

MONTBRAYITE, (Au,Ag,Sb,Pb,Bi)₂₃(Te,Sb,Pb,Bi)₃₈, FROM THE ROBB-MONTBRAY MINE, MONTBRAY, QUÉBEC: CRYSTAL STRUCTURE AND REVISION OF THE CHEMICAL FORMULA

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ABSTRACT

The crystal structure of the mineral montbrayite, a rare gold telluride, was solved using intensity data collected from a crystal of the co-type material from the Robb-Montbray mine, Montbray, Abitibi County, Québec, Canada. The study revealed that the structure is triclinic, space group $P\bar{1}$, with cell parameters: a 10.8045(6), b 12.1470(6), c 13.4480(7) Å, α 108.091(5), β 104.362(5), γ 97.471(5)°, and V 1583.65(15) Å³. The refinement of an anisotropic model led to an R index of 6.36% for 5145 independent reflections with $F_o > 4\sigma(F_o)$, GooF 1.023. There are 19 Te sites and 12 Au sites in the crystal structure of montbrayite. The Au sites host variable amounts of Sb, whereas all the Te sites but one host only Te. All the Au atoms can be considered to be in octahedral coordination forming more regular AuTe₆ or more distorted AuTe₄₊₂ polyhedra, with the exception of one Au position which links five Te atoms and closes its coordination sphere with a contact with itself. Crystal-chemical features of the Au and Te atoms are discussed in relation to other gold and silver tellurides. Electron microprobe analyses of the crystal used for the structural study led to the formula Au_{21.60}Sb_{0.68}Te_{37.41}Bi_{1.31}, calculated on the basis of 61 atoms per formula unit. On the basis of information gained from the structural and chemical characterization, the crystal-chemical formula was revised, yielding (Au,Ag,Sb,Bi,Pb)₂₃(Te,Sb,Bi,Pb)₃₈ ($Z = 1$) instead of (Au,Sb)₂Te₃ ($Z = 12$) as previously reported. The redefinition of montbrayite has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (voting proposal 17-F).

Keywords: montbrayite, crystal structure, gold tellurides, gold, silver, Robb-Montbray, Québec.

INTRODUCTION

Montbrayite was defined as a new mineral species by Peacock & Thompson (1946) during a study of the ores from the Robb-Montbray mine, Montbray, Abitibi County, Québec (Canada). The mineral was given the chemical formula (Au,Sb)₂Te₃ although Pb, Bi, Sb, and Ag were also reported in the chemical analysis. The uncertainty in the attribution of the minor elements was due to the coexistence of

tellurobismuthite (Bi₂Te₃), altaite (PbTe), and petzite (Ag₃AuTe₂) in the analyzed fragment, and for this reason only Sb was included in the formula. Later, Bachechi (1972) was able to synthesize montbrayite and showed that the minor isomorphous substitutions, namely Bi, Pb, and Sb, play a key role for the stability of the mineral. The key role of such minor elements for montbrayite stability, especially Sb, has recently been confirmed by Nakamura & Ikeda (2002), who

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TABLE 1. ELECTRON MICROPROBE DATA (IN wt.% OF ELEMENTS) AND ATOMIC RATIOS (ON THE BASIS OF 61 ATOMS PER FORMULA UNIT) FOR THE SELECTED MONTBRAYITE CRYSTAL TOGETHER WITH DATA FROM THE LITERATURE

	1	2	3	4	5	6	7	8	9	10
Au	44.30	47.70	47.40	46.05	45.09	46.80	49.45	48.30	47.03	47.97
Ag	0.60	0.60	0.40	0.00	0.00	0.45	0.00	0.00	0.03	0.03
Pb	1.60	1.30	1.00	1.10	0.02	0.00	0.00	0.16	0.10	0.00
Bi	2.80	2.90	1.10	3.90	3.68	1.90	3.50	0.02	0.03	0.00
Sb	0.90	0.30	3.20	1.05	1.79	4.65	0.00	6.34	7.33	4.83
Te	49.80	47.00	46.70	47.25	49.15	46.10	46.65	46.40	46.10	45.43
Total	100.00	99.80	99.80	99.35	99.73	99.90	99.60	101.20	100.63	98.27
Au	21.17	23.12	22.69	22.39	21.60	22.33	24.22	22.62	22.04	23.20
Ag	0.49	0.55	0.31	0.00	0.00	0.40	0.00	0.01	0.02	0.06
Pb	0.73	0.61	0.49	0.49	0.00	0.00	0.00	0.07	0.04	0.00
Bi	1.28	1.34	0.49	1.80	1.31	0.85	1.62	0.01	0.02	0.00
Sb	0.67	0.24	2.50	0.82	0.68	3.60	0.00	4.78	5.55	3.78
Te	36.66	35.14	34.53	35.50	37.41	33.82	35.17	33.50	33.33	33.96
	61.00	61.00	61.00	61.00	61.00	61.00	61.00	61.00	61.00	61.00

1: Robb-Montbray, Québec, Canada (Peacock & Thompson 1946); 2: Robb-Montbray, Québec, Canada (Rucklidge 1968); 3: Robb-Montbray, Québec, Canada (Bachechi 1972); 4: Robb-Montbray, Québec, Canada (Criddle *et al.* 1991), average of two analyses; 5: Robb-Montbray, Québec, Canada, this study, average of five analyses; 6: Enasen, Sweden (Nysten & Annersten 1984), average of two analyses; 7: Voronezhsky Massif, Russia (Genkin *et al.* 1999), average of two analyses; 8: Golden Mile, Western Australia (Shackleton & Spry 2003), average of five analyses; 9: Golden Mile, Western Australia (Shackleton & Spry 2003), average of three analyses; 10: Golden Mile, Western Australia (Golding 1978), average of three analyses.

studied isothermal phase relations in the Au–Sb–Te system.

