

Markwelchite, TlPbSbS_3 , a new Tl-Pb sulfosalt from the hydrothermal deposit of Jas Roux, Hautes-Alpes, France

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ABSTRACT

Markwelchite, ideally TlPbSbS_3 , is a new mineral from the hydrothermal deposit of Jas Roux, Hautes-Alpes, France. It occurs as a black anhedral crystal closely associated with protochabournéite. Microhardness measurements (VHN_{15}) gave a mean value of 197 kg/mm^2 corresponding to a Mohs hardness of about 3–4. In plane-polarized incident light, markwelchite is grey in colour. Under crossed polars, it is distinctly anisotropic with greyish white to bluish rotation tints, with bright red internal reflections. Reflectance percentages (R_{\min} and R_{\max}) are: 28.5, 31.5 (471.1 nm), 28.3, 30.7 (548.3 nm), 27.9, 30.3 (586.6 nm), 27.6, 29.8 (652.3 nm). The mean of 5 electron microprobe spot analyses gave Tl 34.67(45), Pb 31.86(25), Sb 15.06(15), As 2.37(5), S 15.35(20), total 99.31 wt%, corresponding, on the basis of a total of 6



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atoms per formula unit and structural results, to $\text{Tl}_{1.063}\text{Pb}_{0.964}(\text{Sb}_{0.775}\text{As}_{0.198})_{\Sigma 0.973}\text{S}_3_{0.000}$. Single-crystal X-ray diffraction studies revealed that markwelchite is isotypic with richardsollyite, TlPbAsS_3 . It is monoclinic, space group $P2_1/c$, with the following unit-cell parameters: $a = 8.9144(3)$, $b = 8.4513(3)$, $c = 8.6511(3)$ Å, $\beta = 108.723(4)^\circ$, $V = 617.27(4)$ Å³ and $Z = 4$. The five strongest observed powder-diffraction lines [d in Å (I_{rel}) (hkl)] are: 3.88 (100) (-211); 3.78 (90) (210); 3.29 (90) (102); 2.73 (85) (-113); 2.93 (75) (022). The crystal structure can be described as formed by (100) $[\text{Me}_2(\text{SbS}_3)]^-$ layers sandwiching the $\text{Me}1^+$ cations. The $\text{Me}1$ site has a seven-fold coordination, whereas the $\text{Me}2$ site has an 6+2 coordination corresponding to a distorted, bicapped trigonal prismatic coordination, and the Sb site displays a trigonal pyramidal coordination with three S atoms and Sb at the apex.

The name markwelchite honours Dr. Mark D. Welch of the Natural History Museum, London (UK).

The new mineral has been approved by the IMA-CNMNC (No. 2024–001). A discussion on the relationships between markwelchite and synthetic TlPbSbS_3 is also provided.

Keywords: markwelchite, TlPbSbS_3 , new mineral, sulfosalt, thallium, richardsollyite, Jas Roux, France.

INTRODUCTION

During a mineralogical study of newly collected samples from the Tl-rich hydrothermal mineralization of Jas Roux, La Chapelle-en-Valgaudemar, Gap, Hautes-Alpes, Provence-Alpes-Côte d'Azur, France (44°44'45''N, 6°19'18''E), a new Tl–Pb mineral was discovered. Details of the geological background of the Jas Roux deposit are given in Johan and Mantiene (2000). The Tl–Hg–Sb–As mineralization occurs within baryte layers mainly hosted in metadolostone and marbles. Johan and Mantiene (2000) gave a full account of the mineralogy of this deposit. Later, Favreau *et al.* (2011) reported an update, citing a total of 57 different

mineral species. Jas Roux is known for the occurrence of ten Tl-mineral species, among which eight have their type locality there: chabournéite (Johan *et al.*, 1981), dewitite (Topa *et al.*, 2020), écrinsite (Topa *et al.*, 2017), ginelfite (Biagioni *et al.*, 2023), jasrouxite (Topa *et al.*, 2013), pierrotite (Guillemin *et al.*, 1970), routhierite (Johan *et al.*, 1974), and vallouiseite (Topa *et al.*, 2023a). Other species first discovered at Jas Roux are laffittite (Johan *et al.*, 1974) and montpelvouxite (Topa *et al.*, 2023b).

This study reports the description of the new mineral markwelchite, together with data on its crystal structure. The new mineral has been approved by the IMA-CNMNC (No. 2024–001). Holotype material is deposited in the Mineralogical Collections of the Natural History Museum of the University of Florence, Italy, under catalogue number 3739/I. Its mineral abbreviation is Mrw.

