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NEW DATA ON NATURAL PHASES IN THE SYSTEM AG-TE

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ABSTRACT

Electron probe investigation of hessite from various deposits did not reveal significant deviations from its stoichiometric composition, Ag_2Te. "Empressite" from the type locality consists of two optically distinct phases with the formulae AgTe and $Ag_{5-x}Te_3$. Other occurrences of the latter phase have been found and analyses show that x varies from 0.24 to 0.36. The coexistence of these two phases cannot be reconciled with experimental data since AgTe has not been synthesized. Coexistence of $Ag_{5-x}Te_3$ with near-stoichiometric sylvanite, $AuAgTe_4$ (23.6% Au) in one deposit and the Au-rich sylvanite (26.0% Au) in another suggests temperatures of formation of 230°C and 300°C, respectively. AgTe, like petzite, is unstable under prolonged electron bombardment at normal operating conditions. Fleischer's recent definition of empressite as AgTe is supported by the analytical data, the formula $Ag_{5-x}Te_3$ (rather than Ag_5Te_3) is suggested for stützite.

INTRODUCTION

In the course of electron probe studies of ores from a number of telluride deposits it became obvious that compositions of naturally occurring phases cannot always be reconciled with descriptive data so far available or with the results of experimental work. An outline of the development of the understanding of the Ag-Te system (which has been the cause of much controversy in recent years) may serve as a useful background for the results of the present investigation.

The only well-established and generally accepted phase in this system has for a long time been hessite, Ag_2Te, first described by G. Rose in 1830 in samples from the Zavodinskii Mine, Altai Mountains. The polymorph stable at surface temperature is monoclinic (Frueh, 1959). In 1914 Bradley first described empressite, AgTe, which he considered hexagonal. Thompson *et al.* (1951) suggested that the formula for empressite should be $Ag_{2-x}Te_{1-x}$, though Donnay *et al.* (1956) showed that, on the basis of X-ray diffraction and density data, the formula was best expressed by $Ag_{5-x}Te_3$. Honea (1964) suggested that the composition of empressite (orthorhombic, with $a=8.90$ Å, $b=20.07$ Å, $c=4.62$ Å) is actually AgTe, and that what he considered to be Ag_5Te_3 (hexagonal, $a=13.38$ Å, $c=8.45$ Å) should be termed stützite. However, Thompson *et al.* (1951) have found that the X-ray powder patterns of empressite and stützite—a name introduced by Schrauf (1878) for a mineral supposed to be Ag_4Te—are identical. Cabri's discussion of Honea's work (1965a) and his excellent investigation of the Ag-Te system (with Kracek

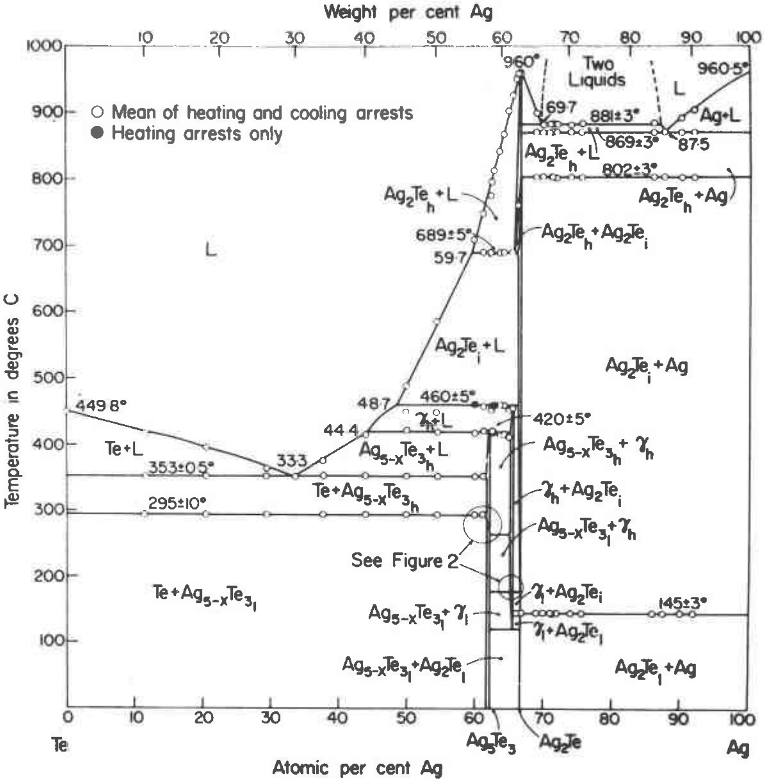

FIG. 1. The phase diagram for the Ag-Te system in the presence of vapor after Kracek, Ksanda, and Cabri (1966) p. 17. AgTe was not included since its stability field was not determined in the synthetic system.

