



Article

Thunderbayite, $\text{TlAg}_3\text{Au}_3\text{Sb}_7\text{S}_6$, a new gold-bearing mineral from the Hemlo gold deposit, Marathon, Ontario, Canada

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Abstract

Thunderbayite (IMA2020–042), ideally $\text{TlAg}_3\text{Au}_3\text{Sb}_7\text{S}_6$, is a new mineral from the Hemlo gold deposit, Marathon, Ontario, Canada. It occurs as very rare anhedral rims up to 70 μm across in contact with aurostibite and associated spatially with stibarsen, biagioniite and native gold in a calcite matrix. Thunderbayite is opaque with a metallic lustre and shows a black streak. In reflected light, thunderbayite is weakly bireflectant and faintly pleochroic from grey–blue to slightly greenish grey–blue. Under crossed polars, it is weakly anisotropic with bluish to light-blue rotation tints. Internal reflections are absent. Reflectance percentages for the four Commission on Ore Mineralogy wavelengths (R_{min} , R_{max}) are: 37.9, 38.4 (471.1 nm); 35.3, 36.0 (548.3 nm); 33.9, 34.4 (586.6 nm); and 32.0, 32.5 (652.3 nm), respectively. A mean of five electron-microprobe analyses gave Ag 14.91(16), Au 27.40(22), Tl 9.37(9), Sb 39.80(34) and S 8.61(7), for a total of 100.09 wt.%, corresponding, on the basis of a total of 20 atoms, to $\text{Tl}_{1.00}\text{Ag}_{3.01}\text{Au}_{3.03}\text{Sb}_{7.12}\text{S}_{5.84}$. Thunderbayite is triclinic, space group $P1$, with $a = 8.0882(5)$, $b = 7.8492(5)$, $c = 20.078(1)$ Å, $\alpha = 92.518(5)$, $\beta = 93.739(5)$, $\gamma = 90.028(6)^\circ$, $V = 1270.73(9)$ Å³ and $Z = 2$. The five strongest powder-diffraction lines [d in Å (hkl)] are: 4.04 (100) (200); 3.92 (80) (020); 2.815 (50) (220/220); 2.566 (45) (117); and 2.727 (40) (017). The crystal structure [$R_1 = 0.0220$ for 5521 reflections with $I > 2\sigma(I)$] can be considered as a strongly deformed pyrite-type structure with several metal–metal bonds. Thunderbayite shows close similarities with criddleite, $\text{TlAg}_2\text{Au}_3\text{Sb}_{10}\text{S}_{10}$, from an optical, chemical and structural point of view. The new mineral is named for the Thunder Bay district, Ontario, in which the Hemlo gold deposit is located.

Keywords: thunderbayite, new mineral, thallium, criddleite, Hemlo deposit, Canada

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Introduction

In the course of a research project dealing with the description and structural characterisation of natural Tl–Ag-sulfides/sulfosalts (i.e. Biagioni *et al.*, 2016; Bindi and Biagioni, 2018; Bindi *et al.*, 2012a, 2012b, 2013, 2015a, 2015b, 2020), we examined a sample from the Hemlo gold deposit, Marathon, Ontario, Canada (Harris, 1989), belonging to the mineralogical collections of the Museo di Storia Naturale of the University of Florence, Italy (catalogue number 46582/G). This is also the type material for the recently approved biagioniite, $\text{Tl}_2\text{Sb}_2\text{S}_2$ (IMA2019-120; Bindi and Moëlo, 2020). We were interested in the solution of the crystal structure of criddleite, $\text{TlAg}_2\text{Au}_3\text{Sb}_{10}\text{S}_{10}$ (Harris *et al.*, 1988), and tested several fragments by single-crystal X-ray diffraction. During this search, a few small grains turned out to be the new mineral thunderbayite, $\text{TlAg}_3\text{Au}_3\text{Sb}_7\text{S}_6$.

Thunderbayite was approved as a new mineral by the International Mineralogical Association Commission on New

Minerals, Nomenclature and Classification (IMA2020-042, Bindi and Roberts, 2020). The mineral name is for the Thunder Bay district, Ontario, Canada in which the Hemlo gold deposit is located. The holotype material is deposited in the mineralogical collection of the Museo di Storia Naturale of the University of Florence, Italy, under catalogue number 46582/G.

Here we report the description of the new mineral thunderbayite, together with its crystal structure.

Material studied

The sample containing thunderbayite, which is preserved in the collections of the Museo di Storia Naturale of the University of Florence, comes from the Hemlo gold deposit. Hemlo is an Archean-aged gold deposit (48°41'41"N, 85°54'13"W) located near the north-east shore of Lake Superior, ~35 km east of Marathon, Ontario, Canada and ~350 km east of Thunder Bay. It is situated in the Hemlo–Schreiber greenstone belt of the Wawa sub-province of the Superior Province (Tomkins *et al.*, 2004, and references therein), is located within a zone of strong deformation that essentially parallels the regional west-northwest trend, and is stratiform within Archean-aged metamorphosed

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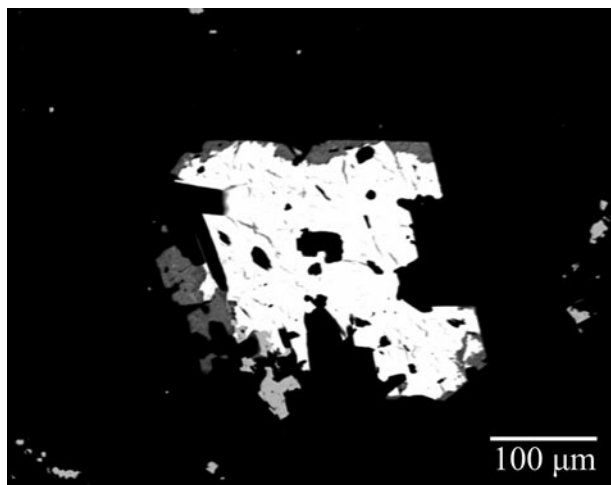


Fig. 1. Scanning electron microscopy back-scatter electron image of thunderbayite (grey) associated with aurostibite (white) in a calcite matrix (black). The light grey phase at the bottom centre is thunderbayite with a slightly higher Au/Ag ratio. Type specimen (cat. numb. 46582/G).

volcano–sedimentary rocks. The deposit has produced more than 21 million oz of gold and consists of several mineralised zones in which the ore minerals were formed from hydrothermal fluids that is related spatially to the shear zone.

The sample consists of tiny thunderbayite grains up to 70 μm across, associated spatially with aurostibite, stibarsen, biagioniite

and native gold in a calcite matrix. Thunderbayite was misidentified initially as criddleite.