The name markwelchite honors Dr Mark D. Welch (b. 1960) of the Natural History Museum, London, United Kingdom. Dr. Welch is a well-known mineralogical crystallographer who has researched a wide range of minerals, many of which have complex structures and unusual crystal chemistry.

MATERIAL STUDIED

The geological outcrop, where the sample containing markwelchite was discovered, is located on the north flank of the Torrent de Chabournéou, a small alpine valley at about 2100 m of altitude in the Les Écrins National Park, Hautes-Alpes, France. Jas Roux is a hydrothermal stratiform deposit hosted in dolomitic metalimestones of Triassic age and appears as several sedimentary lenses embedded in the Pigeonnier anatexites. These lenses protrude and form small cliffs parallel to the valley (Boulliard *et al.*, 2010). Samples from this study consist of

boulders weathered out of the cliffs which contained small veinlets of primary sulfosalts accompanied by a variety of secondary minerals.

The sampling site is at 44°48'43.2"N 6°19'20.1"E (Fig. 1). It is at the top of a boulder heap below the middle part of the Jas Roux cliffs and is located at approximately 2,156 m of altitude. The yellow areas outline the Jas Roux cliffs (Fig. 1). Sampling was done by one of us (HGA) in July 2014 with PN authorization no. 280/2014.

Markwelchite is associated with stibnite, twinnite, guettardite, pierrotite, realgar and protochabournéite (Fig. 2), the latter was verified by single-crystal X-ray diffraction.

The formation of markwelchite is linked to the activity of Tl–Pb–Sb-rich fluids during the hydrothermal evolution of the Jas Roux deposit.

PHYSICAL AND OPTICAL PROPERTIES

Markwelchite occurs as a black anhedral crystals up to 40 microns in size and shows a black streak. The mineral is opaque in transmitted light and exhibits a metallic luster. No cleavage is observed, and the fracture is uneven. The calculated density (for $Z = 4$) for the empirical formula and unit-cell parameters obtained by single-crystal X-ray diffraction (see below) is 6.696 g/cm³. The density could not be measured owing to the small grain size. Five micro-indentation measurements carried out with a VHN load of 15 g give a mean value of 197 kg/mm² (range: 188 – 218), corresponding to a Mohs hardness of about 3–4.

In plane-polarized incident light, markwelchite is grey in colour. Under crossed polars, it is distinctly anisotropic, with grayish white to bluish tint rotation tints and bright red internal reflections. Reflectance was measured in air using a Zeiss MPM-200 microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was approximately 3350 K. Readings were taken for specimen and standard (SiC)

maintained under the same focus conditions. Reflectance percentages (R_{\min} and R_{\max}) for the four COM wavelengths are: 28.5, 31.5 (471.1 nm), 28.3, 30.7 (548.3 nm), 27.9, 30.3 (586.6 nm), 27.6, 29.8 (652.3 nm).

CHEMICAL COMPOSITION

A preliminary EDS chemical analysis of the crystal used for the structural study did not indicate the presence of elements ($Z > 9$) other than Tl, Pb, Sb, As, and S. Quantitative analyses (5 spots) were performed using a JEOL 8200 microprobe (WDS mode, 20 kV, 40 nA, focussed beam (1 μm), counting times 20 s for peak and 10 s for background). For the WDS analyses, the following lines were used: $\text{PbM}\alpha$, $\text{TlM}\alpha$, $\text{SbL}\alpha$, $\text{AsL}\alpha$, $\text{SK}\alpha$. Iron, Cu, Zn, Ag, and Se were sought but found below the detection limit (0.02 wt%). The crystal fragment was homogeneous within analytical error. Chemical data and analytical details are given in Table 1.

The empirical chemical formula based on 6 atoms per formula unit and structural (see below) is $\text{Tl}_{1.063}\text{Pb}_{0.964}(\text{Sb}_{0.775}\text{As}_{0.198})\Sigma_{0.973}\text{S}_{3.000}$. The simplified formula is $\text{TlPb}(\text{Sb,As})\text{S}_3$. The ideal chemical formula is TlPbSbS_3 , which requires Tl 32.47, Pb 32.91, Sb 19.34, S 15.28, total 100.00 wt%.

X-RAY DIFFRACTION STUDIES

Single-crystal X-ray studies were conducted using a Bruker D8 Venture diffractometer equipped with a Photon III detector using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Markwelchite is monoclinic, with the following unit-cell parameters: $a = 8.9144(3)$, $b = 8.4513(3)$, $c = 8.6511(3) \text{ \AA}$, $\beta = 108.723(4)^\circ$, $V = 617.27(4) \text{ \AA}^3$ and $Z = 4$.