and Ksanda, 1966) has done much to clarify the confusion (see phase diagram, Fig. 1). He pointed out distinct similarities between the X-ray patterns of synthetic $Ag_{5-x}Te_3$ and Honea's AgTe, and suggested it might be premature to redefine empressite. However, this step was taken in the most recent index of New Mineral Names (Fleischer, 1966) which defines empressite as AgTe, and stützite as Ag_5Te_3. Kracek *et al.* (1966) established experimentally the existence of Ag_2Te and of $Ag_{5-x}Te_3$. The composition of the latter is near to Ag_5Te_3, with a small solid solution field from 57.95–58.39 weight percent Ag. They discussed the γ-phase, intermediate in composition between $Ag_{5-5}Te_3$ and Ag_2Te, which was originally described by Kiukkola and Wagner (1957). γ-phase is stable between the temperature limits 120 ± 15°C and 460 ± 5°C, ranging in composition from 61.38 to 61.75 weight percent Ag at 300°C. It can be preserved at room temperature with very rapid cooling.

Experimental difficulties have so far prevented synthesis of one natural member of the Ag-Te system. This is the phase AgTe (orthorhombic) which, according to Honea (1964) does occur in natural ores. Furthermore, Luo and Klement (1962) described a simple cubic metastable Ag-Te alloy with 20.5–30.5 at weight percent Ag. The most recent textbook (Sindeeva, 1964) confines discussion of silver tellurides to hessite and the phase $Ag_{5-x}Te_3$. Considering the apparently divergent views held by different authors, one can only agree with Cabri (1965a), who states that the mineralogy of the silver tellurides "is still far from completely understood."

Silver tellurides serve as raw materials not only for the extraction of silver, but of tellurium too, which is increasingly sought because of its application in the electronics and semiconductor industry. In addition they may be of value as geological thermometers. The significance of further work does not appear to be limited to theoretical aspects.

The electron probe has proved of special value for nondestructive quantitative analysis of microscopic grains. For the first time, it provides a means of correlating optical and compositional data in the frequently complex and fine intergrowths of tellurides. The main aim of the present paper is to present a survey of the compositional variations of naturally occurring phases in the system Ag-Te, and to correlate these data with the results of previous workers.

EXPERIMENTAL RESULTS

An ARL-EMX electron probe microanalyser has been used for the investigations. Synthetic gold and silver tellurides, kindly lent by Dr. L. J. Cabri, were used as standards, and the results were processed by a computer program (Rucklidge, 1967).

The quantitative optical data quoted have been obtained using a LEITZ Durimet microhardness tester and a ZEISS microphotometer with Veril S 200 continuous band interference filter. Elba pyrite cut parallel to (111) served as reflectivity standard; it was calibrated against the NPL-measured pyrite "b" as quoted by Bowie (1967, p. 125). The spectral reflectivities of the two standards proved to be virtually identical. Relative errors are in the range of 2 percent of the values measured.

Hessite. A number of typical analyses of hessites from different localities are given in Table 1. These show good agreement with the theoretical composition of hessite, and with the results of experimental work which indicates negligible solid solution of gold in hessite. Gold was detected in an amount greater than 0.1 percent in only one sample of hessite, and in this instance the hessite was intimately intergrown with native gold. This is in agreement with the synthetic work of Cabri (1965b). It is

TABLE 1. ELECTRON PROBE MICROANALYSES OF HESSITE Ag_2Te

	1	2	3	4	5	6	7
Au	0.00	0.0±0.1	0.2±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.1
Ag	62.86	61.7± .7	62.6± .6	63.5± .8	61.6± .8	62.6± .5	62.6± .5
Te	37.14	37.2± .6	37.6± .6	36.8± .5	36.3± .6	37.6± .5	37.0± .5
	100.00	98.9	100.4	100.3	98.2	100.6	99.6

1. Ag_2Te, theoretical.
2. Tough Oakes Mine, Kirkland Lake, Ont. (M1 3536).
3. San Antonio Mine, Bissett, Man. (R530). Intergrown with native gold of composition Au 87.6%, Ag 12.4%.
4. Hollinger Mine, Ont. (R427).
5. Lake of the Woods, Ont. (E507).
6. Burwash Creek, Yukon. (R358).
7. Cripple Creek, Colo. (M18767).

interesting to note this occurrence of an almost pure silver telluride with gold containing only 12.4 percent Ag. Dana (1958, p. 185) quotes an analysis of hessite from Botes which shows 4.73 percent Au. Such high gold contents have to be considered suspect in the light of recent evidence. Similarly, Dana's comment on hessite "with some Au and thus possibly grading into petzite" (1958, p. 184) has to be viewed with reserve.