Physical and optical properties

Thunderbayite occurs as very rare anhedral rims around aurostibite in a calcite matrix (Fig. 1). The mineral exhibits a subhedral to anhedral grain morphology, and shows no inclusions of, or intergrowths with, other minerals. It is black in colour and has a black streak. The mineral is opaque in transmitted light and exhibits a metallic lustre. No cleavage is observed and the fracture is irregular. The calculated density (for $Z=2$) for the empirical formula (see below) is 5.693 g/cm^3 . Unfortunately, the density could not be measured because of the small grain size. The Mohs hardness, estimated with respect to the surrounding calcite (by scratching both minerals), is ~ 3 .

In plane-polarised incident light, thunderbayite is grey in colour, weakly bireflectant and weakly pleochroic from grey–blue to slightly greenish grey–blue. Between crossed polars, thunderbayite is weakly anisotropic with bluish to light-blue rotation tints. Internal reflections are absent and there is no optical evidence of growth zonation.

Reflectance measurements were performed in air by means of a MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was $\sim 3350\text{ K}$. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3,

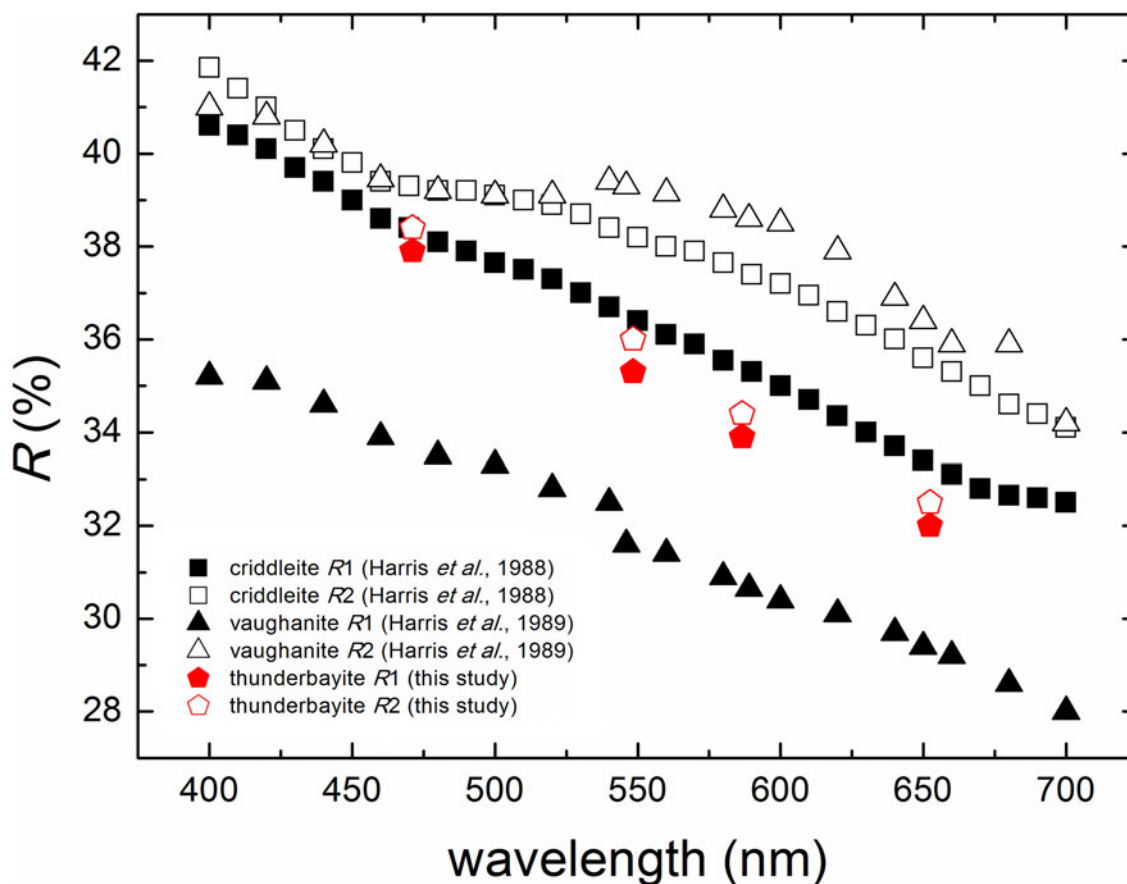


Fig. 2. Reflectivity curves for thunderbayite in air (red symbols, the four wavelengths required by the Commission on Ore Mineralogy) compared to criddleite (black squares; Harris *et al.*, 1988) and vaughanite (black triangles; Harris *et al.*, 1989). Filled and open symbols refer to R1 and R2 values, respectively.

Table 1. Electron-microprobe analysis (wt.% of elements) of thunderbayite.

Constituent	Mean	Range	Standard deviation (σ)
Ag	14.91	14.79–15.03	0.16
Au	27.40	27.22–27.61	0.22
Tl	9.37	9.12–9.50	0.09
Sb	39.80	39.51–40.05	0.34
S	8.61	8.40–8.79	0.07
Total	100.09	99.0–100.16	

586.6 and 652.3 nm). Readings were taken for both the specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.04 mm. Reflectance percentages for R_{\min} and R_{\max} are: 37.9, 38.4 (471.1 nm); 35.3, 36.0 (548.3 nm); 33.9, 34.4 (586.6 nm); and 32.0, 32.5 (652.3 nm), respectively.

In Fig. 2, the reflectance values (measured in air) for criddleite (TlAg₂Au₃Sb₁₀S₁₀; Harris *et al.*, 1988), vaughanite (TlHgSb₄S₇; Harris *et al.*, 1989) and thunderbayite are compared. Although only a limited set of values (only for the four wavelengths required by the Commission on Ore Mineralogy) have been obtained for thunderbayite, it appears evident that its reflectance is similar to that of criddleite.

Chemical composition

A preliminary chemical analysis using energy dispersive spectrometry, performed on the crystal fragment used for the structural study, did not indicate the presence of elements ($Z > 9$) other than Ag, Au, Tl, Sb and S. Quantitative electron-microprobe analyses were carried out using a JEOL 8200 microprobe (wavelength

Table 2. Crystallographic data and refinement parameters for thunderbayite.

