GOLD-SILVER TELLURIDES: RELATION BETWEEN COMPOSITION AND X-RAY DIFFRACTION DATA

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ABSTRACT

Electron-probe microanalyses of natural krennerites and sylvanites, containing no minor elements, have supported previous estimates of silver content using a *d*-value curve obtained from synthetic samples. The correspondence for the silver content of natural calaverite is not as well established.

Examples of krennerite and calaverite containing minor elements have been found. Krennerite can incorporate minor Cu in its structure which permits the mineral to have a lower percentage silver than normal krennerite. Calaverite has been found to contain both Cu and Sb in minor amounts permitting the structure to exist with more silver than in the Au-Ag-Te system.

INTRODUCTION

The relationships between *d*-values for certain *x*-ray reflections and the silver contents of synthetic calaverite, krennerite, and sylvanite were studied by Cabri (1965), and curves of *d*-value *vs.* composition were presented. He also examined several natural gold-silver tellurides by *x*-ray diffraction and estimated their silver contents by relating the *d*-values so obtained to the determinative curves of their synthetic counterparts. The assumption was made that minor element content would not affect these values. All the natural tellurides thus examined, except two, gave silver contents consistent with the experimental phase equilibrium work in the Au-Ag-Te system. In order to explain these two discrepancies (i.e. apparently anomalous *d*-values), a quantitative electron microprobe analysis has been made on these and other natural gold-silver tellurides.

PROCEDURE

An ARL, type EMX, electron microprobe was used for these analyses. Preliminary work using pure elements as standards gave adequate results but the use of synthetic standards in the composition range of the unknowns gave increased confidence in the values obtained. One of these was synthetic krennerite synthesized at 350°C, in the manner described by Cabri (1965), and had the composition 37.68_5 Au, 4.02_1 Ag, and 58.29_2 Te, all in wt. %. This krennerite was confirmed by *x*-ray diffraction

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(Guinier camera) and was found to be homogeneous. It was used for all the calaverite and krennerite determinations. The other standard was prepared from a bulk composition of 7.81 Ag, 28.10 Au, 64.09 Te, all in wt. %, which lay in the stability field of sylvanite + Te + liquid at the temperature of synthesis (350°C). This sample had previously been used to determine the silver-rich side of the sylvanite solvus at 350°C by Cabri. From the *d*-values obtained, the silver content of the sylvanite in this sample was estimated to be 8.4 wt. %. This sylvanite was analyzed using the krennerite standard with the following results, all in wt. %.

	1. (15 spots)	2. (16 spots)
Au	31.3	31.5
Ag	8.7	8.4
Te	60.7	60.7
	100.7	100.6

These results provide such a good check on the value obtained from the *x*-ray determinative curve that the correct composition of the sylvanite standard was assumed to be that obtained from the determinative curve. (8.4 Ag, 31.2 Au, 60.4 Te, all wt. %.)

The operating conditions were: accelerating voltage 25kv, sample current 0.01 or 0.015 μA, with Au L_α, Ag L_α, and Te L_α being the *x*-ray lines measured simultaneously for the principal components. At least five spots on each sample were measured. Data were processed by the computer programme and corrections described by Rucklidge (1967).

ANALYTICAL RESULTS

Besides determining the major elements Au, Ag, and Te with the microprobe, the following elements were also sought: Cu, Sb, Bi, Pb, As, Hg, and Se. The detection threshold for most of these minor elements is probably 0.1% in this material. Of all these, only Cu and Sb in one sample, and only Cu in another, were detected and measured. These two samples turned out to be the very ones that had given anomalous *d*-values.

Table 1 shows the microprobe results for calaverite compared to the estimated silver contents reported in Table 8 of Cabri (1965).

It can readily be seen that there is no *close* correspondence between the silver contents obtained by the two methods, especially for the lower silver contents. This may be because the silver content of the standard used was closer to the higher silver values, but there is a general relation between low silver obtained by both methods though the exact values

TABLE 1.* NATURAL CALAVERITES EXAMINED

Probe No.	Sample No.	Wt. % Ag from *d*-value	Wt. % (electron microprobe analysis)					
			Ag	Au	Te	Cu	Sb	Total
13	ROM-M18767	0.92	0.04	42.3	56.1	—	—	98.44
16	ROM-M19301	1.46	0.5	40.7	56.1	—	—	97.3
3	PRM-F.716	1.54	0.85	41.7	56.5	—	—	99.05
5	PRM-N.S.716A	1.54	0.75	41.8	56.6	—	—	99.15
18	ROM-E1924	1.94	0.88	42.1	56.6	—	—	99.58
4	PRM-F.712	2.24	1.6	40.3	56.8	—	—	98.7
12	ROM-M22591	2.30	2.3	39.5	57.7	—	—	99.5
15	ROM-M13812	2.80	1.2	41.8	57.3	—	—	100.3
20	ROM-E2569	3.80	3.5	37.9	57.5	0.3	0.77	99.97

*Abbreviations used in this and subsequent tables: ROM, Royal Ontario Museum; PRM, Peter Redpath Museum, McGill University; McG, Department of Geological Sciences, Reference Collection, McGill University.

do not agree. Since it could not be determined if other elements were present in amounts below the detection capability of the probe, the values obtained were not recalculated to 100%. Figure 1 shows the "triangle of error" for these analyses and it can readily be seen that there can be a significant range in silver values for most of the samples, as indicated by the length of intersection, in the triangle, of the calaverite-sylvanite tie line. Thus, if no other elements are present, sample No. 13 could conceivably have a silver content of up to 0.9 wt. %, which is practically identical to the value obtained from the *x*-ray determinative curve. Similar reasoning will show that most, but not all, values can be "improved" to show closer correspondence between the *x*-ray and the probe values.