Criddle *et al.* (1991) re-analyzed montbrayite from the type locality from the chemical and optical points of view. Their chemical analyses were in agreement with those originally reported (Peacock & Thompson 1946), differing only in the absence of detectable Ag. More recently, Shackleton & Spry (2003) reported an Sb-rich montbrayite from the Golden Mile, Western Australia, and analyzed all the published compositional data for montbrayite. They concluded that: (1) Sb and Bi substitute at both the Te and Au sites; (2) Ag likely substitutes at the Au site but it is not known at which site Pb substitutes; (3) Bi, Ag, and Pb appear to stabilize montbrayite in much the same manner as does Sb. Shackleton & Spry (2003) also suggested a revision of the chemical formula of montbrayite from $(\text{Au,Sb})_2\text{Te}_3$ to $(\text{Au,Ag,Sb})_2(\text{Te,Sb,Bi})_3$ or, more likely, $(\text{Au,Ag,Sb,Bi})_2(\text{Te,Sb,Bi})_3$. However, as also noted by Criddle *et al.* (1991), the resolution of the uncertainty concerning the mode of substitution of Sb, or Sb, Pb, and Bi, for Au or Te, or both elements, should await the findings from a structure determination of the mineral.

The first X-ray diffraction studies of montbrayite were reported in the original new mineral study (Peacock & Thompson 1946). These authors, by

means of X-ray photographic techniques (Weissenberg and rotation methods), observed a triclinic symmetry with unit-cell parameters a 12.08, b 13.43, c 10.78 Å, α 104.30, β 97.34, γ 107.53°. However, the crystal structure remained unsolved. The first attempt to solve the montbrayite structure was by Bachechi (1971), by means of the precession method, using a sample from the type locality. Bachechi (1971) confirmed the triclinic unit-cell observed by Peacock & Thompson (1946) and hypothesized a structural model in the acentric space group $P1$ consisting of rows of atoms running along [340]. The refinement of the structure, however, led to an R index of about 25% and, although Bachechi (1971) mentioned a full data set being collected with an automated four-circle single-crystal diffractometer, the final structural model was never reported. Finally, Edenharter *et al.* (1991) studied from the structural point of view a crystal from the same sample from the type locality as that used in this study [the sample was provided to them by one of us (WHP)]. They confirmed the triclinic nature of the structure and solved it in the non-centrosymmetric $P1$ space group, as previously attempted by Bachechi (1971). Although the R index was satisfactory ($\sim 7.5\%$, but with several atoms exhibiting negative temperature factors), their structural model showed several partially occupied sites, which led to large discrepancies

TABLE 2. DATA AND EXPERIMENTAL DETAILS FOR THE SELECTED MONTBRAYITE CRYSTAL

Crystal data	
Formula	(Au,Sb) ₂₃ Te ₃₆ Bi ₂
Crystal size (mm ³)	0.050 × 0.065 × 0.085
Form	block
Color	black
Crystal system	triclinic
Space group	<i>P</i> 1̄ (#2)
<i>a</i> (Å)	10.8045(6)
<i>b</i> (Å)	12.1470(6)
<i>c</i> (Å)	13.4480(7)
α (°)	108.091(5)
β (°)	104.362(5)
γ (°)	97.471(5)
<i>V</i> (Å ³)	1583.65(15)
<i>Z</i>	1
Data collection	
Instrument	Oxford Diffraction Xcalibur 3
Radiation type	MoK α ($\lambda = 0.71073$)
Temperature (K)	293(3)
Detector to sample distance (cm)	6
Number of frames	2415
Measuring time (s)	40
Maximum covered 2 θ (°)	60.00
Absorption correction	multi-scan (<i>ABSPACK</i> ; Oxford Diffraction 2006)
Collected reflections	30597
Unique reflections	9195
Reflections with $F_o > 4\sigma(F_o)$	5145
R_{int}	0.0702
R_σ	0.0811
Range of <i>h</i> , <i>k</i> , <i>l</i>	-15 ≤ <i>h</i> ≤ 15, -17 ≤ <i>k</i> ≤ 17, -18 ≤ <i>l</i> ≤ 18
Refinement	
Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4\sigma(F_o)$]	0.0636
Final R_1 (all data)	0.1141
<i>S</i>	1.02
Number refined parameters	291
$\Delta\rho_{max}$ (e Å ⁻³)	1.30
$\Delta\rho_{min}$ (e Å ⁻³)	-1.64

between the formula computed from the structure refinement and that obtained from chemical analyses. Nevertheless, the structural model given by Edenharter *et al.* (1991) includes 61 atoms (as in our study) and exhibits features which are in agreement with what has been found in this study (see below).

In the course of a research project dealing with the description and structural characterization of

natural gold, silver, and copper tellurides (Bindi 2008, 2009, 2014, Bindi & Cipriani 2004a, 2004b, 2004c, Bindi & Keutsch 2018, Bindi & Pinch 2014, Bindi *et al.* 2004, 2005, 2009, 2013, 2015), we examined a fragment from the co-type material obtained by one of us (WHP) from the Royal Ontario Museum (Mineralogy Department) in 1982. The sample was originally acquired from the Royal Ontario Museum (by exchange) and it was labeled "Frohbergite, Robb Montbray, Canada". It measured 27 × 20 × 20 mm, weighed 21 g, and was registered as M37271 (originally M-15815-B); this was part of the material donated to the ROM by Hugh Park in 1928 and later studied by Peacock & Thompson (1946). The sample consists of large montbrayite grains associated with tellurobismuthite, frohbergite, petzite, altaite, melonite, chalcopyrite, and tiny wires of gold.

To help resolve the concerns relating to the structure of montbrayite and those related to the role of minor elements raised in the previous literature, we present here new crystal-structure data for the mineral from its type locality, together with new chemical data.

CHEMICAL COMPOSITION

The chemical composition was determined using wavelength dispersive analysis (WDS) by means of an JEOL JXA-8200 electron microprobe, from the same crystal used for the structural study. Concentrations of major and minor elements were determined at an accelerating voltage of 20 kV and a beam current of 40 nA, with 10 s as the counting time. For the WDS analyses the following lines were used: AuM α , AgL α , SbL β , PbM α , BiM β , and TeL α . The standards employed were: native elements for Au and Ag, galena for Pb, synthetic Bi₂S₃ for Bi, and synthetic Sb₂Te₃ for Sb and Te. The crystal fragment was found to be homogeneous within analytical uncertainty. The average chemical composition (five analyses of different spots) is reported in Table 1, together with chemical data for montbrayite from other occurrences taken from literature. On the basis of 61 atoms (see below for the structure solution), the chemical formula for montbrayite can be written as Au_{21.60}Sb_{0.68}Te_{37.41}Bi_{1.31}.