Crystal data	
Formula	TlAg ₃ Au ₃ Sb ₇ S ₆
Crystal size (mm)	0.020 × 0.020 × 0.030
Form	block
Colour	black
Crystal system	triclinic
Space group	<i>P</i> 1 (#1)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.088(3), 7.854(3), 20.078(8)
α , β , γ (°)	92.52(3), 93.71(3), 90.15(4)
<i>V</i> (Å ³)	1271.5(8)
<i>Z</i>	2
Data collection	
Instrument	Bruker D8 Venture
Radiation type	MoK α ($\lambda = 0.71073$)
Temperature (K)	293(3)
Detector-to-sample distance (cm)	6
Number of frames	1055
Measuring time (s)	50
Maximum covered 2θ (°)	67.48
Absorption correction	multi-scan
Collected reflections	18,799
Unique reflections	6799
Reflections with $F_o > 4\sigma(F_o)$	5521
R_{int} , R_{σ}	0.0208, 0.0145
Range of <i>h</i> , <i>k</i> , <i>l</i>	$-7 \leq h \leq 9$, $-9 \leq k \leq 9$, $-30 \leq l \leq 30$
Refinement	
Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4\sigma(F_o)$]	0.0220
Final R_1 (all data)	0.0245
Number refined parameters	361
GoF	1.058
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e ⁻ Å ⁻³)	0.56, -0.46

dispersive spectroscopy mode, 25 kV, 20 nA, 1 μm beam size, counting times 20 s for peak and 10 s for background). The following lines were used: AgL α , AuM α , TlM α , SbL β and SK α . The standards employed were: synthetic TlI (Tl), Ag-pure element (Ag), Au-pure element (Au), synthetic Sb₂Te₃ (Sb) and pyrite (S). The crystal fragment was found to be homogeneous within analytical error. The average chemical compositions (5 analyses on different spots) together with wt.% ranges of elements are reported in Table 1. On the basis of 20 atoms, the empirical formula of thunderbayite is Tl_{1.00}Ag_{3.01}Au_{3.03}Sb_{7.12}S_{5.84}. The ideal formula is TlAg₃Au₃Sb₇S₆, which requires Tl 9.45, Ag 14.96, Au 27.31, Sb 39.39, S 8.89, for a total 100 wt.%.

X-ray crystallography and crystal-structure determination

The same crystal fragment (20 μm × 20 μm × 30 μm) used to obtain the chemical data was selected for single-crystal X-ray diffraction using a Bruker D8 Venture diffractometer equipped with a Photon II CCD detector, and graphite-monochromatised MoK α radiation ($\lambda = 0.71073$ Å). Thunderbayite is triclinic, with $a = 8.088(3)$, $b = 7.854(3)$, $c = 20.078(8)$ Å, $\alpha = 92.52(3)$, $\beta = 93.71(3)$,

Table 3. Atoms, fractional atom coordinates (Å), and atomic displacement parameters (Å²) for thunderbayite.

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
Tl1	0.51983(10)	0.01613(9)	0.98984(4)	0.0874(2)
Tl2	0.48208(9)	0.51764(9)	0.04759(3)	0.07683(19)
Ag1	-0.01841(13)	-0.01304(12)	0.23420(5)	0.0506(2)
Ag2	-0.01990(12)	-0.01104(11)	0.52154(4)	0.0431(2)
Ag3	-0.0225(2)	-0.0150(2)	0.81150(8)	0.0932(4)
Ag4	0.47704(16)	0.51585(16)	0.33949(6)	0.0694(3)
Ag5	0.48161(13)	0.52001(13)	0.60460(5)	0.0520(2)
Ag6	0.4800(2)	0.5239(2)	0.90808(7)	0.0919(4)
Au1	0.51393(9)	0.01835(9)	0.13515(4)	0.07904(19)
Au2	0.51381(8)	0.02540(8)	0.42869(3)	0.06754(17)
Au3	0.51237(6)	0.02224(6)	0.69923(2)	0.04881(13)
Au4	0.01811(7)	0.48143(7)	0.14738(3)	0.05465(15)
Au5	0.01606(8)	0.48648(8)	0.44131(3)	0.06506(17)
Au6	0.01594(9)	0.48543(9)	0.70939(3)	0.07471(19)
Sb1	0.62225(13)	0.62812(13)	0.17843(5)	0.0636(3)
Sb2	0.62487(18)	0.63013(18)	0.46532(7)	0.0897(4)
Sb3	0.62270(15)	0.62770(15)	0.75223(6)	0.0754(3)
Sb4	0.87755(14)	0.35372(13)	0.00921(5)	0.0624(2)
Sb5	0.87418(13)	0.37729(12)	0.32541(5)	0.0588(2)
Sb6	0.87037(16)	0.37047(16)	0.58138(6)	0.0825(4)
Sb7	0.87271(12)	0.37430(12)	0.87835(4)	0.0551(2)
Sb8	0.12319(17)	0.87655(17)	0.10718(6)	0.0860(3)
Sb9	0.12482(14)	0.87839(14)	0.39822(5)	0.0717(3)
Sb10	0.12395(13)	0.87710(13)	0.66835(5)	0.0611(2)
Sb11	0.12450(11)	0.87638(11)	0.95727(4)	0.0503(2)
Sb12	0.37074(14)	0.12834(14)	0.24922(5)	0.0695(3)
Sb13	0.37429(12)	0.12933(12)	0.53772(4)	0.0533(2)
Sb14	0.37250(19)	0.12923(19)	0.82125(7)	0.0972(4)
S1	0.3705(7)	0.3825(6)	0.1687(2)	0.0900(13)
S2	0.3752(5)	0.3884(4)	0.45807(16)	0.0568(8)
S3	0.3827(4)	0.3870(4)	0.71542(14)	0.0464(7)
S4	0.1269(6)	0.6182(5)	0.2757(2)	0.0730(11)
S5	0.1230(7)	0.6249(7)	0.5723(2)	0.0872(13)
S6	0.1251(4)	0.6231(4)	0.84379(14)	0.0474(7)
S7	0.8750(3)	0.1206(3)	0.11298(12)	0.0361(6)
S8	0.8792(7)	0.1167(7)	0.3989(3)	0.0933(14)
S9	0.8795(5)	0.1237(5)	0.69460(19)	0.0703(10)
S10	0.6162(6)	0.8830(6)	0.3086(2)	0.0753(11)
S11	0.6170(5)	0.8860(5)	0.57502(17)	0.0625(9)
S12	0.6227(5)	0.8803(4)	0.85802(16)	0.0550(8)

Table 4. Selected bond distances (Å) for thunderbayite.

