

SYNTHESIS AND STABILITY OF MONTBRAYITE, Au_2Te_3

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ABSTRACT

An accurate electron microprobe analysis of the mineral montbrayite from the Robb-Montbray mine, Québec, yielded the empirical formula $(\text{Au}_{1.80}, \text{Ag}_{0.08}, \text{Pb}_{0.04}, \text{Sb}_{0.07})_{2.03} (\text{Te}_{2.88}, \text{Bi}_{0.12})_{3.00}$. A stable compound of this composition was synthesized, although the stoichiometric compound Au_2Te_3 breaks down to AuTe_2 and gold. Further experiments have shown that Sb can stabilize the compound by itself. Substitution of Bi, Pb, and Sb or of Sb only, leading to deviations from the stoichiometric Au and Te content, is considered responsible for the stability of montbrayite.

INTRODUCTION

Gold and silver tellurides constitute the largest group among the natural compounds of tellurium and the minerals of this group frequently occur in ore deposits of gold. Montbrayite, however, is a rare mineral species, recently discovered in ore from the Robb-Montbray mine, Québec, and first described by Peacock and Thompson (1946). Only two other occurrences are known: one in Armenia (Shcherbina and Zaryan, 1964) and the other in the ore deposit of Kalgoorlie, Australia (G. Travis, Western Mining Corporation, private communication). Its composition was long assumed to be Au_2Te_3 on the basis of an early chemical analysis, although this analysis also indicated the presence of Ag, Bi, Pb, and Sb in substitutional solid solution for Au and Te up to about 6 percent. Since gold and silver tellurides occur with only trace impurities, these elements were ascribed to mechanical contamination of the original material (Peacock and Thompson, 1946). However, experiments designed to synthesize Au_2Te_3 (Peacock and Thompson, 1946; Markham, 1960; Cabri, 1965) all gave negative results, the compound being unstable with respect to calaverite (AuTe_2) and gold, although the mineral occurs associated with both (Shcherbina and Zaryan, 1964; Rucklidge, 1969). The instability of the compound under the experimental conditions was considered to be substantiated by fusion experiments from preparations containing Bi, Pb and Sb, which also yielded an intergrowth of mostly calaverite and gold (Peacock and Thompson, 1946). These results led to various

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suggestions to account for the stability of the mineral and the conditions necessary for its formations.

Recently some electron microprobe analysis results showed unequivocally that homogeneous crystals of montbrayite contain 3–5 percent of impurities (Rucklidge, 1969; G. Travis, Western Mining Corporation, private communication). The presence of Bi, Pb, and Sb in the mineral and the instability of the compound Au_2Te_3 seemed related and suggested that the stability of montbrayite is controlled by the presence of impurities in its structure.

In this study, the chemical composition of one specimen of natural montbrayite was determined, to obtain accurately the proportions of each element present. Based on these results, experimental work was carried out to investigate the stability of the mineral and the role of the three elements in its composition.

COMPOSITION

The chemical composition of montbrayite was determined on a specimen from the type locality, Robb-Montbray, Québec, taken from the Peacock collection in the University of Toronto. The analyses were carried out with an ARL-EMX electron microprobe using an accelerating voltage of 25 kV and a sample current of about $0.04 \mu\text{A}$. The standard for Au, Ag, and Te was a sample of synthetic calaverite $(\text{Au, Ag})\text{Te}_2$, containing 1.52 percent of Ag, while for Bi, Pt, and Sb the pure elements were used as standards. $L\alpha$ peaks were chosen for the determination of Au, Ag, Sb, and Te, but for Bi and Pb, M peaks were preferred because they were better resolved and had symmetric backgrounds, although no correction could be applied for M fluorescence. The data were processed on a IBM 360 computer using a program designed to apply corrections for fluorescence, absorption, and atomic number (Rucklidge, 1967). The composition is given in Table 1 where it is compared with the results of the previous analyses. The estimated errors of the concentrations of the elements are expressed as standard deviations and are calculated from several independent determinations of the same sample. A sample of synthetic krennerite $(\text{Au, Ag})\text{Te}_2$ was included in each batch of analyses to check the experimental conditions. The determined mean composition, when compared with the known composition, tests the accuracy of the analysis for Au, Ag, and Te. The results, shown in Table 2, are in good agreement.