Powder X-ray diffraction study (PXRD) was carried out using the same instrument but with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The diffraction rings from markwelchite were converted

into a conventional XRD pattern. Crystal-to-detector distance was 7 cm. Observed and calculated X-ray powder diffraction data for markwelchite are given in Table 2. The unit-cell parameters from the PXRD data are: $a = 8.9057(9)$, $b = 8.4376(8)$, $c = 8.6355(10)$ Å, $\beta = 108.646(8)^\circ$, $V = 614.83(7)$ Å³.

CRYSTAL STRUCTURE REFINEMENT

Single-crystal X-ray diffraction intensity data were integrated and corrected for standard Lorentz-polarization factors and absorption with APEX3 (Bruker, 2016). A total of 1803 unique reflections were collected. The statistical tests on the distribution of $|E|$ values ($|E^2-1| = 0.912$) indicated the presence of an inversion center. Systematic absences with the space group $P2_1/c$. Given the similarity of the unit-cell values, space group, and general stoichiometry, the structure was refined using the atomic coordinates given for richardsollyite, TlPbAsS_3 (Meisser *et al.*, 2017), through Shelxl-2014 (Sheldrick, 2015). Table 3 reports details of the selected crystal, data collection, and refinement.

In the crystal structure of markwelchite, similar to richardsollyite, there are three cation and three anion sites. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). Initially, owing to the similar scattering factors of Pb and Tl, only the scattering curve of the first was used. Consequently, the site occupation factor (s.o.f.) of the three independent cation sites were refined using the following curves: Pb vs □ (structural vacancy) for the *Me1* and *Me2* sites, and Sb vs □ for the *Sb* site. All the cation positions but *Sb* were found fully occupied and their s.o.f. were fixed to 1. The *Sb* site was subsequently refined using Sb vs As curves and gave a $\text{Sb}_{0.805(11)}\text{As}_{0.195}$ site occupancy, which is in agreement with that obtained by electron microprobe (i.e., $\text{Sb}_{0.78}\text{As}_{0.20}$).

DISCUSSION

Crystal Structure

Markwelchite is isotopic with richardsollyite. The crystal structure of markwelchite can be described as formed by (100) $[Me_2(SbS_3)]^-$ layers sandwiching the *Me1* cations (Fig. 3). The *Me1* site has a seven-fold coordination, with an eighth ligand at 3.808(2) Å. The *Me2* site has an 6+2 coordination (two ligands > 3.6 Å), corresponding to a distorted, bicapped trigonal prismatic coordination. Finally, the *Sb* site displays a trigonal pyramidal coordination with three S atoms and Sb at the apex.

However, some differences with respect to richardsollyite occur in the coordination of atoms hosted at the *Me2* and *Me1* sites. The average $\langle Me_2-S \rangle$ is 3.191 Å, with a corresponding bond-valence sum (BVS) of 1.49 v.u. (valence units), calculated using the bond-parameter of Brese and O'Keeffe (1991) for the Pb–S bond, also considering the very long *Me2*–S3 bond [3.8077(18) Å]. In richardsollyite, this site has an average $\langle Pb-S \rangle$ distance of 3.122 Å, with distances ranging between 2.91 and 3.45 Å; the corresponding BVS is 1.85 v.u. (Meisser *et al.*, 2017). *Me1* is eight-fold coordinated, with an average $\langle Me_1-S \rangle$ distance of 3.298 Å; in richardsollyite this site is seven-fold coordinated, with average distance of 3.333 Å and a BVS of 0.98 v.u. (Meisser *et al.*, 2017). In markwelchite, the BVS, calculated using the value of 2.55 Å for Tl–S bonds (e.g., Biagioni and Moëlo, 2017), is 1.34 v.u. that could indicate a cross-substitution $Tl^+ + Pb^{2+} = Pb^{2+} + Tl^+$ between *Me1* and *Me2*. A possible fit would give $Me_2 = Pb_{0.55}Tl_{0.45}$ and $Me_1 = Tl_{0.55}Pb_{0.45}$, corresponding to mean formal charges of 1.55 and 1.45 v.u., respectively. The disorder of Tl and Pb at the *Me1* and *Me2* sites is larger than that possibly occurring in richardsollyite, where a virtually ordered distribution of these two elements was reported (Meisser *et al.*, 2017). This is probably a consequence of the Sb–for–As replacement in markwelchite with respect to richardsollyite. Indeed, the *Sb* site has a site occupancy

(Sb_{0.80}As_{0.20}), in accord with electron microprobe data; in richardsollyite this site was virtually As-pure (Meisser *et al.*, 2017). The occurrence of Sb may allow an increase in the size of the *Me2* polyhedron, favouring the partial replacement of Pb²⁺ by Tl⁺ (Fig. 4).

