

EMPRESSITE AND STUETZITE REDEFINED

RUSSELL M. HONEA, *Department of Geology and Mineralogy,
University of Colorado, Boulder, Colorado.*

ABSTRACT

The name empressite, originally applied to a mineral having the composition AgTe , has been applied by Thompson *et al.* (1951) to material identical with type stuetzite and a synthetic product with the composition Ag_5Te_3 . New *x*-ray single crystal, DTA, and chemical analysis data substantiate the original definition. Empressite has the composition AgTe ; is orthorhombic with space group $Pmmm$ or Pmn , $a=8.90\text{A}$, $b=20.07$, $c=4.62$, $Z=16$. Measured and calculated specific gravity is 7.61. Strongest lines of the *X*-ray powder pattern are 2.70(10), 2.23(8), 3.81(6), and 3.33(6). Empressite decomposes to Ag_5Te_3 plus Te at 210°C . The type locality at the Empress Josephine mine, Kerber Creek district, Saguache County, Colorado, remains the only described locality.

The name stuetzite is here applied to the type material which has been shown to be identical with synthetic Ag_5Te_3 and with material from several natural occurrences. A new analysis of material from the May Day mine, La Plata district, Colorado, confirms the above composition. Stuetzite is hexagonal, space group $C6/mmm$, $a=13.38\text{A}$, $c=8.45$, $Z=7$, calculated specific gravity 8.18 (8.00 measured). Strongest lines of the powder pattern are 2.16(10), 2.55(8), 3.03(7), and 2.62(7). New occurrences of stuetzite are described from the analysis locality and the Golden Fleece mine, Lake City, Hinsdale County, Colorado.

INTRODUCTION

Stuetzite was described by Schrauf (1878) as a silver telluride with the possible composition Ag_4Te , and empressite by Bradley (1914, 1915) as having the composition AgTe . Investigations of the synthetic system Ag-Te failed to prove phases with such compositions, but indicated the presence of a binary phase with the composition of hessite (Ag_2Te) and a second phase variously assigned the formulae AgTe , Ag_3Te_2 , $\text{Ag}_{12}\text{Te}_7$, Ag_7Te_4 , $\text{Ag}_{2-x}\text{Te}_{1+x}$, Ag_5Te_3 , $\text{Ag}_{5-x}\text{Te}_3$. Using a combined study of natural and synthetic material Thompson *et al.* (1951) showed the identity of synthetic material (from run with composition Ag_5Te_3) with type stuetzite and supposed "type empressite," and applied the name empressite to this material. *X*-ray data and a new chemical analysis of the supposed type empressite are given in support of the identity, and the formula $\text{Ag}_{2-x}\text{Te}_{1+x}$ is proposed. These authors recognized the presence of still another silver telluride mineral with a completely different *x*-ray powder pattern, and designate the mineral as empressite (?), or later as empressite II (Berry and Thompson, 1962).

Further study by Kracek and Rowland (1955) of the synthetic material designated empressite led to assignment of the composition Ag_5Te_3 . Donnay *et al.* (1956) modified the formula to $\text{Ag}_{5-x}\text{Te}_3$ and proposed omission of silver from the lattice to account for the wide discrepancy between the measured specific gravity of natural material (7.61) and the

calculated value (8.07) while maintaining constancy of cell dimensions with those of synthetic material. Markham (1960) determined a value for x of 0.2 in his study of the synthetic system, while the analysis reported by Thompson *et al.* (1951) yields the formula $\text{Ag}_{4.29}\text{Te}_3$.

The present study was undertaken to establish the identity of the empressite (?) of Thompson *et al.* (1951). Chemical analysis, differential thermal analysis, and x -ray single crystal data on natural material from the type locality show that Bradley's original composition of AgTe was correct, and it is proposed that the name empressite be retained for this material. Since type stuetzite has been shown by x -ray methods to be identical with synthetic Ag_5Te_3 , and since there are several natural occurrences of identical material, it is proposed that the name stuetzite be applied to the silver telluride of that composition. While the original description of stuetzite is inadequate in several regards the mineral as here redefined is fully characterized in the literature and use of the name eliminates the necessity of introducing still another into the synonymy.

SOURCE OF STUDY MATERIAL

The nature of this study makes it imperative that the material described be carefully authenticated for purposes of future reference. For this reason a description of the samples used for analysis and x -ray data is given below.

Empressite. Type material could not be located in the collections of Yale University (A. N. Winchell, personal communication, 1962). A few fragments of the material described by Thompson *et al.* (1951) as type material (USNM, R7243) was provided by P. E. Desautels of the U. S. National Museum. This material is described by Desautels (personal communication, 1962) as having been supplied to Colonel Roebbling by Mr. Frank Leavitt, who removed the material from the Empress Josephine mine, Kerber Creek district, Colorado, and who supplied Prof. R. D. George with the material sent to Bradley for analysis and description. This specimen is described in some detail by Thompson *et al.* (1951) as their Material 1. A second specimen of empressite from the type locality is from the collections of the University of Colorado (UC1649) and was donated by Professor George as part of the material sent to Bradley. The specimen consists of a massive aggregate of empressite with a small amount of galena, altaite, and stuetzite on one corner. Much of the surface is covered by a fine grained aggregate of sericite containing small pyrite euhedrons. Except for color, which in this specimen is pale bronze with a darker bronze tarnish, the above description is the same as that given by Thompson *et al.* (1951) for Material 1. This sample (UC 1649)

is the source of the Material 4 of Thompson *et al.* (1951) which is designated empressite (?). Additional samples of empressite were furnished by Dr. J. R. Hayes of the Colorado School of Mines and by Mr. H. E. Miller, a private collector. Both samples proved to be portions of UC1649.