The unit cell content of montbrayite is shown in Table 1 along with the assumed grouping of the atoms, and was calculated from the following experimental data: chemical analysis (Table 1–3), cell

TABLE 1 - CHEMICAL COMPOSITION OF MONTBRAYITE FROM ROBB-MONTRAY, QUE

	(1)	(2)	(3)	(4)	(5)
Au	44.32	47.7	47.36 ± 0.19	22.707	} 24.360
Ag	0.55	0.6	0.37 ± 0.05	0.321	
Pb	1.61	1.3	1.02 ± 0.08	0.463	
Sb	0.90	0.3	1.12 ± 0.04	0.669	
Bi	2.81	2.9	3.23 ± 0.14	1.454	} 35.996
Te	49.80	47.0	46.66 ± 0.15	34.542	
	99.99	99.8	99.76		100.00

(1) - chemical analysis, Peacock and Thompson, 1946

(2) - electron microprobe, Rucklidge, 1969

(3) - electron microprobe, this study

(4) - unit cell content: analysis c, $V = 1577.4 \text{ \AA}^3$, $d = 9.94$

(5) - Au_2Te_3 , theoretical composition

dimensions (Bachechi, 1970), density (Peacock and Thompson, 1946). The empirical formula is accordingly: $(\text{Au}_{1.89}, \text{Ag}_{0.03}, \text{Pb}_{0.04}, \text{Sb}_{0.07})_{2.03} (\text{Te}_{2.88}, \text{Bi}_{0.12})_{3.00}$.

PREVIOUS WORK

The Au-Te system, discussed and investigated on the 300°C isotherm by Markham (1960), shows only one compound, calaverite (AuTe_2), and this compound has no detectable solid solution range (Cabri, 1965). Two eutectic points exist in the system, between Au- AuTe_2 at 447°C and AuTe_2 -Te at 416°C. Several experiments on the Au-Te system were also made at the composition of Au_2Te_3 ; by Markham at 300°C, by Cabri in the temperature range 320–440°C, and by Peacock and Thompson using a fusion technique, all of which yielded

TABLE 2. CHEMICAL COMPOSITION OF SYNTHETIC KRENNERITE

	(1)	(2)
Au	37.70 ± 0.14	37.68
Ag	3.91 ± 0.11	4.02
Te	58.09 ± 0.35	58.29
	99.70	99.99

(1)—electron microprobe

(2)—known composition

calaverite and gold. Fusion experiments with fragments of natural montbrayite and a mixture of the same composition (Table 1-1) gave quench products consisting mostly of calaverite and gold (Peacock and Thompson, 1946). The study of the ternary system Au-Ag-Te, by Markham and Cabri did not reveal a compound corresponding to montbrayite. Furthermore, a mixture of Au_2Te_3 bulk composition with 1 percent Ag, when heated to 315° and 385°C in a high temperature camera, gave only the powder pattern of calaverite and gold (Cabri, 1965).

EXPERIMENTAL

All the experiments were conducted in evacuated silica tubes. The starting material for the runs was prepared by melting a mixture of the pure elements at 600°C. The liquid was rapidly quenched at room temperature to form a compact mass of mostly calaverite and gold. The quench products were ground in an agate mortar under acetone and pelletized in a small press for use in the synthesis of montbrayite. This procedure proved to be essential for the attainment of equilibrium in the runs, since solid state reactions proceed very slowly when gold is one of the main reactants. The reaction rates were improved by the use of calaverite, which reduces the amount of free gold as reactant, and by the use of pellets, which brings the reacting grains into close contact. The charges were heated in horizontal cylindrical furnaces which maintain the temperature constant to within $\pm 3^\circ\text{C}$. The experiments were conducted in the temperature range 200°-440°C. The products were identified exclusively by electron microprobe and X-ray diffraction, since calaverite and montbrayite have similar optical properties. A Guinier-DeWolff camera was of fundamental importance in showing three feeble low angle lines ($d = 11.22; 9.35; 7.43$), which allow the unequivocal identification of montbrayite from an intergrowth of similarly diffracting tellurides.

EXPERIMENTAL RESULTS

Under the experimental conditions montbrayite was readily synthesized in the temperature interval 360°-400°C from preparations of its composition (Table 1-3, neglecting the Ag content) and persisted as a single phase when heated for an additional three weeks. Some samples were annealed for four months at 300°, 250°, and 200°C and no changes were detected. In Table 3 the diffraction lines of the synthetic compound, calibrated using PbS as standard, are compared with those of natural montbrayite and with the calculated spacings. Figure 1 shows large polycrystalline grains of synthetic montbrayite. Two runs, at 440° and 420°C, showed evidence of melting, the resulting quench products being mainly calaverite and gold¹ in agreement

¹ Bi_2Te_3 was also identified, and Sb in variable amounts was found in the calaverite. PbTe, however, was not detected.