Structural and chemical information allow to propose the idealized structural formula $Me1(Tl_{0.55}Pb_{0.45})_{\Sigma 1.00}Me2(Pb_{0.55}Tl_{0.45})_{\Sigma 1.00}^{Sb}(Sb_{0.82}As_{0.18})_{\Sigma 1.00}S_3$.

Possible stacking faults cannot be excluded, and these could be responsible for the presence of the residual maxima in the difference Fourier map around *Me1* and *Me2* (highest peak 5.04 e Å⁻³ at 0.95 Å from *Me2*).

Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table 4, whereas selected bond distances and bond valences are provided in Tables 5 and 6, respectively.

Relation to other species

Markwelchite is the Sb-analogue of richardsollyite, TIPbAsS₃, and is isostructural with three synthetic compounds, i.e., KEuAsS₃, RbEuAsS₃, and CsEuAsS₃ (Bera and Kanatzidis, 2008).

Synthetic TIPbSbS₃ shows two polymorphs. The high-temperature one is stable over 620 K and has a structure of TII type (orthorhombic *Cmcm*) with a disorder of cations occupying the same structural site (crystal structure determined from single-crystal X-ray data by Balić Žunić *et al.*, 1992). In the low-temperature form the disorder of cations is retained although the symmetry is lowered to monoclinic, space group *P2₁/c* (structure determination from X-ray powder data by Balić Žunić and Bente, 1995). This is mainly due to a side movement in the stacking of tightly bonded two-layer slabs. The structures of the two polymorphs are influenced by the activities of the lone electron pairs of the cations involved.

The side movement in the stacking of tightly-bonded slabs in the low temperature polymorph is probably caused by cation repulsions upon decreasing the slab separation. The structural differences with respect to markwelchite are likely due to differences in the formation conditions (temperature, pressure, time).

To elucidate the structural evolution of markwelchite as a function of temperature, *in situ* low- and high-temperature single-crystal X-ray diffraction studies are planned to conduct, provided that more suitable fragments will become available.

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Competing interests. The authors declare that there are no competing interests.

Supplementary material. To view the supplementary material for this article, please visit xxx.

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Table 1. Results of electron microprobe analyses (in elemental wt%) of markwelchite.

	mean	range	SD	probe standard
Tl	34.67	33.55–35.19	0.45	Tl-metal
Pb	31.86	30.95–32.27	0.25	Pb-metal
Sb	15.06	14.69–15.20	0.15	Sb-metal
As	2.37	2.19–2.51	0.05	As-metal
S	15.35	15.09–15.88	0.20	Pb-metal
Total	99.31			

Table 2. Observed and calculated X-ray powder diffraction data (on the basis of the structural model given in Table 4) for markwelchite; only reflections with $I_{\text{calc}} > 4$ are listed. The five strongest reflections are given in bold.

