

NEW DATA ON NATURAL PHASES IN THE
SYSTEM Ag-Te

E. F. STUMPFEL, *Department of Geology, University of Manchester*

AND

J. RUCKLIDGE, *Department of Geology, University of Toronto.*

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 $\text{Ag}_{5-x}\text{Te}_3$. 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 $\text{Ag}_{5-x}\text{Te}_3$ 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 $\text{Ag}_{5-x}\text{Te}_3$ (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 $\text{Ag}_{2-x}\text{Te}_{1-x}$, though Donnay *et al.* (1956) showed that, on the basis of X-ray diffraction and density data, the formula was best expressed by $\text{Ag}_{5-x}\text{Te}_3$. 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

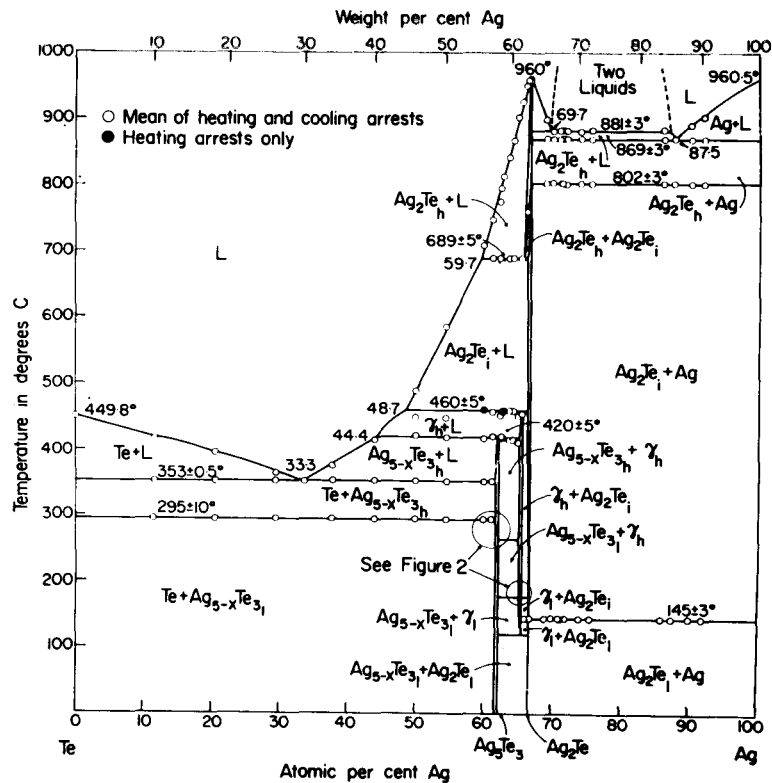


FIG. 1. The phase diagram for the Ag-Te system in the presence of vapor after Kracek, Ksanda, and Cabri (1966) p. 17. $AgTe$ was not included since its stability field was not determined in the synthetic system.

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 $120 \pm 15^\circ C$ and $460 \pm 5^\circ C$, ranging in composition from 61.38 to 61.75 weight percent Ag at $300^\circ C$. 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 $\text{Ag}_{5-x}\text{Te}_3$. 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

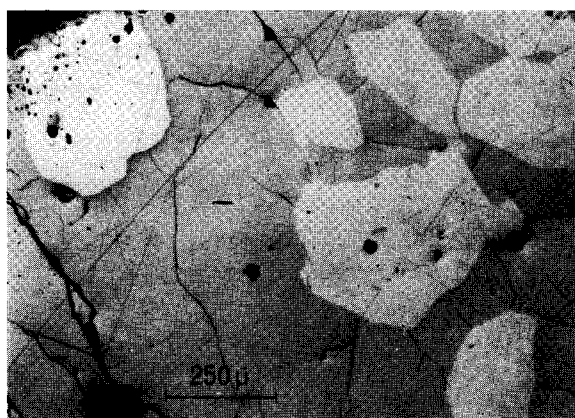


FIG. 2. Empress Josephine Mine, Colorado (USNM R 7243) $\text{Ag}_{5-x}\text{Te}_3$ (medium gray), AgTe (light gray), PbTe (white). Black is gangue.

Thompson *et al.* (1951) fits “1” regarding anisotropy, and “2” regarding bireflection.

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 $\text{Ag}_{5-x}\text{Te}_3$ range with $x=0.24\text{--}0.36$ (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

$\text{Ag}_{5-x}\text{Te}_3$ 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 dis-

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	$\text{Ag}_{0.96}\text{Te}$	$\text{Ag}_{4.64}\text{Te}_3$	$\text{Ag}_{4.76}\text{Te}_3$	$\text{Ag}_{4.70}\text{Te}_3$

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.

crepancy 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.

There is now proof that the phases $\text{Ag}_{5-x}\text{Te}_3$ 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 ₉ Te 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}Te₃, "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}Te₃, 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}Te₃ are (a) AgTe and Ag_{5-x}Te₃ in R359, (Fig. 3), and (b) sylvanite and Ag_{5-x}Te₃ in R267 from Red Cloud Mine, Boulder, Colorado and

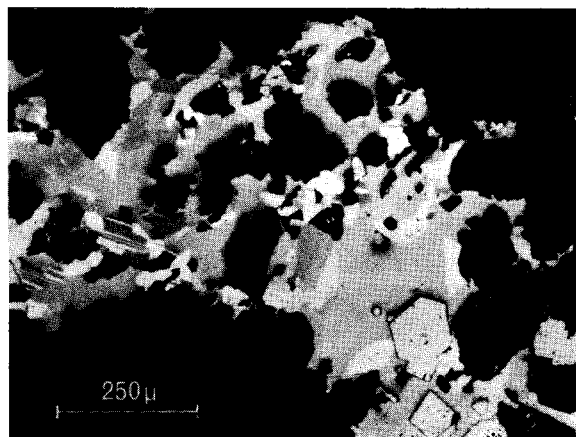


FIG. 3. Red Cloud Mine, Colorado (R267). Pyrite (euhedral grains, off-white), Ag_{5-x}Te₃ with *x*=0.24 (medium gray). AuAgTe₄ (with 23.6% Au) twinned grains, dark gray and whitish). Partly crossed polarizers.