CRYSTAL-STRUCTURE SOLUTION AND REFINEMENT

A small crystal fragment (50 × 65 × 85 μm^3) was selected for the single-crystal X-ray diffraction study. The intensity data collection (see Table 2 for details) was carried out by means of an Oxford Diffraction Xcalibur 3 single-crystal diffractometer (enhanced X-ray source, MoK α X-ray radiation, $\lambda = 0.71073$ Å)

TABLE 3. ATOMS, SITE OCCUPANCY FACTORS (s.o.f.), FRACTIONAL ATOMIC COORDINATES, AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (\AA^2) FOR THE SELECTED MONTBRAYITE CRYSTAL

Atom	s.o.f.	x	y	z	U_{eq}
Au1	Au _{0.872(9)} Sb _{0.128}	0.15833(7)	0.42458(7)	0.32381(6)	0.0129(3)
Au2	Au _{0.960(9)} Sb _{0.040}	-0.09742(7)	0.34589(7)	0.01427(6)	0.0133(3)
Au3	Au _{0.951(9)} Sb _{0.049}	0.64203(7)	0.26047(7)	0.69800(6)	0.0137(3)
Au4	Au _{0.879(9)} Sb _{0.121}	0.37677(7)	0.17845(8)	0.38274(6)	0.0131(3)
Au5	Au _{0.93(1)} Sb _{0.07}	0.42152(7)	0.50241(7)	0.63161(6)	0.0138(3)
Au6	Au _{0.942(9)} Sb _{0.058}	0.12410(7)	0.10291(8)	0.07485(6)	0.0136(3)
Au7	Au _{0.97(1)} Sb _{0.03}	0.68990(7)	0.58561(7)	0.93528(6)	0.0131(3)
Au8	Au _{0.97(1)} Sb _{0.03}	0.21231(6)	0.75086(7)	0.56850(6)	0.0131(3)
Au9	Au _{0.96(1)} Sb _{0.04}	-0.04847(7)	0.67199(7)	0.25444(6)	0.0137(3)
Au10	Au _{0.98(1)} Sb _{0.02}	0.47876(6)	0.82643(7)	0.87477(6)	0.0132(3)
Au11	Au _{0.95(1)} Sb _{0.05}	-0.73828(6)	0.08731(7)	-0.18652(6)	0.0128(3)
Au12	Au _{0.96(1)} Sb _{0.04}	0	0	½	0.0147(4)
Te1	Te _{1.00}	0.01945(11)	0.56304(12)	0.42757(11)	0.0139(3)
Te2	Te _{1.00}	-0.54179(11)	0.26403(12)	-0.03781(11)	0.0145(3)
Te3	Te _{1.00}	0.12471(12)	0.53845(12)	0.16493(11)	0.0186(3)
Te4	Te _{1.00}	0.09102(11)	0.24570(12)	-0.04981(11)	0.0148(3)
Te5	Te _{1.00}	-0.30731(11)	-0.00740(12)	0.01131(10)	0.0146(3)
Te6	Te _{1.00}	-0.19436(11)	0.82191(12)	0.35247(10)	0.0136(3)
Te7	Te _{1.00}	0.27542(12)	0.64944(13)	0.73849(11)	0.0164(3)
Te8	Te _{1.00}	-0.06447(11)	0.09440(12)	0.32360(10)	0.0141(3)
Te9	Te _{1.00}	0.35301(12)	0.33300(14)	0.25998(13)	0.0246(4)
Te10	Te _{1.00}	-0.31010(12)	0.16036(12)	-0.13046(10)	0.0143(3)
Te11	Te _{1.00}	0.17414(11)	-0.17029(12)	0.38476(11)	0.0153(3)
Te12	Te _{1.00}	0.43687(11)	-0.09305(12)	0.70308(11)	0.0147(3)
Te13	Te _{1.00}	0.23487(12)	0.31847(13)	0.48178(11)	0.0171(3)
Te14	Te _{1.00}	0.50009(11)	0.40106(12)	0.79286(10)	0.0134(3)
Te15	Te _{1.00}	0.42700(11)	0.07926(12)	0.54567(10)	0.0138(3)
Te16	Te _{1.00}	-0.03401(12)	0.22026(13)	0.17294(11)	0.0167(3)
Te17	Te _{1.00}	0.16059(11)	-0.00696(12)	0.22455(11)	0.0149(3)
Te18	Te _{1.00}	-0.23927(11)	0.48704(12)	0.10831(10)	0.0132(3)
Bi	Bi _{0.74(1)} Te _{0.26}	0.60688(9)	0.38095(10)	0.53111(9)	0.0321(4)

fitted with a Sapphire 2 CCD detector. A total of 3142 frames of data were collected at room temperature as six sets of omega runs with an exposure time of 40 s per frame and a frame width of 1.00° . This afforded an overall data collection of 30,597 reflections (9195 unique). The refined triclinic unit-cell parameters are a 10.8045(6), b 12.1470(6), c 13.4480(7) Å, α 108.091(5), β 104.362(5), γ 97.471(5)°, and V 1583.65(15) Å³, which, neglecting the orientation, are similar to those originally reported by Peacock & Thompson (1946), and subsequently by Bachechi (1971) and Edenharter *et al.* (1991).

Data frames were processed using the *CrysAlis* software package (Oxford Diffraction 2006) running on the Xcalibur 3 control PC. The program ABSPACK (Oxford Diffraction 2006) was used for the absorption correction. The merging R for the data set decreased from 15.69% before the absorption correction to

7.02% after the correction. Although the statistical tests on the distribution of $|E|$ values strongly indicated the presence of an inversion center ($|E^2 - 1| = 0.985$), pointing to the choice of the space group $P\bar{1}$, the first attempt to refine the structure was done in the non-centrosymmetric $P1$ space group using the atomic coordinates reported by Edenharter *et al.* (1991). The refinement of this model ($R1 \sim 17\%$) showed: (1) high correlation matrices between couples of atoms that are equivalent in the corresponding centrosymmetric space group; (2) Flack parameter = 0.51, strongly indicating a centrosymmetric space group; and (3) absence of partially occupied sites as predicted in the model of Edenharter *et al.* (1991).