<i>h</i>	<i>k</i>	<i>l</i>	d_{calc}	I_{calc}	d_{obs}	I_{obs}							
-1	0	2	4.2619	35				-3	2	3	2.0725	18	
2	0	0	4.2213	9				-2	1	4	2.0663	11	
-2	1	1	3.8792	100	3.88	100		1	4	0	2.0496	11	
-1	1	2	3.8054	37	3.80	40		0	0	4	2.0483	5	
1	2	0	3.7788	56				4	1	0	2.0478	17	
2	1	0	3.7764	94	3.78	90		-1	4	1	2.0259	4	
0	2	1	3.7556	29				-1	3	3	2.0151	5	
0	1	2	3.6864	8				3	3	0	1.9910	18	
-1	2	1	3.6358	47	3.64	50		-3	0	4	1.9872	5	
-2	0	2	3.5673	8				3	1	2	1.9782	20	1.98
1	0	2	3.2937	97	3.29	90		-4	2	1	1.9678	17	
1	2	1	3.2580	8				1	4	1	1.9528	7	
1	1	2	3.0689	33	3.06	30		-4	2	2	1.9396	7	
-1	2	2	3.0007	33	2.99	40		-1	2	4	1.9201	7	
2	2	0	2.9865	9				-2	4	1	1.9019	25	1.90
0	2	2	2.9413	87	2.93	75		2	3	2	1.8938	24	
-3	1	1	2.8025	55	2.79	50		4	2	0	1.8882	8	
-1	1	3	2.7292	94	2.73	85		0	4	2	1.8778	6	
-2	2	2	2.7259	19				4	1	1	1.8554	14	
1	3	0	2.6723	64	2.67	60		0	2	4	1.8432	8	
3	1	0	2.6701	21				1	1	4	1.8152	17	
0	3	1	2.6640	27				-4	0	4	1.7837	13	
-3	1	2	2.6337	78	2.63	70		-5	0	2	1.7747	18	
2	2	1	2.6209	75	2.61	60		-4	1	4	1.7452	7	
-1	3	1	2.6202	14				-4	3	2	1.7256	15	
-2	1	3	2.5950	21				-3	4	1	1.7218	15	
2	0	2	2.5580	5				-1	4	3	1.7043	6	
1	3	1	2.4677	17				1	2	4	1.7013	8	
2	1	2	2.4483	4				-1	1	5	1.6806	8	
-1	3	2	2.3501	8				0	4	3	1.6711	14	
3	1	1	2.3376	33	2.34	25		4	0	2	1.6706	4	
0	3	2	2.3212	7				-2	4	3	1.6701	9	
0	2	3	2.2937	11				0	3	4	1.6567	5	
-2	3	2	2.2109	16				2	0	4	1.6469	8	
2	2	2	2.1883	6				-1	5	1	1.6447	14	
-1	0	4	2.1554	4				-4	2	4	1.6433	5	
-2	0	4	2.1310	12				-3	3	4	1.6238	21	
1	2	3	2.0764	13				2	1	4	1.6165	6	
								0	1	5	1.6087	7	

-2	2	5	1.5978	5
3	4	1	1.5951	8
3	2	3	1.5814	6
-5	2	3	1.5780	4
5	2	0	1.5680	9
-5	1	4	1.5477	7
2	2	4	1.5345	5
0	2	5	1.5278	6
2	5	1	1.5082	5
-1	3	5	1.4648	5
-4	2	5	1.4629	7
5	2	1	1.4617	5
2	4	3	1.4588	9
-4	4	3	1.4568	8
5	3	0	1.4483	6
-2	0	6	1.4418	7
4	1	3	1.4375	4
0	5	3	1.4373	8
4	3	2	1.4369	5
-2	5	3	1.4366	8
4	4	1	1.4135	6
6	0	0	1.4071	10
3	5	1	1.3881	5

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Table 3. Crystal and experimental data for markwelchite.

Crystal data	
Crystal size (mm)	0.025 × 0.020 × 0.018
Cell setting, space group	Monoclinic, $P2_1/c$
a (Å)	8.9144(3)
b (Å)	8.4513(3)
c (Å)	8.6511(3)
β (°)	108.723(3)
V (Å ³)	617.27(4)
Z	4
Data collection and refinement	
Radiation, wavelength (Å)	MoK α , $\lambda = 0.71073$
Temperature (K)	293
$2\theta_{\max}$ (°)	60.06
Measured reflections	16162
Unique reflections	1803
Reflections with $F_o > 4\sigma(F_o)$	1525
R_{int}	0.0327
$R\sigma$	0.0319
Range of h, k, l	$-12 \leq h \leq 12,$ $-11 \leq k \leq 11,$ $-12 \leq l \leq 12$
$R [F_o > 4\sigma(F_o)]$	0.0225
R (all data)	0.0245
wR (on F^2)	0.0485
Goof	1.008
Number of least-squares parameters	58
Maximum and minimum residual peak ($e \text{ \AA}^{-3}$)	5.04 (at 0.95 Å from Me_2) -0.68 (at 1.17 Å from Me_2)

Table 4. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for markwelchite.

Site	x/a	y/b	z/c	U_{eq}
<i>Me1</i>	0.41633(3)	0.41732(3)	0.78400(3)	0.03302(10)
<i>Me2</i>	0.91462(3)	0.29497(3)	0.98226(3)	0.02430(9)
<i>Sb</i>	0.75784(5)	0.55110(5)	0.62968(5)	0.01872(12)
S1	0.7130(2)	0.6230(2)	0.8803(2)	0.0215(3)
S2	0.0212(2)	0.4672(2)	0.6847(2)	0.0206(3)
S3	0.6158(2)	0.3039(2)	0.5538(2)	0.0283(4)

Table 5. Selected bond distances (\AA) for markwelchite.