TABLE 3. X-RAY DIFFRACTION LINES OF MONTBRAYITE
FROM POWDER PHOTOGRAPH

(1)		(2)		(3)	(4)
I	d Å(meas.)	I	d Å(meas.)	d Å(calc.)	hkl
		1	11.212	11.223	100
		1	9.302	9.348	011
1	7.48	2	7.363	7.427	111
2	4.47	4	4.425	4.419	121
0.5	4.07	0.5	4.009	3.995	310
0.5	3.81	1	3.812	3.814	121
		0.5	3.644	3.648	131
0.5	3.52	1	3.535	3.536	113
		0.5	3.442	3.445	130
1	3.22	1	3.196	3.197	041
		0.5	3.062	3.065	103
8	2.97	8	2.983	{ 2.975 2.974	{ 223 212
8	2.92	6	2.922	2.922	340
		0.5	2.588	2.588	243
0.5	2.47	0.5	2.469	2.468	332
		1	2.456	2.456	312
1	2.37	1	2.352	2.353	014
		1	2.320	2.319	042
1	2.27	1	2.274	2.273	303
1	2.12	4	2.119	2.118	015
10	2.08	10	2.087	{ 2.088 2.082	{ 143 152

(1) Natural, Peacock, and Thompson, 1946.

(2) Synthetic, this study.

(3) Space group $P1$, $a = 12.11$, $b = 13.44$, $c = 10.80$, $\alpha = 104^\circ 23'$,
 $\beta = 97^\circ 30'$, $\gamma = 107^\circ 56'$, $V = 1577.4$.

(4) The indices are unequivocally assigned with the help of single crystal photographs of natural specimens.

with the results of the fusion experiments made by Peacock and Thompson (1946). Subsequently a melting temperature of $410^{\circ} \pm 5^{\circ}\text{C}$ was estimated by heating experiments on a sample of coarsely ground synthetic material of the same composition, sealed in a evacuated silica tube.

To substantiate these results, several experiments were made on the Au-Te system at the Au_2Te_3 composition in the temperature range 250° – 440°C . Two runs, at 440° and 430°C , showed indications of melting, although they lie in the subsolidus region of the Au-AuTe₂ system, suggesting that the accepted temperature for the Au-AuTe₂ eutectic (447°C) is too high. In the other runs, subsolidus reactions yielded an intergrowth of calaverite and gold in agreement with previous work. However a detailed examination of the samples in a polished section showed the presence of two kinds of calaverite. Large grains of homogeneous calaverite with round grains of gold at the margins were found associated with calaverite grains, containing numerous small particles of gold (Fig. 2). This texture, visible in less than 30 percent of the calaverite present, suggests that a simultaneous growth of calaverite and metastable montbrayite occurred, followed

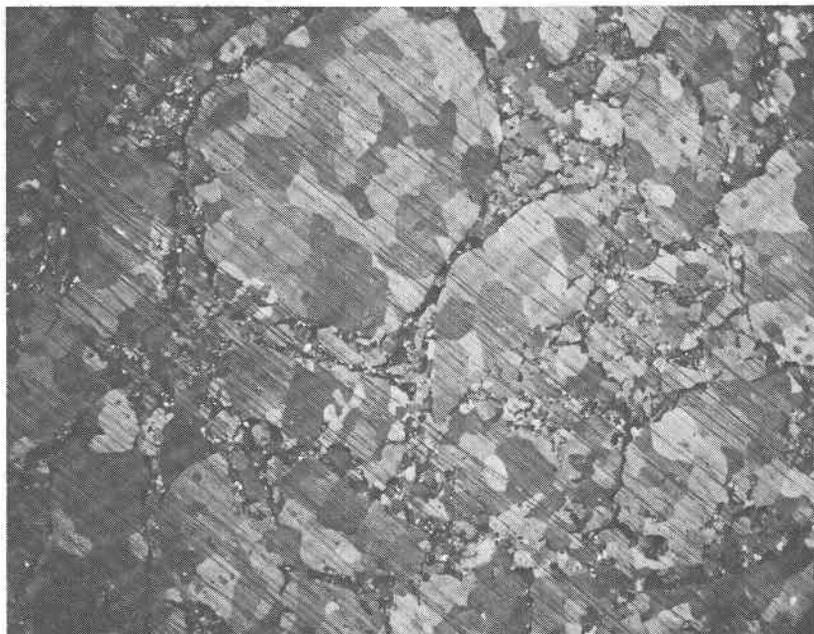


FIG. 1. Polycrystalline grains of montbrayite (reflected light, crossed nicols, $128\times$).