Given these features, the structure solution was then initiated in the space group $P\bar{1}$. The positions of most of the atoms (all the Au positions and most of the Te atoms) were determined by means of direct

TABLE 4. ANISOTROPIC DISPLACEMENT PARAMETERS OF THE ATOMS FOR THE SELECTED MONTBRAYITE CRYSTAL

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.0138(4)	0.0125(5)	0.0152(5)	0.0035(3)	0.0058(3)	0.0075(4)
Au2	0.0138(4)	0.0118(5)	0.0155(4)	0.0037(3)	0.0049(3)	0.0060(3)
Au3	0.0139(4)	0.0116(5)	0.0166(4)	0.0031(3)	0.0059(3)	0.0055(3)
Au4	0.0149(4)	0.0118(5)	0.0158(5)	0.0048(3)	0.0069(3)	0.0069(3)
Au5	0.0135(4)	0.0107(5)	0.0163(5)	0.0008(3)	0.0033(3)	0.0053(3)
Au6	0.0159(4)	0.0128(4)	0.0152(4)	0.0054(3)	0.0061(3)	0.0074(3)
Au7	0.0128(4)	0.0105(5)	0.0148(4)	0.0011(3)	0.0033(3)	0.0042(3)
Au8	0.0132(4)	0.0117(5)	0.0142(4)	0.0003(3)	0.0037(3)	0.0056(3)
Au9	0.0132(4)	0.0107(5)	0.0162(5)	0.0015(3)	0.0037(3)	0.0042(3)
Au10	0.0136(4)	0.0123(5)	0.0137(4)	-0.0007(3)	0.0033(3)	0.0066(3)
Au11	0.0140(4)	0.0105(5)	0.0131(4)	0.0000(3)	0.0028(3)	0.0052(3)
Au12	0.0163(5)	0.0113(6)	0.0135(6)	0.0003(4)	0.0005(4)	0.0048(5)
Te1	0.0122(5)	0.0125(7)	0.0170(6)	0.0001(5)	0.0049(5)	0.0061(5)
Te2	0.0134(5)	0.0127(7)	0.0172(6)	0.0025(5)	0.0032(5)	0.0065(5)
Te3	0.0232(6)	0.0170(8)	0.0232(7)	0.0068(6)	0.0088(5)	0.0148(6)
Te4	0.0132(5)	0.0128(7)	0.0189(7)	0.0019(5)	0.0059(5)	0.0060(6)
Te5	0.0140(5)	0.0121(7)	0.0167(6)	-0.0013(5)	0.0047(5)	0.0053(5)
Te6	0.0142(5)	0.0122(7)	0.0153(6)	0.0001(5)	0.0051(5)	0.0068(5)
Te7	0.0135(5)	0.0154(7)	0.0182(7)	0.0023(5)	0.0035(5)	0.0047(6)
Te8	0.0152(5)	0.0122(7)	0.0152(6)	0.0007(5)	0.0052(5)	0.0056(5)
Te9	0.0159(6)	0.0215(8)	0.0310(8)	0.0006(6)	0.0091(5)	0.0018(7)
Te10	0.0169(6)	0.0140(7)	0.0147(6)	0.0048(5)	0.0060(5)	0.0073(5)
Te11	0.0138(5)	0.0128(7)	0.0188(7)	0.0000(5)	0.0060(5)	0.0053(6)
Te12	0.0131(5)	0.0140(7)	0.0172(6)	-0.0001(5)	0.0054(5)	0.0064(5)
Te13	0.0135(6)	0.0137(7)	0.0204(7)	0.0017(5)	0.0045(5)	0.0022(6)
Te14	0.0147(6)	0.0096(6)	0.0150(6)	0.0015(5)	0.0039(5)	0.0042(5)
Te15	0.0153(5)	0.0113(7)	0.0172(6)	0.0033(5)	0.0058(5)	0.0076(5)
Te16	0.0158(6)	0.0177(7)	0.0179(7)	0.0018(5)	0.0053(5)	0.0088(6)
Te17	0.0156(6)	0.0119(7)	0.0162(6)	0.0038(5)	0.0036(5)	0.0043(5)
Te18	0.0137(5)	0.0101(6)	0.0158(6)	0.0023(5)	0.0054(5)	0.0043(5)
Bi	0.0321(6)	0.0339(7)	0.0406(7)	0.0106(5)	0.0172(5)	0.0211(6)

methods (Sheldrick 2008). A least-squares refinement on F^2 using these heavy-atom positions and isotropic temperature factors resulted in an R factor of $\sim 18\%$. Three-dimensional difference Fourier synthesis yielded the position of the remaining tellurium atoms. The SHELXL program (Sheldrick 2008) was used for the refinement of the structure. The occupancy of all the sites was left free to vary (Au *versus* vacancy and Te *versus* vacancy). The electron density at all the Au sites was found to be systematically < 79 , indicating substitution by a lighter element. Given the absence of Ag in our sample (see above), we thus refined the occupancy of all the Au sites using the scattering curves of Au *versus* Sb (Table 2). All the Te sites but one were found to be consistent with a pure occupation by Te and then were fixed to the resulting value. One Te site was found to exhibit a mean electron number of $74.9 e^-$, and, given the chemical data obtained from the same crystal, was thought to be a Bi/Te site. The

refinement using the scattering curves of Bi *versus* Te gave the $\text{Bi}_{0.74}\text{Te}_{0.26}$ site population (Table 2). Neutral scattering curves for Au, Sb, Bi, and Te were taken from the *International Tables for X-ray Crystallography* (Ibers & Hamilton 1974). At the last stage, with anisotropic atomic displacement parameters for all atoms and no constraints, the residual value settled at $R1 = 6.36\%$ for 5145 observed reflections [$F_o > 4\sigma(F_o)$ level] and 291 parameters and at $R1 = 11.41\%$ for all 9195 independent reflections. Inspection of the difference Fourier map revealed that maximum positive and negative peaks were 1.30 and $1.64 e^-/\text{\AA}^3$, respectively. The formula obtained from the structure refinement, $(\text{Au}_{21.69}\text{Sb}_{1.31})_{\Sigma 23}(\text{Te}_{36.52}\text{Bi}_{1.48})_{\Sigma 38}$, is in excellent agreement with that obtained from the electron microprobe data $(\text{Au}_{21.60}\text{Sb}_{0.68})_{\Sigma 22.28}(\text{Te}_{37.41}\text{Bi}_{1.31})_{\Sigma 38.72}$. Although it is possible that minor Te (given its close atomic number with Sb) could enter the Au sites [according to

