., Penco, A. M., Rinaldi, R.: Saneroite, a new natural hydrate Mn-silicate. *Neues Jahrb. Mineral. Monatsh.* (1981) 161–168.
- Lutz, H. D., El-Suradi, S., Engelev, B.: Zur Kenntnis der Sulfite und Sulfithydrate der zink-, mangan-, magnesium- und cobalt-röntgenographischen, spektroskopischen und thermoanalytischen Untersuchungen. *Z. Naturforsch.* **B32** (1977) 1230–1238.
- Mandarino, J. A.: The Gladstone-Dale relationship: part IV. The compatibility concept and its applications. *Can. Mineral.* **19** (1981) 441–450.
- North, A. C. T., Phillips, D. C., Scott Mathews, F.: A semiempirical method of absorption correction. *Acta Crystallogr.* **A24** (1968) 351–359.
- Paar, W. H., Braithwaite, R. S., Chen, T. T., Keller, P.: A new mineral, scotlandite ($PbSO_3$), from Leadhills, Scotland; the first naturally occurring sulphite. *Mineral. Mag.* **48** (1984) 283–288.
- Pertlik, F., Zemann, J.: The crystal structure of scotlandite, $PbSO_3$. *Tschermaks Mineral. Petrogr. Mitt.* **34** (1985) 289–295.
- Sarp, H., Burri, G.: Seconde occurrence du nouveau minéral scotlandite $PbSO_3$. *Schweiz. Mineral. Petrogr. Mitt.* **64** (1984) 317–321.
- Teller, R. G., Bau, R., Gutlich, P.: *Structure and bonding – Metal complexes*. Vol. 44, p. 1–82, Berlin, Heidelberg, New York: Springer-Verlag 1981.
- Yvon, K., Jeitschko, W., Parthé, E.: LAZY PULVERIX, a computer program, for calculating X-ray and neutron diffraction powder patterns. *J. Appl. Crystallogr.* **10** (1977) 73–74.