Tl1–Au1	2.920(2)	Au2–Sb2	3.334(3)	Sb5–Au5	2.635(2)	S1–Tl2	2.891(3)	S9–Ag3	2.704(2)
Tl1–Sb11	3.392(1)	Au2–Sb9	3.358(2)	Sb5–S4	3.027(3)	S1–Au1	3.151(2)	S9–Au3	3.081(3)
Tl1–Sb14	3.663(2)	Au2–Sb13	2.627(3)	Sb5–S8	2.574(2)	S1–Au4	2.965(2)	S9–Au6	3.041(3)
Tl1–S12	2.979(2)	Au2–S2	3.113(2)			S1–Sb1	2.793(3)	S9–Sb6	3.049(4)
		Au2–S8	3.140(4)	Sb6–Ag2	3.323(2)	S1–Sb12	2.623(3)	S9–Sb10	2.829(2)
Tl2–Ag6	2.803(2)	Au2–S10	2.789(2)	Sb6–Au5	3.283(3)				
Tl2–Sb1	2.889(3)	Au2–S11	3.240(2)	Sb6–Au6	2.865(4)	S2–Ag4	2.794(3)	S10–Ag4	3.193(2)
Tl2–Sb4	3.569(2)			Sb6–S5	2.874(3)	S2–Ag5	3.141(2)	S10–Au2	2.789(2)
Tl2–S1	2.891(3)	Au3–Sb10	3.350(4)	Sb6–S9	3.049(2)	S2–Au2	3.113(4)	S10–Sb1	3.225(4)
		Au3–Sb14	2.858(2)			S2–Au5	3.009(2)	S10–Sb12	2.999(3)
Ag1–Sb8	2.959(2)	Au3–S3	3.064(3)	Sb7–Ag3	3.416(3)	S2–Sb2	2.761(3)	S10–S8	3.220(2)
Ag1–Sb12	3.326(3)	Au3–S9	3.081(4)	Sb7–Sb4	2.637(2)	S2–Sb13	2.643(2)		
Ag1–S4	3.251(2)	Au3–S11	2.850(2)	Sb7–S6	2.958(3)			S11–Ag2	3.302(3)
Ag1–S7	2.780(4)					S3–Ag5	2.667(2)	S11–Ag5	3.167(2)
		Au4–Sb4	3.055(3)	Sb8–Ag1	2.959(3)	S3–Au3	3.064(3)	S11–Au2	3.240(3)
Ag2–Sb6	3.323(2)	Au4–Sb8	3.361(2)	Sb8–Au1	3.353(2)	S3–Au6	3.064(2)	S11–Au3	2.850(2)
Ag2–Sb9	2.906(4)	Au4–S1	2.965(4)	Sb8–Au4	3.361(3)	S3–Sb3	2.750(3)	S11–Sb2	2.920(4)
Ag2–Sb10	3.256(2)	Au4–S4	2.833(2)	Sb8–Sb11	3.011(3)			S11–Sb13	2.832(2)
Ag2–Sb13	3.362(4)	Au4–S7	3.091(4)	Sb8–S7	2.784(2)	S4–Ag1	3.251(2)		
Ag2–S5	3.267(2)					S4–Ag4	3.153(3)	S12–Tl1	2.979(2)
Ag2–S8	2.774(3)	Au5–Sb5	2.635(2)	Sb9–Ag2	2.906(3)	S4–Au4	2.833(2)	S12–Ag3	3.192(4)
Ag2–S11	3.302(2)	Au5–Sb6	3.283(4)	Sb9–Au2	3.358(2)	S4–Sb5	3.027(3)	S12–Ag6	3.249(3)
		Au5–Sb9	3.364(2)	Sb9–Au5	3.364(5)	S4–Sb9	3.129(2)	S12–Sb3	2.842(2)
Ag3–Sb10	3.258(2)	Au5–S2	3.009(3)	Sb9–S4	3.129(4)			S12–Sb14	2.901(3)
Ag3–Sb11	3.238(3)	Au5–S5	2.880(3)	Sb9–S8	2.733(2)	S5–Ag2	3.267(2)		
Ag3–Sb14	3.378(2)	Au5–S8	3.167(2)			S5–Ag5	3.054(3)		
Ag3–S6	3.163(3)			Sb10–Ag2	3.256(2)	S5–Au5	2.880(4)		
Ag3–S9	2.704(2)	Au6–Sb6	2.865(3)	Sb10–Ag3	3.258(3)	S5–Au6	3.177(3)		
Ag3–S12	3.192(3)	Au6–Sb10	3.348(2)	Sb10–Au3	3.350(2)	S5–Sb6	2.874(2)		
		Au6–S3	3.064(2)	Sb10–Au6	3.348(3)	S5–Sb10	2.703(2)		
Ag4–Sb2	2.832(2)	Au6–S5	3.177(2)	Sb10–S5	2.703(2)				
Ag4–S2	2.794(3)	Au6–S6	2.943(3)	Sb10–S9	2.829(4)	S6–Ag3	3.163(4)		
Ag4–S4	3.153(2)	Au6–S9	3.041(2)			S6–Ag6	3.183(2)		
Ag4–S10	3.193(5)			Sb11–Tl1	3.392(2)	S6–Au6	2.943(4)		
		Sb1–Tl2	2.889(5)	Sb11–Ag3	3.238(4)	S6–Sb7	2.958(3)		
Ag5–Sb2	3.246(2)	Sb1–Au1	3.327(3)	Sb11–Sb8	3.011(3)	S6–Sb11	2.958(2)		
Ag5–Sb3	3.184(4)	Sb1–S1	2.793(2)	Sb11–S6	2.958(2)				
Ag5–Sb13	3.383(2)	Sb1–S10	3.225(3)			S7–Ag1	2.780(3)		
Ag5–S2	3.141(4)			Sb12–Ag1	3.326(2)	S7–Au1	3.092(3)		
Ag5–S3	2.667(2)	Sb2–Ag4	2.832(3)	Sb12–Au1	2.740(4)	S7–Au4	3.091(2)		
Ag5–S5	3.054(3)	Sb2–Ag5	3.246(2)	Sb12–S1	2.623(5)	S7–Sb4	2.835(2)		
Ag5–S11	3.167(3)	Sb2–Au2	3.334(4)	Sb12–S10	2.999(2)	S7–Sb8	2.784(4)		
		Sb2–S2	2.761(4)						
Ag6–Tl2	2.803(3)	Sb2–S11	2.920(2)	Sb13–Ag2	3.362(5)	S8–Ag2	2.774(2)		
Ag6–S6	3.183(2)			Sb13–Ag5	3.383(3)	S8–Au2	3.140(4)		
Ag6–S12	3.249(3)	Sb3–Ag5	3.184(3)	Sb13–Au2	2.627(2)	S8–Au5	3.167(2)		
		Sb3–S3	2.750(3)	Sb13–S2	2.643(3)	S8–Sb5	2.574(4)		
Au1–Tl1	2.920(2)	Sb3–S12	2.842(2)	Sb13–S11	2.832(2)	S8–Sb9	2.733(3)		
Au1–Sb1	3.327(4)					S8–S10	3.220(2)		
Au1–Sb8	3.353(4)	Sb4–Au4	3.055(3)	Sb14–Ag3	3.378(3)				
Au1–Sb12	2.740(2)	Sb4–Sb7	2.637(2)	Sb14–Au3	2.858(2)				
Au1–S1	3.151(3)	Sb4–S7	2.835(3)	Sb14–S3	3.003(3)				
Au1–S7	3.092(3)			Sb14–S12	2.901(2)				