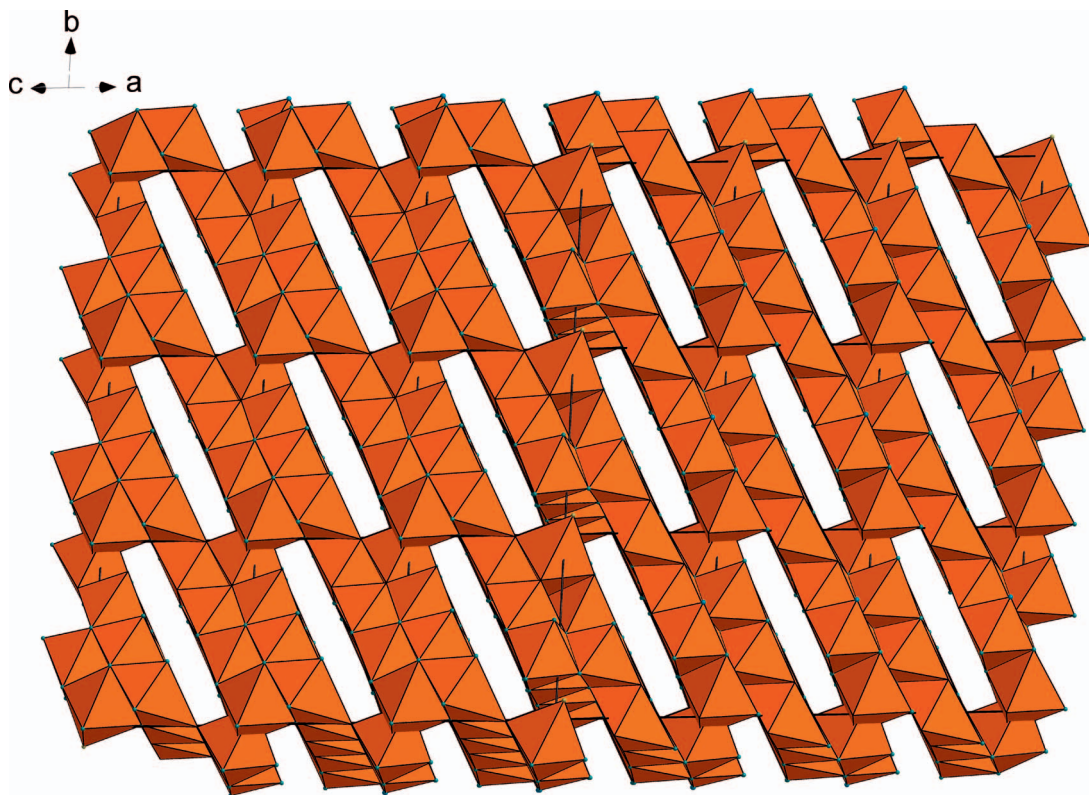


Fig. 2. The crystal structure of montbrayite with Au atoms depicted as polyhedra. Edge-sharing octahedral chains along [101] generating empty spaces (hosting Te–Te contacts) are evident. The unit cell and the orientation of the structure are outlined.

Au–Te–Bi–Te–Au–Au–Te–Te–Te–Au–Au–Te–Te, corresponding to $(0\bar{3}10)$ -sheets that give rise to a sort of commensurate modulation of ~ 52.6 Å along $[3010]$.

Relationships with other gold tellurides

Montbrayite is structurally related to the group of gold-silver tellurides with the chemical formula $Au_{1-x}Ag_xTe_2$, the most important group of minerals from an economic standpoint in the Au–Ag–Te system. This group comprises calaverite, $AuTe_2$, krennerite, Au_3AgTe_8 , muthmannite, $AuAgTe_2$, and sylvanite, $AuAgTe_4$. Petzite, Ag_3AuTe_2 , cannot be grouped with the structures above since it shows intermetallic behavior. Indeed, it exhibits a garnet-like structure consisting of edge-sharing $Ag[Te_4Ag_2Au_2]$ and $Au[Ag_6Te_2]$ polyhedra.

The crystal-chemical environment of Au is very similar in these structures. The $AuTe_6$ polyhedra in montbrayite show a mean bond-distance ranging from 2.82 to 2.95 Å (Table 5). As described above, we

observed $AuTe_6$ and more-distorted $AuTe_{4+2}$ polyhedra. Such a feature poses montbrayite as an intermediate compound between muthmannite (quite regular $AuTe_6$ octahedra) and krennerite/sylvanite (Au in a [4+2] coordination). The Au(1) and Au(2) sites in muthmannite show distances in the range 2.67–2.98 Å [Au(1)] and 2.66–2.90 Å [(Au(2))] (Bindi & Cipriani 2004a), whereas the $[4+2]Au$ distances in the crystal structure of krennerite vary from 2.93 to 2.96 Å (Dye & Smyth 2012) and in sylvanite vary from 2.88 to 2.91 Å (Pertlik 1984). In calaverite the Au atoms show a [2+4] coordination with Au–Te distances ranging from 2.68 to 2.97 Å (Reithmayer *et al.* 1993).

Interesting crystal-chemical features among the Au, Ag-tellurides also concern the environment of the tellurium atoms. Krennerite (Dye & Smyth 2012) and empressite (Bindi *et al.* 2004a) exhibit a Te_3 group in their structures. In contrast, Te–Te contacts < 2.9 Å forming Te_2 dumbbells are observed in calaverite (Reithmayer *et al.* 1993), sylvanite (Pertlik 1984), muthmannite (Bindi & Cipriani 2004a), and stützite (Peters *et al.* 1996, Bindi & Keutsch 2018). In