Empressite. Investigation of the type material of empressite from the Empress Josephine Mine proved to be of particular interest. The polished section R359, obtained from the Peacock collection at the University of Toronto, through the kindness of Professor E. W. Nuffield, is believed to be the material "1" of Thompson *et al.* (1951) and was derived from the type specimen USNM R7243. Thompson *et al.* (1951, p. 460) describe polished sections of empressite as having "a smooth surface which shows intense reflection pleochroism, light gray-mauve to creamy-white," and very strong anisotropism under crossed nicols, with white, yellowish-green, russet-brown, brown and dark-blue colors. Twinning and evidence of cleavage are absent.

Re-examination of this material in reflected light revealed the presence of two phases in roughly equal amounts (Fig. 2). Their optical properties agree only partly with those mentioned by Thompson *et al.* (1951). Coarse-grained telluride aggregates consist of:

1. A light gray, soft mineral, with noticeable but not distinct bireflection. Under crossed nicols, there are anisotropy colors changing from a

brownish to a strong bluish tint. Reflectivity at 546 nm 37.2–38.9%, at 589 nm 36.7–38.3%. Microhardness VHN 75–90.

2. A white mineral, harder than "1", with distinct bireflection (white to brownish-gray). In contrast to "1", there are no colors under crossed nicols, only a distinct change from light to dark. Reflectivity at 546 nm 34.1–49.9%, at 589 nm 34.4–50.1%. Microhardness VHN 108–133.

A comprehensive survey of the optical properties of these phases will appear elsewhere.

It is interesting to note the very strong bireflection of phase "2". These observations show that the original description of empressite by Thompson *et al.* (1951) fits "1" regarding anisotropy, and "2" regarding bireflection.

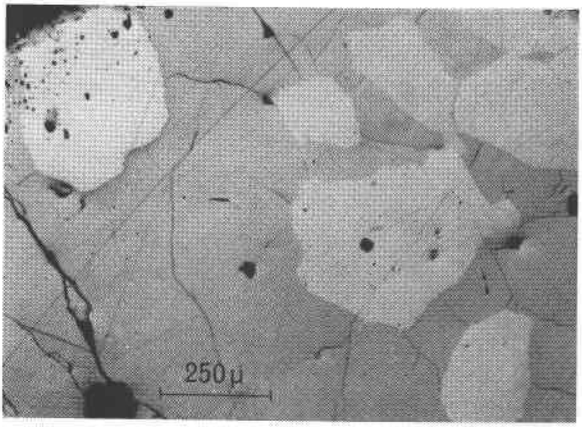

FIG. 2. Empress Josephine Mine, Colorado (USNM R 7243) $Ag_{5-x}Te_3$ (medium gray), AgTe (light gray), PbTe (white). Black is gangue.

Electron probe analyses of these phases appear in Table 2, and from these data it becomes obvious that two phases occur.

The gray phase ("1") corresponds to compositions in the $Ag_{5-x}Te_3$ range with $x=0.24$–0.36 (analyses 4–6). The white phase ("2") has a composition very close to AgTe (analysis 3). This is in good agreement with a chemical analysis of "empressite type locality" quoted by Honea (1964, p. 332): Ag 44.9%, Te 53.6%, traces of Pb, Cu, Fe, S. The existence, and, in fact, coexistence of these two phases is a particular interest for our understanding of the Ag-Te system. The traditional discrepancies regarding the composition of empressite might possibly have been caused by different phases having been investigated by different authors, who considered them identical. The values for x in the three samples of

$Ag_{5-x}Te_3$ are larger than the maximum of 0.11 found by Kracek *et al.* (1966) and Kiukkola and Wagner (1957) in experiments at 300°C. However Markham (1960) obtained a value as high as 0.2 in his experimental work, and Donnay *et al.* (1956) suggested that Thompson's natural material had an x value of 0.71. This latter value is subject to question for reasons discussed below. The only other comparable data are given by Honea (1964) for impure material from La Plata district, Colorado. The values obtained for x by electron probe methods in this study are considered to be reliable, even though synthetic Ag_2Te was used as a standard rather than a material of closer composition. The fact that a discrepancy occurs between natural and synthetic compositions of this phase need not be too disturbing, since at present the other phase under discussion, AgTe, has not been synthesized at all.