<i>Me1</i> – S1	3.049(2)	<i>Me2</i> – S3	3.040(2)	<i>Sb</i> – S1	2.405(2)
– S1	2.913(2)	– S1	3.222(2)	– S2	2.350(2)
– S3	3.073(2)	– S2	2.795(2)	– S3	2.421(2)
– S3	3.213(2)	– S1	3.267(2)		
– S2	3.374(2)	– S2	3.259(2)		
– S1	3.469(2)	– S2	3.349(2)		
– S3	3.604(2)	– S2	3.407(2)		
– S3	3.692(2)	– S3	3.808(2)		

Table 6. Bond valences (in valence units, v.u.) according to the parameters given by Brese and O'Keeffe (1991).

	<i>Me1</i>	<i>Me2</i>	<i>Sb</i>	Σ anions
S1	0.38	0.16 0.14	1.04	2.06
	0.26			
	0.08			
S2	0.11	0.52	1.21	2.21
		0.15		
		0.12		
		0.10		
S3	0.24	0.27 0.03	0.99	1.81
	0.17			
	0.06			
	0.05			
Σ cations	1.35	1.49	3.24	

Note: the bond parameters of Pb–S and Tl–S bonds were assumed as 2.55 \AA . The site occupancy at the *Sb* site is ($\text{Sb}_{0.80}\text{As}_{0.20}$).

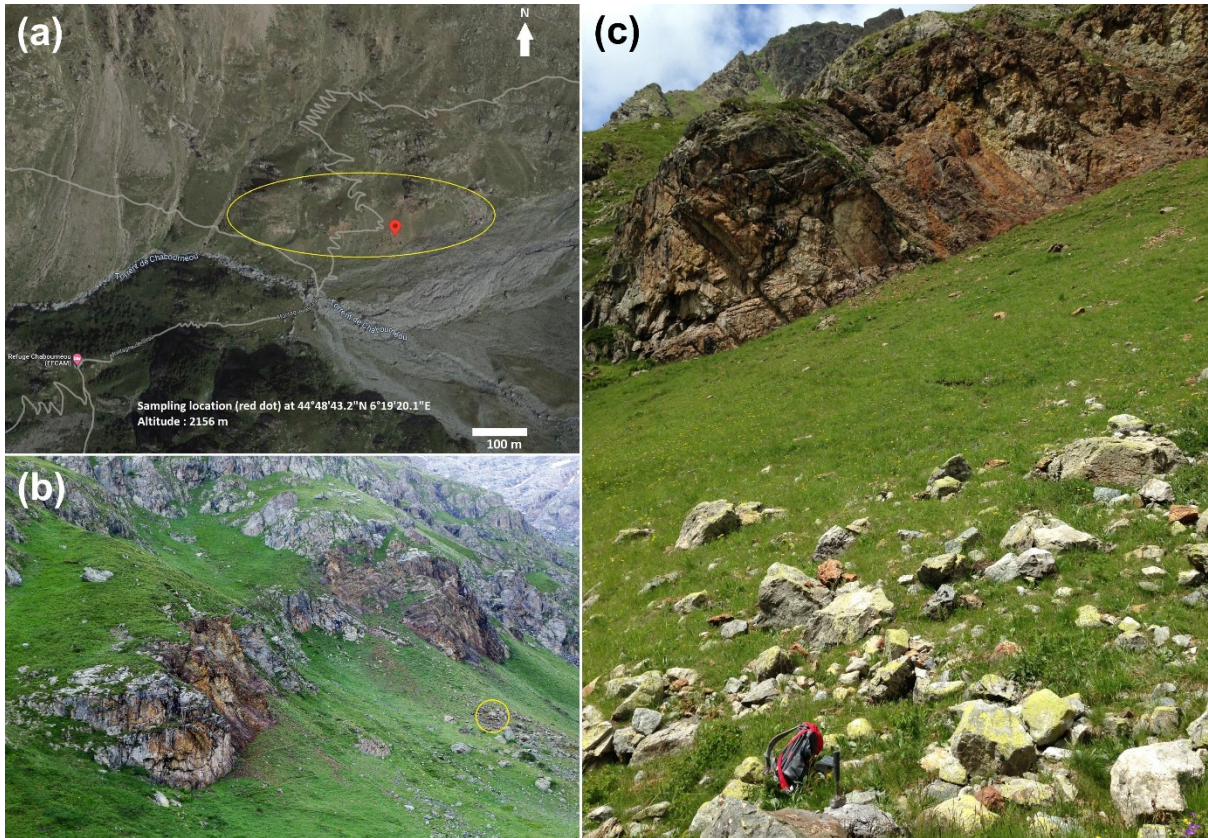


FIGURE 1 – (a) The location where the sample containing markwelchite was collected ($44^{\circ}48'43.2''\text{N}$ $6^{\circ}19'20.1''\text{E}$). (b) Photograph indicating the sampling site below the cliff, looking to the East. (c) Photograph showing the sampling site by looking W towards the westmost cliff.