TABLE 5. BOND DISTANCES (IN Å) IN THE STRUCTURE OF MONTBRAYITE

Au1-Te1	2.695(2)	Au7-Te14	2.663(1)
Au1-Te9	2.704(2)	Au7-Te4	2.673(1)
Au1-Te13	2.822(2)	Au7-Te2	2.844(1)
Au1-Te16	2.835(2)	Au7-Te18	2.919(2)
Au1-Te3	2.862(2)	Au7-Te3	2.994(2)
Au1-Bi	2.991(1)	Au7-Te9	3.036(2)
<Au1-Te/Bi>	2.818	<Au7-Te>	2.855
Au2-Te18	2.681(1)	Au8-Te12	2.693(1)
Au2-Te4	2.689(1)	Au8-Te1	2.694(1)
Au2-Te10	2.803(2)	Au8-Te11	2.874(2)
Au2-Te3	2.919(2)	Au8-Te7	2.899(2)
Au2-Te16	2.987(2)	Au8-Te8	2.903(1)
Au2-Te3	3.119(2)	Au8-Bi	2.992(1)
<Au2-Te>	2.866	<Au8-Te/Bi>	2.843
Au3-Te14	2.682(2)	Au9-Te11	2.674(1)
Au3-Te11	2.700(1)	Au9-Te18	2.684(1)
Au3-Te15	2.819(2)	Au9-Te6	2.797(2)
Au3-Te10	2.895(2)	Au9-Te3	2.877(1)
Au3-Te3i	3.002(2)	Au9-Te1	3.005(2)
Au3-Bi	3.014(2)	Au9-Te4	3.160(2)
<Au3-Te/Bi>	2.852	<Au9-Te>	2.866
Au4-Te13	2.702(2)	Au10-Te7	2.671(2)
Au4-Te12	2.723(1)	Au10-Te5	2.677(1)
Au4-Te15	2.787(2)	Au10-Te2	2.726(2)
Au4-Te9	2.856(2)	Au10-Te12	2.737(2)
Au4-Te17	2.871(2)	Au10-Te9	3.272(2)
Au4-Bi	3.019(1)	Au10-Te5	3.315(2)
<Au4-Te/Bi>	2.826	<Au10-Te>	2.900
Au5-Te13	2.671(2)	Au11-Te8	2.667(1)
Au5-Te9	2.687(2)	Au11-Te2	2.675(1)
Au5-Te14	2.821(2)	Au11-Te6	2.767(2)
Au5-Te7	2.831(2)	Au11-Te5	2.776(2)
Au5-Bi	2.932(2)	Au11-Te4	3.300(1)
Au5-Bi	2.981(1)	Au11-Te12	3.322(2)
<Au5-Te/Bi>	2.821	<Au11-Te>	2.918
Au6-Te16	2.697(2)	Au12-Te6	2.667(1)
Au6-Te17	2.721(2)	Au12-Te6	2.667(1)
Au6-Te5	2.740(2)	Au12-Te8	2.916(2)
Au6-Te4	2.760(2)	Au12-Te8	2.916(2)
Au6-Te9	3.310(2)	Au12-Te11	3.269(1)
Au6-Au6	3.154(2)	Au12-Te11	3.269(1)
<Au6-Te>	2.897	<Au12-Te>	2.951

montbrayite the shortest Te-Te contacts are 2.83 Å (Te15-Te15 and Te10-Te17), 2.90 Å (Te1-Te1), and 2.95 Å (Te8-Te16). Such values are comparable to those observed in native tellurium (Te-Te = 2.835 Å; Cherin & Unger 1967).

X-ray powder pattern

The X-ray powder pattern calculated using the structural data obtained in this study is shown in Table

6. It appears very similar to both that originally reported (Peacock & Thompson 1946) and that given for the synthetic analogue of montbrayite (Bachechi 1972). The absence of the high-intensity low- θ peaks (at $d > 8$ Å) in the original study (Peacock & Thompson 1946) is ascribed to the fact that these authors used over-exposed photographic methods for the X-ray characterization. With such methods, the low- θ region has a very high background (as it is also

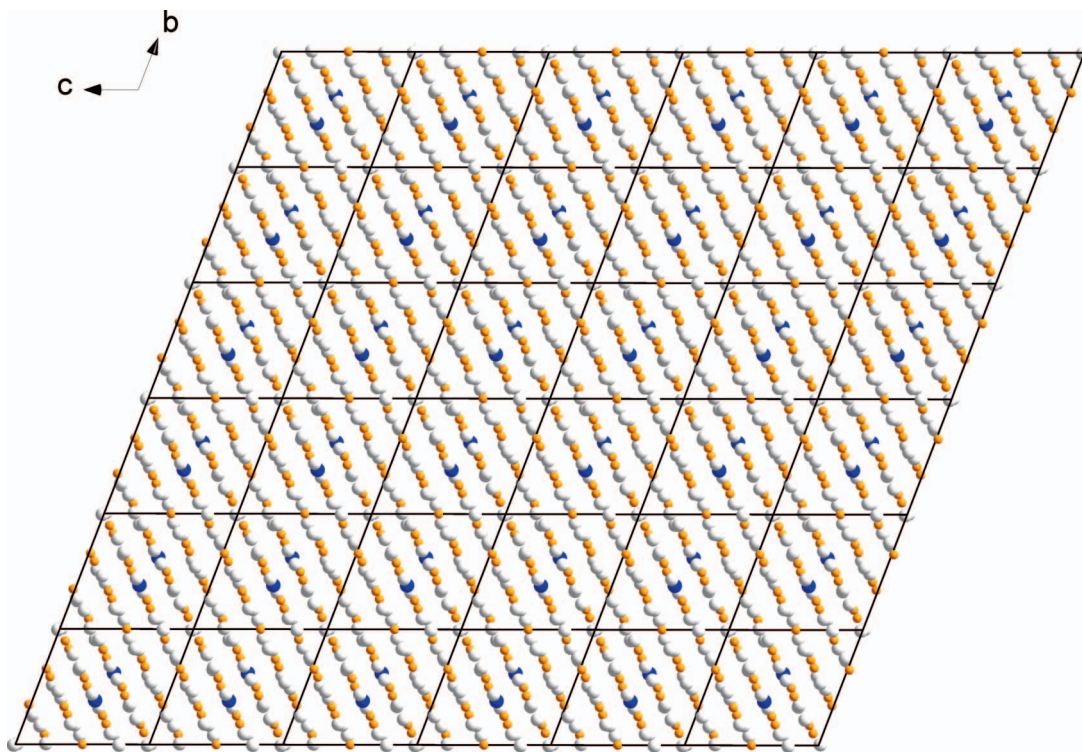


FIG. 3. A portion of the structure of montbrayite ($1 \times 6 \times 6$ unit cells) down [100] showing rows of atoms running along [034] with a complex sequence (see text for explanation). Atoms colors as in Figure 1. The unit cell and the orientation of the structure are outlined.

well visible in the diffraction photographs reported in their paper). However, the peaks at $d \sim 9.3$ and 11.2 \AA were confirmed by Bachechi (1972) during her studies of the synthetic analogue of montbrayite.