$\gamma = 90.15(4)^\circ$, $V = 1271.5(8) \text{ \AA}^3$ and $Z = 2$. Systematic absences were consistent with the space groups $P1$ and $P\bar{1}$. The statistical tests on the distribution of $|E|$ values ($|E^2 - 1| = 0.729$) indicated the absence of an inversion centre and so the $P1$ space group was chosen. The structure was solved and refined using the program *SHELXL* (Sheldrick, 2008). The occupancy of all the sites was left free to vary (Tl vs. \square ; Ag vs. \square ; Au vs. \square ; Sb vs. \square ; S vs. \square) but all the positions were found to be fully occupied and then fixed in the subsequent refinement cycles. Neutral scattering curves for Tl, Ag, Au, Sb and S were taken from the *International Tables for X-ray Crystallography* (Wilson, 1992). At the last stage, with anisotropic atomic displacement parameters for all the atoms and no constraints, the residual value settled at $R_1 = 0.0220$ for 5521 observed reflections [$2\sigma(I)$ level] and 361 parameters and at $R_1 = 0.0245$ for all 6799 independent reflections.

Experimental details and R indices are given in Table 2. Fractional atomic coordinates and atomic displacement parameters are reported in Table 3. Bond distances are given in Table 4. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

X-ray powder-diffraction data (Table 5) were collected with a Bruker D8 Venture diffractometer equipped with a Photon II CCD detector and using copper radiation ($\text{CuK}\alpha$, $\lambda = 1.54138 \text{ \AA}$). The program *Apex3* (Bruker, 2016) was used to convert the observed diffraction rings to a conventional powder-diffraction pattern. The least squares refinement gave the following values: $a = 8.0882(5)$, $b = 7.8492(5)$, $c = 20.078(1) \text{ \AA}$, $\alpha = 92.518(5)$, $\beta = 93.739(5)$, $\gamma = 90.028(6)^\circ$ and $V = 1270.73(9) \text{ \AA}^3$.

Table 5. Observed and calculated* X-ray powder-diffraction data (*d* in Å) for thunderbayite.

<i>l_{calc}</i>	<i>l_{meas}</i>	<i>d_{calc}</i>	<i>d_{meas}</i>	<i>h k l</i>	<i>l_{calc}</i>	<i>l_{meas}</i>	<i>d_{calc}</i>	<i>d_{meas}</i>	<i>h k l</i>
10	-	10.0082	-	0 0 2	10	10	2.3766	2.375	$\bar{1}$ $\bar{3}$ 3
18	10	6.6721	6.67	0 0 3	10	-	2.3706	-	2 2 4
22	30	5.6414	5.63	$\bar{1}$ 1 0	9	10	2.3516	2.351	1 $\bar{3}$ 3
11	-	5.6106	-	1 1 0	9	-	2.3447	-	3 $\bar{1}$ 3
6	-	5.4492	-	$\bar{1}$ 1 1	16	15	2.3378	2.338	$\bar{3}$ $\bar{1}$ 4
9	10	5.0041	4.98	0 0 4	12	10	2.3243	2.325	$\bar{2}$ $\bar{1}$ 7
7	-	4.8862	-	1 $\bar{1}$ 2	8	-	2.3178	-	$\bar{1}$ 3 3
9	-	4.4663	-	$\bar{1}$ $\bar{1}$ 3	11	-	2.3168	-	3 1 3
8	-	4.3370	-	$\bar{1}$ 1 3	15	15	2.3160	2.315	$\bar{3}$ 1 4
9	10	4.3063	4.31	0 $\bar{1}$ 4	5	5	2.3079	2.306	3 0 4
7	15	4.2794	4.21	1 $\bar{1}$ 3	8	20	2.2822	2.281	1 3 3
11	-	4.1405	-	1 1 3	18	-	2.2820	-	$\bar{1}$ $\bar{3}$ 4
100	100	4.0355	4.04	2 0 0	16	15	2.2507	2.252	1 $\bar{3}$ 4
90	80	3.9231	3.92	0 2 0	14	10	2.2293	2.227	3 $\bar{1}$ 4
8	-	3.7690	-	$\bar{1}$ 1 4	12	-	2.2113	-	$\bar{1}$ 3 4
12	10	3.7186	3.72	1 $\bar{1}$ 4	6	-	2.2003	-	$\bar{2}$ 3 0
12	-	3.5998	-	1 1 4	13	10	2.1992	2.200	3 1 4
33	30	3.5967	3.60	$\bar{2}$ 1 0	6	-	2.1893	-	2 3 0
34	-	3.5807	-	2 1 0	10	-	2.1720	-	1 3 4
12	-	3.5567	-	$\bar{2}$ 0 3	6	5	2.1241	2.124	$\bar{1}$ $\bar{1}$ 9
32	30	3.5360	3.53	$\bar{1}$ 2 0	13	-	2.0841	-	$\bar{2}$ $\bar{2}$ 7
28	-	3.5208	-	1 2 0	10	-	2.0261	-	$\bar{3}$ 0 7
19	15	3.4492	3.44	0 $\bar{2}$ 3	7	-	2.0218	-	$\bar{2}$ 2 7
9	10	3.3579	3.331	2 0 3	15	15	1.9946	1.995	2 $\bar{2}$ 7
9	-	3.2625	-	$\bar{2}$ $\bar{1}$ 3	12	10	1.9748	1.974	$\bar{3}$ $\bar{1}$ 7
11	-	3.2459	-	$\bar{2}$ 0 4	10	10	1.9588	1.959	$\bar{2}$ $\bar{1}$ 9
7	-	3.2168	-	$\bar{2}$ 1 3	5	-	1.9299	-	2 2 7
12	-	3.2051	-	$\bar{1}$ $\bar{2}$ 3	5	-	1.9085	-	$\bar{1}$ 4 0
13	-	3.1559	-	0 $\bar{2}$ 4	7	-	1.8905	-	$\bar{1}$ 4 2
15	15	3.1393	3.125	1 $\bar{2}$ 3	6	-	1.8805	-	$\bar{3}$ 3 0
5	-	3.1174	-	2 $\bar{1}$ 3	10	-	1.8598	-	3 $\bar{1}$ 7
11	-	3.1097	-	$\bar{1}$ 2 3	13	10	1.8585	1.857	$\bar{1}$ 3 7
13	-	3.0462	-	2 0 4	6	-	1.8485	-	1 4 3
10	-	3.0300	-	1 2 3	11	-	1.8203	-	1 3 7
9	-	2.9763	-	$\bar{1}$ $\bar{2}$ 4	8	-	1.7983	-	$\bar{4}$ 2 0
7	-	2.9035	-	1 $\bar{2}$ 4	8	-	1.7903	-	4 2 0
15	10	2.8595	2.860	0 0 7	7	-	1.7680	-	$\bar{2}$ 4 0
37	50	2.8207	2.815	$\bar{2}$ 2 0	8	-	1.7604	-	2 4 0
37	-	2.8053	-	2 2 0	5	-	1.7416	-	1 4 5
9	5	2.7915	2.774	1 2 4	5	-	1.7274	-	$\bar{4}$ 1 6
7	-	2.7521	-	$\bar{1}$ 0 7	5	-	1.7164	-	$\bar{3}$ 1 9
49	40	2.7257	2.727	0 $\bar{1}$ 7	5	-	1.7007	-	$\bar{2}$ 0 11
5	-	2.6903	-	3 0 0	5	-	1.6919	-	$\bar{2}$ $\bar{2}$ 10
22	15	2.6492	2.650	0 1 7	7	-	1.6793	-	0 $\bar{2}$ 11
10	-	2.6419	-	1 0 7	5	-	1.6611	-	$\bar{2}$ 4 4
7	-	2.6306	-	$\bar{1}$ $\bar{1}$ 7	8	-	1.6477	-	$\bar{3}$ 3 6
5	5	2.6108	2.612	$\bar{2}$ 2 3	5	-	1.6114	-	$\bar{1}$ 3 9
54	45	2.5646	2.566	$\bar{1}$ 1 7	6	-	1.6233	-	$\bar{3}$ $\bar{3}$ 7
10	-	2.5532	-	$\bar{3}$ 0 3	5	-	1.5891	-	$\bar{3}$ 4 0
7	-	2.5367	-	1 $\bar{1}$ 7	5	-	1.5810	-	$\bar{3}$ 3 7
6	-	2.4921	-	$\bar{1}$ 3 0	6	-	1.5615	-	3 $\bar{3}$ 7
6	-	2.4841	-	1 3 0	5	-	1.5468	-	$\bar{3}$ 4 3
35	30	2.4721	2.473	1 1 7	8	-	1.5365	-	$\bar{4}$ 3 4
9	-	2.4408	-	3 0 3	5	-	1.4867	-	1 5 4
9	-	2.4363	-	$\bar{3}$ $\bar{1}$ 3	8	-	1.4238	-	$\bar{1}$ 0 14
5	-	2.4309	-	1 $\bar{3}$ 2	5	-	1.4406	-	$\bar{4}$ $\bar{3}$ 7
11	10	2.4196	2.420	$\bar{3}$ 1 3	12	-	1.4103	-	$\bar{4}$ 1 4
5	-	2.3922	-	0 3 3	12	-	1.4026	-	4 4 0