Table 2. Electron Probe Analyses of Ag-Te Phases

	1	2	3	4	5	6
Ag	45.81	58.49	44.9±0.7	56.5±0.4	57.1±0.6	56.7±0.7
Au	0.0	0.0	0.0± .1	0.0± .1	0.0± .1	0.0± .1
Te	54.19	41.51	55.8± .4	43.2± .4	42.6± .6	42.9± .4
	100.00	100.00	100.7	99.7	99.7	99.6
Formula	AgTe	Ag_5Te_3	$Ag_{0.96}Te$	$Ag_{4.64}Te_3$	$Ag_{4.76}Te_3$	$Ag_{4.70}Te_3$

1. AgTe, theoretical.
2. Ag_5Te_3, theoretical.
3. White phase, Empress Josephine Mine, Kerber Creek District, Colo. R359. (USNM R 7243).
4. Grey Phase, R359.
5. Grey Phase, Red Cloud Mine, Boulder Co., Colo. R267.
6. Grey phase, Lindquist Lake, B. C. R622.

There is now proof that the phases $Ag_{5-x}Te_3$ and AgTe both exist and coexist in nature. It is unfortunate that the present synthetic data cannot explain the existence of AgTe, and the conclusion is forced that some natural processes defy reproduction in the laboratory. Honea (1964), on the basis of DTA information, has suggested that a stability field exists for AgTe below 210°C, and has presented a modified phase diagram for the system Ag-Te. This is probably close to the truth, but we have refrained from altering Figure 1, which contains only the data for the synthetic system.

Thompson *et al.* (1951) made X-ray powder patterns of their sample no. 4, empressite, which was "probably part of the original material collected by Dr. George from Empress Josephine Mine." However, this

TABLE 3. CHANGE IN COMPOSITION OF AgTe ON PROLONGED EXPOSURE TO ELECTRON BEAM

	1	2
Ag	44.9	48.9
Te	55.8	50.8
	100.7	99.7
Formula	$Ag_{0.96}Te$	Ag_9Te_8 approx.

1. Initial composition of phase.
2. Composition after 3 minutes exposure to electron beam.

material, which was not analyzed, gave an X-ray pattern different from that of the other empressite specimens and has been listed as "empressite II" by Berry and Thompson (1962). Honea (1964) has shown that this pattern is AgTe. Fusion in vacuo resulted in a product which gave the powder pattern of $Ag_{5-x}Te_3$, "plus the strong lines of clausthalite." This may be misleading since the two strongest lines of clausthalite have almost identical *d* values to prominent lines in the pattern of $Ag_{5-x}Te_3$, and similarities exist with the pattern of Te. Electron probe analyses have failed to give any indication of Se being present in any of the R359 material.

The coexisting Au-Ag-Te phases in the three samples containing $Ag_{5-x}Te_3$ are (a) AgTe and $Ag_{5-x}Te_3$ in R359, (Fig. 3), and (b) sylvanite and $Ag_{5-x}Te_3$ in R267 from Red Cloud Mine, Boulder, Colorado and

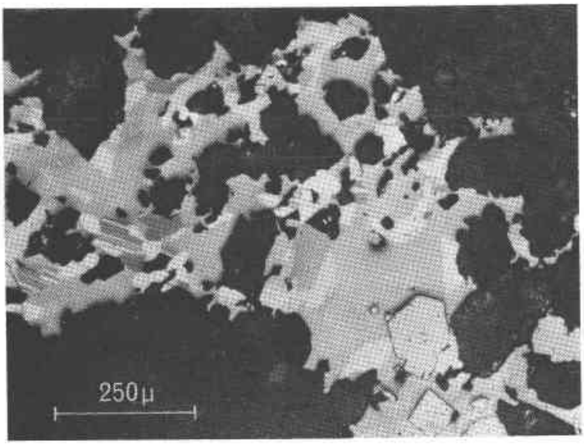

FIG. 3. Red Cloud Mine, Colorado (R267). Pyrite (euhedral grains, off-white), $Ag_{5-x}Te_3$ with x=0.24 (medium gray). $AuAgTe_4$ (with 23.6% Au) twinned grains, dark gray and whitish). Partly crossed polarizers.