Nomenclature remarks

Although the structural formula obtained here for montbrayite from the type locality, ideally $(\text{Au,Sb})_{23}\text{Bi}_2\text{Te}_{36}$, matches very well the chemistry obtained (from the same crystal), we think that a revision of the chemical formula from $(\text{Au,Sb})_2\text{Te}_3$ to $(\text{Au,Sb})_{23}\text{Bi}_2\text{Te}_{36}$ would not be correct. Indeed, even if we do not consider the original chemical data by Peacock & Thompson (1946), who clearly state that their analyses could be contaminated by surrounding tellurobismuthite, altaite, and petzite, there are several chemical data from other occurrences (Table 1) which show Bi and/or Sb contents too high to satisfy our proposed formula. Especially illuminating is the case of Sb-rich montbrayite from the Golden Mile (Shackleton & Spry 2003), where there is only Sb besides Au and Te (no Pb, Bi, or Ag). The Sb content in the formula, when

normalized to 61 atoms, is about 4.7 (as an average, in *apfu*). This, together with the fact that Au is slightly $< 23 \text{ apfu}$ and Te $< 38 \text{ apfu}$, implies that Sb replaces both Au and Te in the Australian montbrayite. This substitution scheme does not work with our proposed (structural) formula. It appears clear that montbrayite needs a much more flexible formula.

What is clearly evident from our structure refinement is that (1) an element lighter than 79 (atomic number) substitutes (in a disordered fashion) for Au; (2) an element heavier than 51 (atomic number) substitutes (in an ordered fashion) for Te. The lighter element substituting for Au is surely Sb (taking into account our chemical data), but the heavier element substituting for Te could be Pb or Bi, or both (for the fragment studied here it is surely Bi, as Pb is almost absent, but this cannot be conclusive). Analogously, given the very close scattering power, minor Pb/Bi could randomly substitute for Au, and minor Sb could randomly substitute for Te and thus be invisible to X-rays. Furthermore, given the fact that we are dealing with a complex mineral with a quasi-intermetallic behavior, bond valence and cation-size considerations

TABLE 6. X-RAY POWDER DIFFRACTION DATA FOR MONTBRAYITE

1					2		3	
d_{calc}	l_{calc}	h	k	l	d_{meas}	l_{meas}	d_{meas}	l_{meas}
12.1699	1	0	0	1	-	-	-	-
11.2509	19	0	1	0	-	-	11.212	1
10.2928	4	0	$\bar{1}$	1	-	-	-	-
10.1988	11	1	0	0	-	-	-	-
9.3516	100	$\bar{1}$	0	1	-	-	9.302	1
8.5765	5	$\bar{1}$	1	0	-	-	-	-
7.4451	44	$\bar{1}$	$\bar{1}$	1	7.48	1	7.363	2
6.9625	8	$\bar{1}$	1	1	-	-	-	-
6.8524	7	1	0	1	-	-	-	-
6.3911	4	0	$\bar{1}$	2	-	-	-	-
6.1131	2	$\bar{1}$	0	2	-	-	-	-
6.0850	2	0	0	2	-	-	-	-
5.9599	2	$\bar{1}$	$\bar{1}$	2	-	-	-	-
5.4737	3	$\bar{1}$	2	0	-	-	-	-
5.1464	2	0	$\bar{2}$	2	-	-	-	-
4.9723	1	$\bar{1}$	$\bar{2}$	1	-	-	-	-
4.9617	4	$\bar{2}$	1	1	-	-	-	-
4.5278	1	0	2	1	-	-	-	-
4.5151	1	1	2	0	-	-	-	-
4.4258	8	$\bar{2}$	$\bar{1}$	2	4.47	2	4.425	4
4.2414	1	$\bar{1}$	0	3	-	-	-	-
4.2173	2	$\bar{2}$	1	2	-	-	-	-
4.0633	2	2	$\bar{2}$	1	-	-	-	-
4.0459	1	0	$\bar{2}$	3	-	-	-	-
4.0260	11	$\bar{2}$	2	1	4.07	$\frac{1}{2}$	4.009	$\frac{1}{2}$
4.0092	1	0	3	1	-	-	-	-
3.9223	2	1	$\bar{3}$	1	-	-	-	-
3.8145	5	1	1	2	3.81	$\frac{1}{2}$	3.812	1
3.8081	3	$\bar{1}$	3	0	-	-	-	-
3.7868	2	$\bar{2}$	$\bar{1}$	3	-	-	-	-
3.6269	3	2	1	1	-	-	3.644	$\frac{1}{2}$
3.5884	6	1	$\bar{2}$	3	3.52	$\frac{1}{2}$	3.535	1
3.5298	2	2	$\bar{2}$	2	-	-	-	-
3.3238	1	3	1	2	-	-	-	-
3.3053	1	$\bar{1}$	$\bar{3}$	3	-	-	-	-
3.2333	1	$\bar{1}$	$\bar{2}$	4	-	-	-	-
3.2009	8	1	3	3	3.22	1	3.196	1
3.1851	3	$\bar{2}$	3	1	-	-	-	-
3.0603	8	1	2	2	-	-	3.062	$\frac{1}{2}$
2.9778	30	2	2	1	2.97	8	2.983	8
2.9764	32	$\bar{3}$	2	2	-	-	-	-
2.9288	32	0	$\bar{3}$	4	2.92	8	2.922	6
2.8046	2	$\bar{1}$	4	2	-	-	-	-
2.6867	1	2	$\bar{4}$	2	-	-	-	-
2.6571	4	3	2	0	-	-	-	-
2.6028	4	$\bar{2}$	$\bar{1}$	5	-	-	2.588	$\frac{1}{2}$
2.5497	3	4	0	0	-	-	-	-
2.5124	4	$\bar{1}$	3	5	-	-	-	-
2.4748	4	$\bar{4}$	1	3	2.47	$\frac{1}{2}$	2.469	$\frac{1}{2}$
2.3742	1	4	1	0	2.37	1	2.352	1
2.3129	4	4	2	3	-	-	2.320	1
2.2847	3	$\bar{1}$	4	5	-	-	-	-
2.2838	3	$\bar{1}$	$\bar{5}$	2	-	-	-	-

TABLE 6. CONTINUED.