*Calculated powder pattern and indexing for thunderbayite on the basis of $a=8.088(3)$, $b=7.854(3)$, $c=20.078(8)$ Å, $\alpha=92.52(3)$, $\beta=93.71(3)$, $\gamma=90.15(4)$ ° and with the atom coordinates reported in Table 3 (only reflections with $I_{rel} \geq 5$ are listed).

Results and discussion

Description of the structure

In the crystal structure of thunderbayite there are two Tl sites, six Ag sites, six Au sites, 15 Sb sites and 12 S sites. Notably, the sites

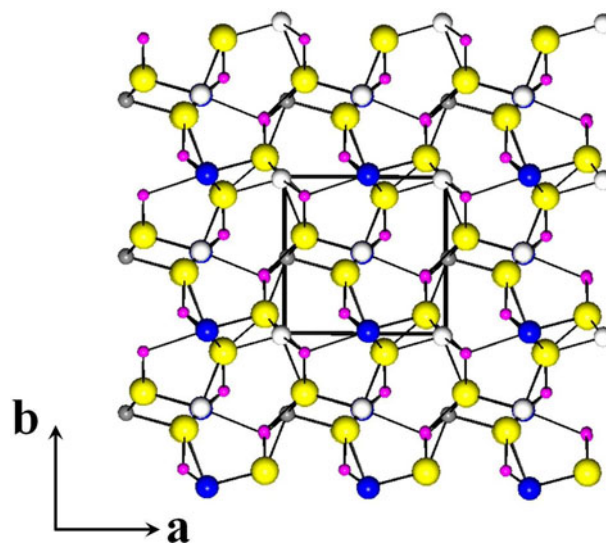


Fig. 3. The crystal structure of thunderbayite down $\sim[001]$. Tl, Ag, Au, Sb and S are given as blue, white, grey, violet and yellow circles, respectively. The unit cell and the orientation of the structure are reported.

appear chemically pure, with no (or limited, if we consider the refinement uncertainties) substitutions. We cannot apply the classical crystal-chemical description that takes into account the metal–anion coordination polyhedra for thunderbayite, as several metal–metal bonds are present. Thallium atoms are three-fold coordinated by Sb, Ag/Au and S, with an additional contact with Sb at distance > 3.55 Å. By considering a limit < 3.4 Å for the coordination environment of Ag, Ag6 is three-fold coordinated, Ag1 and Ag4 are four-fold coordinated, Ag3 and Ag5 are six-fold coordinated, and Ag2 and Ag5 are seven-fold coordinated. Interestingly, all the Ag atoms coordinate Sb and S except Ag6, which shows a short bond with Tl2 equal to $2.803(3)$ Å. Analogously, taking into account the same limit < 3.4 Å for the coordination environment of Au, all the Au atoms coordinate Sb and S except Au1, which shows a short bond with Tl1 equal to $2.920(2)$ Å. In detail, Au3 and Au4 are five-fold coordinated, Au1, Au5 and Au6 are six-fold coordinated and Au2 is seven-fold coordinated. The Sb atoms show several complex environments ranging from a three-fold to a six-fold coordination with Au/Ag, Sb and S. Only Sb1 and Sb11 make bonds with Tl, with distances varying from $2.889(5)$ Å (Sb1–Tl2) to $3.392(2)$ Å (Sb11–Tl1). Sb2, Sb6, Sb9 and Sb13 exhibit a similar coordination environment (five-fold coordination) with mean bond distances of 3.02, 3.08, 3.10 and 2.97 Å, respectively. Sb2 and Sb13 show close values of the mean bond distances as they coordinate to the same set of atoms: 2 Ag, 1 Au, and 2 S. Analogously, Sb6 and Sb9, having an almost identical coordination sphere, coordinate 2 Au, 1 Ag and 2 S atoms.