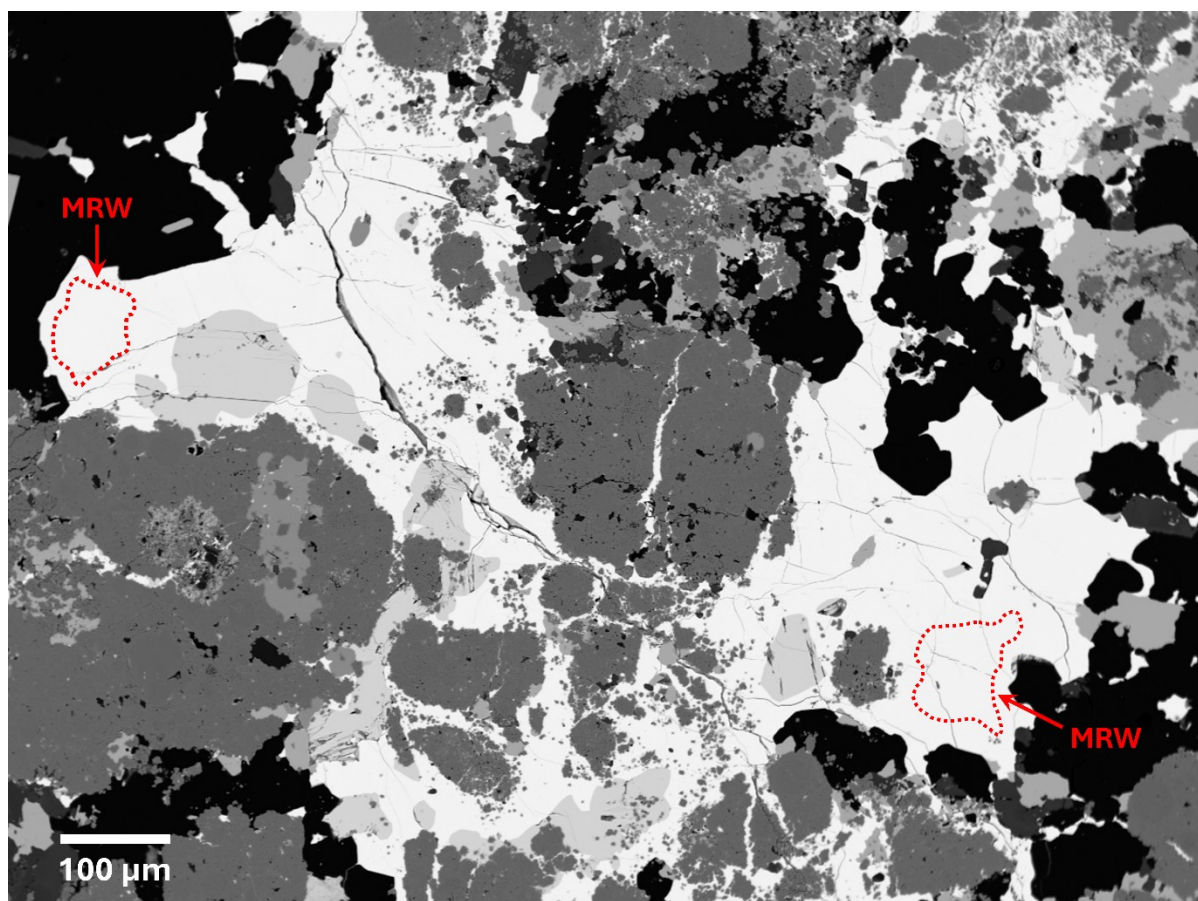


FIGURE 2 – SEM~BSE image of the markwelchite-containing polished section. Small grains of markwelchite occur in the brighter regions, closely associated with protochabournéite.