1					2		3	
d_{calc}	l_{calc}	h	k	l	d_{meas}	l_{meas}	d_{meas}	l_{meas}
2.2769	4	3	3	0	2.27	1	2.274	1
2.2639	2	0	4	2	-	-	-	-
2.1878	2	2	5	3	-	-	-	-
2.1458	2	2	3	4	-	-	-	-
2.1203	10	5	0	1	2.12	1	2.119	4
2.1169	2	4	4	1	-	-	-	-
2.0936	9	2	5	3	-	-	-	-
2.0903	10	1	4	3	-	-	-	-
2.0896	2	3	1	4	-	-	-	-
2.0887	10	3	1	6	2.08	10	2.087	10
2.0865	11	3	5	2	-	-	-	-
2.0826	11	2	1	5	-	-	-	-
2.0475	1	4	3	4	-	-	-	-
2.0272	3	4	3	1	2.03	1	-	-
2.0266	1	1	2	6	-	-	-	-
1.9853	2	3	0	4	-	-	-	-
1.9804	2	1	1	6	1.975	1	-	-
1.9803	1	2	4	6	-	-	-	-
1.9653	2	5	1	4	-	-	-	-
1.9446	2	1	5	1	-	-	-	-
1.9162	1	2	6	3	-	-	-	-
1.9127	2	4	5	1	-	-	-	-
1.9112	2	4	0	3	-	-	-	-
1.9041	1	2	6	0	1.905	1	-	-
1.9013	2	0	5	2	-	-	-	-
1.8823	2	0	1	6	-	-	-	-
1.8716	2	2	4	4	1.857	1/2	-	-
1.8423	1	1	2	5	1.836	1/2	-	-
1.7848	1	6	0	2	1.786	1/2	-	-
1.7311	1	4	1	7	-	-	-	-
1.7279	2	6	1	2	-	-	-	-
1.7237	2	4	2	7	-	-	-	-
1.7212	4	5	3	5	1.717	2	-	-
1.7138	5	5	3	3	-	-	-	-
1.7038	4	1	7	1	-	-	-	-
1.6990	5	1	1	7	1.699	2	-	-
1.6547	2	3	6	4	-	-	-	-
1.6425	1	2	7	0	-	-	-	-
1.5891	1	6	2	2	-	-	-	-
1.4973	1	4	6	5	-	-	-	-
1.4941	1	7	1	3	-	-	-	-
1.4889	2	4	4	2	1.490	2	-	-
1.4882	2	6	4	4	-	-	-	-
1.4644	3	0	6	8	1.459	2	-	-
1.4044	1	6	4	6	1.443	1/2	-	-
1.3392	1	7	2	0	1.339	1/2	-	-
1.3388	1	8	2	3	-	-	-	-
1.3301	1	4	7	2	-	-	-	-
1.3273	1	6	1	8	-	-	-	-
1.3262	2	6	7	0	-	-	-	-

TABLE 6. CONTINUED.

1					2		3	
d_{calc}	l_{calc}	h	k	l	d_{meas}	l_{meas}	d_{meas}	l_{meas}
1.3244	1	4	1	6	1.322	1	-	-
1.3241	1	1	6	4			-	-
1.3237	1	4	6	5			-	-
1.3169	1	2	8	7	-	-	-	-
1.3145	2	3	4	10	1.309	2	-	-
1.3134	2	3	8	6			-	-
1.3114	2	2	4	9			-	-
1.2161	1	8	5	1	1.211	½	-	-
1.2056	1	4	3	9	-	-	-	-
1.2024	1	5	6	7	-	-	-	-
1.2010	1	1	10	5	1.198	2	-	-
1.1977	1	1	2	11			-	-

1 = Calculated powder pattern and indexing for montbrayite on the basis of $a = 10.8045(6)$, $b = 12.1470(6)$, $c = 13.4480(7)$ Å, $\alpha = 108.091(5)$, $\beta = 104.362(5)$, $\gamma = 97.471(5)^\circ$ and with the atom coordinates reported in Table 2. Intensities were calculated using XPOW software, version 2.0 (Downs *et al.* 1993). 2 = observed powder pattern originally reported for natural montbrayite by Peacock & Thompson (1946). 3 = observed powder pattern for synthetic montbrayite reported by Bachechi (1972).

do not help a lot, as there is also the possibility that Au exhibits valence fluctuations (being present in the +1 and +3 valence states), as in calaverite (Schutte & de Boer 1988). So, montbrayite represents a case that cannot be resolved in a straightforward way with a combined X-ray and electron-microprobe study of the same crystal.

In other words, this is the possible scenario in terms of atom-site distribution for montbrayite: (1) Pb can substitute for Au or Te; (2) Bi can substitute for Te (in an ordered fashion) or Au; (3) Sb can substitute for Au (in a disordered fashion) or Te; (4) Ag, when present, substitutes for Au.

It appears evident that a structural study cannot help us to completely decipher the scenario, mainly because there are several elements with very similar scattering power (*i.e.*, Au is close to Pb and Bi; Sb is very close to Te) playing the same crystal-chemical role. So, even in the case that one were able to structurally characterize montbrayite from all the reported occurrences (something nearly impossible given the size of the mineral from some localities) and then carry out electron microprobe analyses of the X-rayed crystals, one would not reach a unique solution.

In conclusion, even if the formula $(\text{Au,Sb})_{23}\text{Bi}_2\text{Te}_{36}$ perfectly matches our structural and chemical data for montbrayite from the type locality, we do not feel confident (for the reasons explained above) to propose it as the revised formula for the mineral. We thus propose a revision of the formula from $(\text{Au,Sb})_2\text{Te}_3$ to $(\text{Au,Ag,Sb,Bi,Pb})_{23}(\text{Te,Sb,Bi,Pb})_{38}$.

Such a formula is also in excellent agreement with that proposed by Shackleton & Spry (2003) on the basis of chemical data. This way to write the formula does not take into account the fact that the ‘anionic’ species replacing Te has been found ordered at a specific site in type montbrayite, but we think it is a good compromise given the complexity of the mineral under investigation. The redefinition of montbrayite has been approved by the Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association (voting proposal 17-F).

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