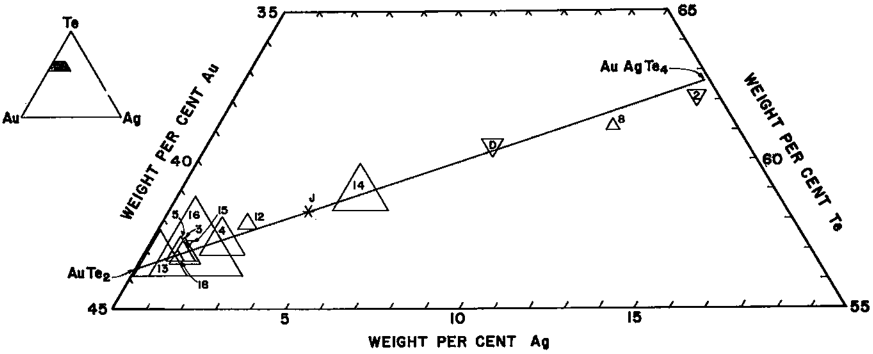

FIG. 1. Part of the Au-Ag-Te system showing the "triangles of error" of the electron microprobe analyses plotted with respect to the $AuTe_2$-$AuAgTe_4$ tie-line. J is the synthetic krennerite standard used for determining all the natural calaverites, krennerites, and the sylvanite standard. D is the synthetic sylvanite standard (analysis No. 2), which was used to determine the natural sylvanites.

The anomalous calaverite, ROM-E2569, however, is of particular interest. The *d*-value, when applied to the determinative curve indicated a silver content of about 3.8 wt. %, which is considerably greater than the 2.8 ± 0.2 wt. % maximum determined by Cabri (1965) for calaverite in the Au-Ag-Te system. The probe analysis also gave a large silver content (3.5%) but the presence of Cu and Sb in this calaverite clearly demonstrates that the calaverite structure will be maintained with larger silver contents in the quinary Au-Ag-Te-Cu-Sb system. Thus the high silver content in this case does not contradict the phase relations in the ternary Au-Ag-Te system, but rather shows that complications exist when one departs from the ternary for a system containing more components.

Only two krennerites were successfully analysed, and these are shown in Table 2.

TABLE 2. NATURAL KRENNERITES ANALYSED

Probe No.	Sample No.	Wt. % Ag from *d*-value	Wt. % Electron Microprobe Analysis				
			Ag	Au	Te	Cu	Total
1	McG2792-R1	2.04	2.4	38.7	58.3	0.6	100.0
14	ROM-M23798	4.56	4.7	35.4	58.3	—	98.4

In this case we have a good correspondence between the silver content estimated from the *d*-value and from the microprobe analysis. The low silver content predicted by the *x*-ray method for sample McG2792-R1 cannot be readily explained from the phase equilibrium work in the Au-Ag-Te system, but, since it really lies in the quaternary Au-Ag-Te-Cu, the ternary phase relations do not strictly apply. It would be most interesting to determine how much Ag in krennerite can be replaced by Cu.

Only two of the sylvanites examined gave reliable analytical results but these do not straddle the calaverite-sylvanite tie line, plotting a little below (see Fig. 1). This may be due to the standard used.

TABLE 3. NATURAL SYLVANITES EXAMINED

Probe No.	Sample No.	Wt. % Ag from *d*-value	Wt. % (Electron Microprobe Analysis)			
			Ag	Au	Te	Total
8	PRM-F.708	11.85	11.2	27.4	61.0	99.6
2	PRM-F.704	not determined	13.4	24.8	62.3	100.5

There are not enough sylvanite analyses to draw any conclusions other than that these appear reasonable and agree with the results of the phase equilibrium work. The 13.4 wt. % Ag for Sample 2 is slightly more than that expected in $AuAgTe_4$(13.23%), but since the total analysis adds up in excess of 100% this is not a source of concern.

SUMMARY

In conclusion, the silver content of natural krennerites and sylvanites can be estimated by measuring the *d*-values of selected reflections used to establish determinative curves for their synthetic equivalents. The correspondence for natural calaverite is not as well established, especially for the silver-poor calaverites. Closer correspondence between the microprobe and the diffraction data could, conceivably, be obtained by reducing analytical errors and by better detection of minor elements.

Of great interest is the fact that both calaverite and krennerite can incorporate elements other than Au, Ag, and Te in their structures, and that these elements affect their silver contents. Calaverite, by incorporating Cu and Sb in its structure, can tolerate more silver than it can in the Au-Ag-Te system. Krennerite, in contrast, by the incorporation of Cu, appears to maintain its structure with less silver than it needs in the Au-Ag-Te system. We believe this to be the first authenticated report of these trace elements in these two tellurides.

REFERENCES

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