The crystal structure of thunderbayite can be viewed as a strongly deformed pyrite-type structure. It is well known that when half of the S atoms in pyrite-type compounds are replaced by other types of atoms, such as pnictogens, they can form different ordered ternary compounds, such as ullmannite (NiSbS)-type structures. The coordination environment of Ni in ullmannite (considering Sb and S as ‘anions’) closely resembles those observed (on average) for Ag and Au in thunderbayite (Figs 3, 4 and Table 4). If we look at Fig. 4, it appears that the structure of thunderbayite consists of ‘slabs’ stacked along

Table 6. X-ray powder-diffraction data (d in Å) for thunderbayite compared to that of criddleite.

Thunderbayite*		Criddleite**			Thunderbayite		Criddleite		
l_{calc}	d_{calc}	$h k l$	d_{meas}	l_{meas}	l_{calc}	d_{calc}	$h k l$	d_{meas}	l_{meas}
10	10.0082	0 0 2	10.01	5	5	2.3922	0 3 3	2.392	3
18	6.6721	0 0 3	6.67	30	10	2.3766	$\bar{1}$ $\bar{3}$ 3	2.385	5
22	5.6414	$\bar{1}$ 1 0	5.63	90	10	2.3706	2 2 4	2.366	10
11	5.6106	1 1 0	-	-	9	2.3516	1 $\bar{3}$ 3	2.351	3
6	5.4492	$\bar{1}$ 1 1	5.45	10	9	2.3447	3 $\bar{1}$ 3	-	-
9	5.0041	0 0 4	5.00	40	16	2.3378	$\bar{3}$ $\bar{1}$ 4	-	-
			4.94	5	12	2.3243	$\bar{2}$ $\bar{1}$ 7	2.329	1
7	4.8862	1 $\bar{1}$ 2	4.85	20	8	2.3178	$\bar{1}$ 3 3	-	-
9	4.4663	$\bar{1}$ $\bar{1}$ 3	-	-	11	2.3168	3 1 3	-	-
8	4.3370	$\bar{1}$ 1 3	4.34	30	15	2.3160	$\bar{3}$ 1 4	-	-
9	4.3063	0 $\bar{1}$ 4	-	-	5	2.3079	3 0 4	2.305	5
7	4.2794	1 $\bar{1}$ 3	4.25	40	8	2.2822	1 3 3	2.278	3
11	4.1405	1 1 3	-	-	18	2.2820	$\bar{1}$ $\bar{3}$ 4	-	-
100	4.0355	2 0 0	4.03	40	16	2.2507	1 $\bar{3}$ 4	-	-
			4.00	15	14	2.2293	3 $\bar{1}$ 4	2.225	5
			3.95	3	12	2.2113	$\bar{1}$ 3 4	-	-
90	3.9231	0 2 0	3.91	50	6	2.2003	$\bar{2}$ 3 0	-	-
11	3.8855	$\bar{1}$ $\bar{1}$ 4	-	-	13	2.1992	3 1 4	-	-
8	3.7690	$\bar{1}$ 1 4	3.75	1	6	2.1893	2 3 0	-	-
12	3.7186	1 $\bar{1}$ 4	3.69	10	10	2.1720	1 3 4	-	-
5	3.7087	0 $\bar{2}$ 2	-	-	6	2.1241	$\bar{1}$ $\bar{1}$ 9	2.125	10
12	3.5998	1 1 4	-	-	13	2.0841	$\bar{2}$ $\bar{2}$ 7	-	-
33	3.5967	$\bar{2}$ 1 0	-	-	10	2.0261	$\bar{3}$ 0 7	2.030	30
34	3.5807	2 1 0	-	-	7	2.0218	$\bar{2}$ 2 7	2.018	60
12	3.5567	$\bar{2}$ 0 3	-	-	15	1.9946	2 $\bar{2}$ 7	2.001	3
32	3.5360	$\bar{1}$ 2 0	-	-	12	1.9748	$\bar{3}$ $\bar{1}$ 7	1.980	35
28	3.5208	1 2 0	-	-	10	1.9588	$\bar{2}$ $\bar{1}$ 9	1.959	70
19	3.4492	0 $\bar{2}$ 3	3.431	10	5	1.9299	2 2 7	1.932	1
9	3.3579	2 0 3	3.331	10	5	1.9085	$\bar{1}$ 4 0	1.909	5
9	3.2625	$\bar{2}$ $\bar{1}$ 3	3.298	1	7	1.8905	$\bar{1}$ 4 2	1.891	10
11	3.2459	$\bar{2}$ 0 4	3.225	3	6	1.8805	$\bar{3}$ 3 0	1.873	10
7	3.2168	$\bar{2}$ 1 3	-	-	10	1.8598	3 $\bar{1}$ 7	-	-
12	3.2051	$\bar{1}$ $\bar{2}$ 3	-	-	13	1.8585	$\bar{1}$ 3 7	-	-
13	3.1559	0 $\bar{2}$ 4	-	-	6	1.8485	1 4 3	1.847	10
15	3.1393	1 $\bar{2}$ 3	3.142	5	11	1.8203	1 3 7	1.815	1
5	3.1174	2 $\bar{1}$ 3	-	-	8	1.7983	4 2 0	1.802	1
11	3.1097	$\bar{1}$ 2 3	-	-	8	1.7903	4 2 0	1.793	15
13	3.0462	2 0 4	-	-	7	1.7680	$\bar{2}$ 4 0	-	-
10	3.0300	1 2 3	-	-	8	1.7604	2 4 0	1.761	10
9	2.9763	$\bar{1}$ $\bar{2}$ 4	-	-	5	1.7416	1 4 5	1.741	10
7	2.9035	1 $\bar{2}$ 4	2.896	5	5	1.7274	4 1 6	1.726	10
15	2.8595	0 0 7	2.860	70	5	1.7164	$\bar{3}$ 1 9	1.715	10
37	2.8207	$\bar{2}$ 2 0	2.813	100	5	1.7007	$\bar{2}$ 0 11	1.697	3
37	2.8053	2 2 0	-	-	5	1.6919	$\bar{2}$ $\bar{2}$ 10	1.689	3
9	2.7915	1 2 4	2.774	3	7	1.6793	0 $\bar{2}$ 11	1.679	3
7	2.7521	$\bar{1}$ 0 7	-	-	5	1.6611	$\bar{2}$ 4 4	1.662	1
49	2.7257	0 $\bar{1}$ 7	-	-	8	1.6477	$\bar{3}$ 3 6	1.648	30
5	2.6903	3 0 0	2.689	1	5	1.6114	$\bar{1}$ 3 9	1.640	5
22	2.6492	0 1 7	-	-	6	1.6233	$\bar{3}$ $\bar{3}$ 7	1.620	3
10	2.6419	1 0 7	-	-	5	1.5891	$\bar{3}$ 4 0	1.588	5
7	2.6306	$\bar{1}$ $\bar{1}$ 7	-	-	5	1.5810	$\bar{3}$ 3 7	1.580	5
5	2.6108	$\bar{2}$ 2 3	2.612	3	6	1.5615	3 $\bar{3}$ 7	1.567	3
54	2.5646	$\bar{1}$ 1 7	2.569	30	5	1.5468	$\bar{3}$ 4 3	1.548	3
10	2.5532	$\bar{3}$ 0 3	5.545	40	8	1.5365	4 3 4	1.536	10
7	2.5367	1 $\bar{1}$ 7	2.522	15	5	1.4867	1 5 4	1.486	5
6	2.4921	$\bar{1}$ 3 0	2.500	10	8	1.4238	$\bar{1}$ 0 14	1.425	15
6	2.4841	1 3 0	2.480	30	5	1.4406	4 $\bar{3}$ 7	-	-
35	2.4721	1 1 7	2.473	20	12	1.4103	4 4 0	1.415	3
9	2.4408	3 0 3	-	-	12	1.4026	4 4 0	1.399	40
9	2.4363	$\bar{3}$ $\bar{1}$ 3	-	-					
5	2.4309	1 $\bar{3}$ 2	2.426	3					
11	2.4196	$\bar{3}$ 1 3	-	-					