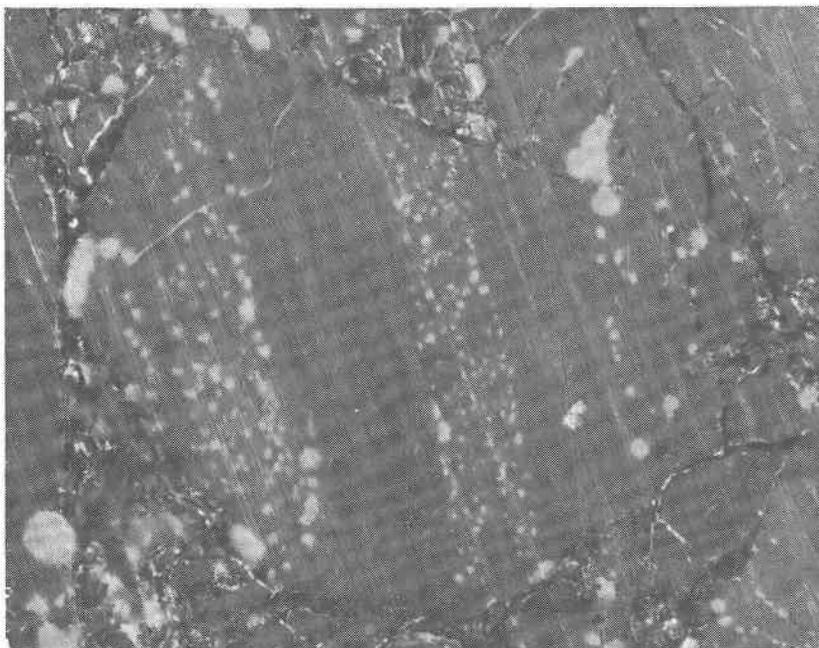


FIG. 2. Calverite with gold inclusions associated with homogeneous calaverite (reflected light, crossed nicols, 800 \times).

by a breakdown of the latter to calaverite and gold. These results indicate that montbrayite is not stable on the Au-Te system, in agreement with previous investigations, and only becomes a stable phase when impurities in the form of Pb, Sb and Bi are present in the structure up to a small fraction of Au and Te.

In order to define the role of the three elements in the mineral more precisely, some experiments were made starting with mixtures of ternary composition. In these preparations the proportions of Au and Te of the natural specimen were preserved while the remaining elements were replaced with one of Bi, Pb, or Sb (Table 4). Montbrayite formed only from the Au-Sb-Te mixture, while in the other two runs intergrowths of tellurides and gold were obtained, indicating that only Sb meets all the requirements to substitute for both Au and Te. The homogeneity range of montbrayite along the Au_2Te_3 -Sb join is now under investigation.

CONCLUSIONS

The pure compound Au_2Te_3 , corresponding to the ideal composition of montbrayite, is not stable but breaks down to AuTe_2 and gold.

TABLE 4. SYNTHESIS EXPERIMENTS FROM TERNARY MIXTURES

Composition	Temp. °C	Days	Run products
Au _{1.89} Sb _{0.23} Te _{2.88}	390	30	mont
Au _{1.89} Pb _{0.23} Te _{2.88}	390	30	cal + alt + Au
Au _{1.89} Bi _{0.23} Te _{2.88}	390	30	cal + tell + Au

alt = altaite, PbTe; cal = calaverite, AuTe₂; mont = montbrayite; tell = tellurbismuth, Bi₂Te₃

However, a stable compound corresponding to the mineral can be synthesized with 5.5 atomic percent of Au substituted by Sb plus Pb, and 4.0 atomic percent of Te substituted by Bi, according to the composition of the natural specimen. With this composition, the synthetic montbrayite melts at 410°C under its vapour pressure and does not undergo any phase transformations in the range of temperature 200°–410°C. Furthermore, it was found that Sb can stabilize the compound by itself. It seems, therefore, that deviations in the content of Au and Te from the stoichiometric ratio 2:3 (caused by substitution of Bi, Pb, and Sb, as in the natural specimens from Robb-Montbray, or of Sb only, as found experimentally) are responsible for the stability of montbrayite.

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