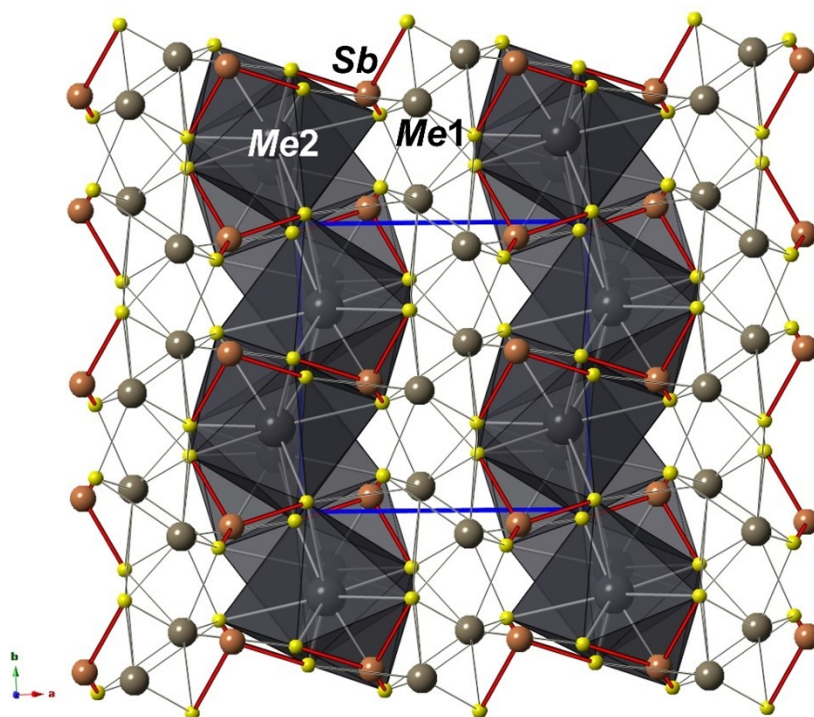


FIGURE 3 – Crystal structure of markwelchite as seen down [001]. Circles: grey = *Me1*; orange = *Sb*; yellow = *S*. *Me2*-centered polyhedra are shown in dark grey.

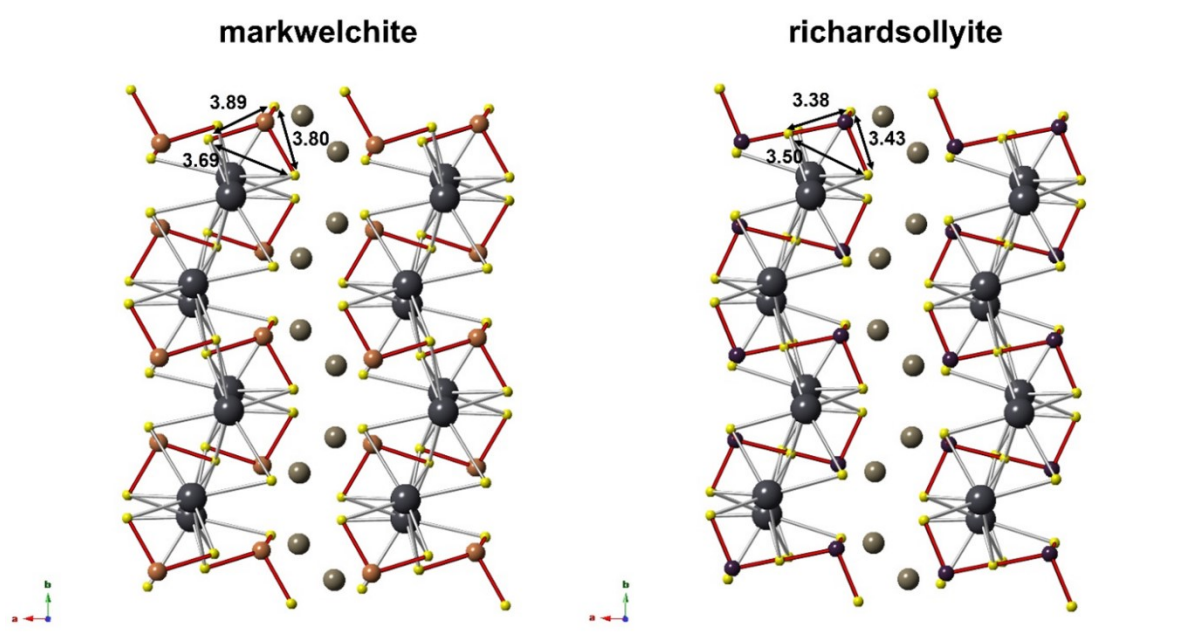


FIGURE 4 – Comparison between the crystal structures of markwelchite (left) and richardsollyite (right). The S–S distances (in Å) forming the base of the trigonal pyramids having Sb and As at their vertex are shown.