R622 from Lindquist Lake, B.C. The compositions of these sylvanites are shown in Table 4. Sylvanite rarely contains as much Ag as is demanded by the ideal formula $AuAgTe_4$, but in most instances Au substitutes considerably for Ag. In sample R267 the sylvanite contains the maximum possible amount of Ag, and appears to be in the process of being replaced by $Ag_{5-x}Te_3$, Cabri (1965b) has shown that sylvanite solid solution, Te and $Ag_{5-x}Te_3$ represent an equilibrium assemblage in the appropriate composition range below 330°C. He has extrapolated his boundaries to suggest that only at temperatures 230°C and below would the ideal sylvanite composition $AuAgTe_4$ be formed. It is of interest to note therefore that in the natural assemblage of R267 this composition is found coexisting with $Ag_{5-x}Te_3$, and conclusions regarding a maximum temperature of formation around 230°C may be inferred.

TABLE 4. ELECTRON PROBE MICROANALYSES OF SYLVANITE COEXISTING WITH $Ag_{5-x}Te_3$

	1	2	3
Au	24.19	23.6±0.3	26.0±0.3
Ag	13.22	13.2± .2	11.4± .3
Te	62.59	61.7± .4	61.4± .4
	100.00	98.5	98.8

1. $AuAgTe_4$.
2. Red Cloud Mine, Boulder Co., Colo. R267.
3. Lindquist Lake B.C. R622.

The other example where sylvanite and $Ag_{5-x}Te_3$ coexist is R622 where the sylvanite has a more Au-rich composition. Cabri's data would suggest that this assemblage equilibrated at about 300°C. Finally, one particular aspect of probe analysis of AgTe (white phase "2") should be mentioned. Continued electron bombardment at normal experimental conditions of 25 kV accelerating voltage and 0.03μA sample current apparently alters the composition of the material in question, but at 15 kV 0.03μA the composition is stable. Table 3 compares analytical data obtained from "white phase" after short and after prolonged exposure to the electron beam. There is a distinct increase in Ag, and a decrease in Te with time. Similar observations have recently been made on petzite (Rucklidge and Stumpfl, 1968) where increases in Ag and, to a lesser degree, Te, and a decrease in Au were noted with time of exposure to the electron beam. In the case of petzite, it was suggested that Au diffuses up an electric field gradient in the area of electron impact, while Ag diffuses down this gradient. This and the apparent presence of a thermal gradient may be related to the semiconductor properties of petzite, which has a resistivity in the order of 10^3 greater than those of other gold- and silver-tellurides. Possibly a similar process is responsible for the changes in the composition of AgTe during prolonged electron bombardment.

SUMMARY AND CONCLUSIONS

Electron probe microanalysis has revealed complex relationships in the tellurium-rich part of the Ag-Te system. A phase of the composition $Ag_{5-x}Te_3$ (with $x = 0.24–0.36$) has bireflection similar to that described by Thompson *et al.* (1951) for empressite. The phase AgTe shows anisotropism similar to that described by Thompson *et al.* (1951) for empressite. Polished section R359 consists of roughly equal amounts of $Ag_{5-x}Te_3$ and AgTe, but the proportions of the two phases vary through the section. Thompson *et al.* (1951) were not aware that both phases were present. Is it possible that the samples taken by Thompson *et al.* for X-ray diffraction, specific gravity determination and chemical analysis did not contain the same proportion of these two phases? The diffraction and compositional data would be obtained from material predominantly $Ag_{5-x}Te_3$ (which would account for their high value of x, 0.71) while the gravity may have been determined on pure AgTe. This explanation would satisfactorily dispose of the inconsistencies observed by Honea (1964, p. 329). Complete understanding of the problems involved is difficult unless the so far unsuccessful attempts to synthesize AgTe finally succeed, or certain limitations in the applicability of synthetic data to natural environments are acknowledged. AgTe is not stable under prolonged electron bombardment at normal operating conditions. It apparently is a semiconductor like petzite which has recently been shown to display similar instability under conditions of electron bombardment. These new data further confirm the existence of a natural phase AgTe and thus indicate that Bradley's original empressite formula was correct. The authors therefore uphold the recent definition of empressite as AgTe (Fleischer, 1966) but they feel that stützite would better be defined as $Ag_{5-x}Te_3$, and not as Ag_5Te_3, since none of the natural phases analysed by electron probe correspond to a composition Ag_5Te_3. The composition of $Ag_{5\ x}Te_3$ for stützite is not inconsistent with recent experimental data in the Ag-Te binary system.

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