*Calculated powder pattern and indexing for thunderbayite on the basis of $a = 8.088(3)$, $b = 7.854(3)$, $c = 20.078(8)$ Å, $\alpha = 92.52(3)$, $\beta = 93.71(3)$, $\gamma = 90.15(4)^\circ$ and with the atom coordinates reported in Table 3.

**Observed powder pattern reported for synthetic criddleite (Harris *et al.*, 1988).

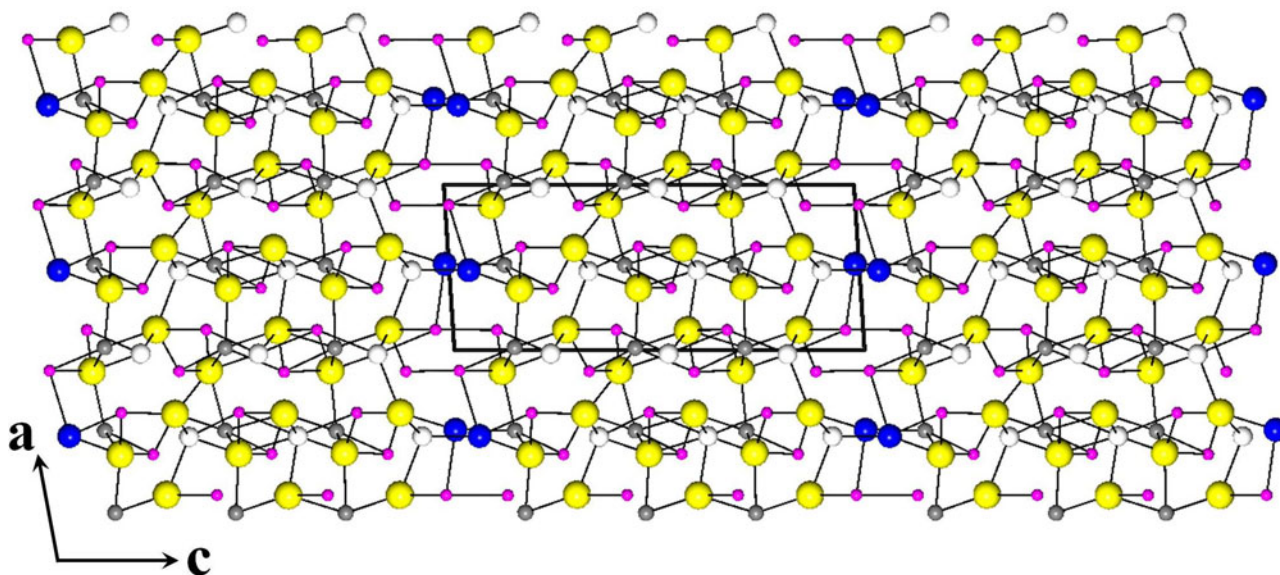


Fig. 4. The crystal structure of thunderbayite down $\sim[010]$. Symbols as in Fig. 2. The unit-cell and the orientation of the structure are shown.

the *c* axis: three alternate Au and Ag slabs with the Tl atoms terminating the unit cell. The Au slab is very similar to the Ni slab in the crystal structure of ullmannite (Bayliss, 1977), with several Sb–S short bonds (Table 4). Therefore, thunderbayite might be regarded as an intergrowth structure of ternary pyrite-type slabs and Tl–Sb/S layers stacked along the *c* axis.

Relationships between thunderbayite and criddleite

Thunderbayite shows close similarities with criddleite, $\text{TlAg}_2\text{Au}_3\text{Sb}_{10}\text{S}_{10}$ (Harris *et al.*, 1988), from an optical, chemical and crystallographic point of view (very similar unit-cell values). As the two minerals come from the same mineral deposit, initially we thought thunderbayite and criddleite to be one and the same phase. However, the strongly different $[\text{Tl}+\text{Ag}+\text{Au}]/(\text{Sb}+\text{S})$ ratio (0.54 and 0.30 for thunderbayite and criddleite, respectively) and the differences in the strongest diffraction peaks [4.04(100), 3.92(90), 2.565(50) Å and 2.813(100), 5.63(90), 2.86(70) Å, for thunderbayite and criddleite, respectively] made us confident that they are different mineral species. Table 6 shows a comparison of the powder-diffraction data of thunderbayite and criddleite.

Although the crystal structure of criddleite is as yet unknown, it is very likely that it possesses the same metal–metal interactions as observed in thunderbayite. Similarly, the unknown structure of vaughanite, $\text{TlHgSb}_4\text{S}_7$ (Harris *et al.*, 1989), might also show the same features. However, discussions on charge balance, degree of metallic bonding and possible structural models must await the availability of suitable crystals for X-ray investigations.

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Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2020.80>

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