Stuetzite. Specimens of this mineral were identified from the May Day mine, La Plata district, La Plata County, Colorado (UC 4128), and from the Golden Fleece mine, Lake City, Hinsdale County, Colorado (UC4129). A small amount of stuetzite (less than one per cent of the samples studied) is associated with empressite in both UC1649 and USNM, R7243.

PHYSICAL PROPERTIES

Empressite has a metallic luster and on fresh surfaces a pale bronze color which tarnishes to a somewhat darker bronze on exposure. The mineral is brittle, has no cleavage, and breaks with an uneven to sub-conchoidal fracture. The hardness of empressite is $3\frac{1}{2}$, and the specific gravity as measured for both UC1649 and USNM, R7243 with the Berman balance is 7.61 ± 0.01 (7.61 calculated). This value compares well with the determination of 7.51 by Bradley (1914) and of 7.61 by Thompson *et al.* (1951) on USNM, R7243, but is higher than the value of 7.30 ± 0.04 reported by Thompson *et al.* on Material 4. Crystals of empressite have not been observed, and the material in the specimens studied is present in compact, granular masses. In polished section empressite is seen to be present in a coarse granular mosaic aggregate which takes a good polish. The mineral shows very strong bireflectance, with the color varying from gray to creamy white depending on orientation. Anisotropism is very strong, with polarization colors of gray—yellowish white—grayish blue. Etch reactions are as follow: HNO_3 —slight effervescence and quickly stains dark gray to black, HCl —negative, KCN —negative, FeCl_3 —quickly stains iridescent, KOH —negative, HgCl_2 —stains brown. The Talmadge hardness is C. Care must be taken in preparing polished sections so that the low decomposition temperature of 210°C is not exceeded. The decomposition products show an abundant host material with the properties of stuetzite enclosing irregularly distributed small grains of tellurium.

Stuetzite has a metallic luster, and on fresh surfaces a dark lead gray color. Exposed surfaces rapidly develop a dark bronze to iridescent tarnish. The mineral is brittle, has no cleavage, and breaks with a sub-conchoidal to uneven fracture. The hardness is $3\frac{1}{2}$, and the specific gravity as measured with a Berman balance on fragments from the May Day mine (UC4128) is 8.00 ± 0.02 (8.18 calculated). This value is con-

siderably higher than the 7.61 reported for the "empressite" of Thompson *et al.* (1951), but as indicated above their measurement is believed by this writer to have been made on empressite proper. The only natural crystal described (Schrauf, 1878; Thompson *et al.*, 1951) is hexagonal, has an equant habit, and is highly modified. Synthetic crystals obtained by the writer are short prismatic and have well developed pyramidal terminations. Natural material observed in this study is present in massive, compact, granular aggregates. Polished sections of stuetzite are very similar in appearance to hessite, except that the inversion twinning so

TABLE 1. X-RAY SINGLE CRYSTAL DATA FOR EMPRESSITE AND STUETZITE

Space Group	Empressite	Stuetzite					
	1	2	3	4	5	6	7
	<i>Pnmm</i> or <i>Pmn</i>			<i>C6/mmm</i>		<i>P6/mmm</i>	
<i>a</i>	8.90 Å	13.429 Å	13.4 kX	13.46 kX	13.49 Å	13.49 Å	13.38 Å
<i>b</i>	20.07						
<i>c</i>	4.62	8.4508	8.5	8.5	8.47	8.48	8.45
Z	16	3		7	7	7	7
SG	7.61			8.03	8.07		8.18

1. Empressite (UC1649), Empress Josephine mine, Kerber Creek district, Colorado.
2. "Ag₁₂Te₇" or synthetic stuetzite, Koern (1939).
3. Stuetzite (type), probably from Nagyag, Transylvania. M. A. Peacock in Thompson *et al.* (1951).
4. Synthetic stuetzite. J. F. Rowland in Thompson *et al.* (1951).
5. Synthetic stuetzite. Donnay *et al.* (1956).
6. "Empressite I" or stuetzite as here redefined (USNM, R7243), Empress Josephine mine, Kerber Creek district, Colorado. Berry and Thompson (1962).
7. Stuetzite (UC4128), May Day mine, La Plata district, Colorado.

commonly seen in hessite was not observed in stuetzite. The Talmadge hardness is B, and the color is light gray. Anisotropism is moderate, with polarization colors of gray-reddish brown-blue. Etch reactions are: HNO₃—quickly stains grayish brown to iridescent, HCl—very slowly stains light brown, most of which rubs off, KCN—negative, FeCl₃—quickly stains iridescent with development of a parallel etch pattern, KOH—negative, HgCl₂—stains brown.

X-RAY DATA

X-ray single crystal data for empressite was obtained from an anhedral single crystal fragment oriented through use of the precession

method. Zero, first, and second level photographs were obtained for the (hk0) and (0kl) orientations, and cone axis photographs with the x -ray beam parallel to the a and c axes. Empressite is orthorhombic, and has cell dimensions and contents as shown in Table 1. Systematic omissions show the space group to be either $Pmmm$ or Pmn . An x -ray powder diffraction pattern was indexed using these dimensions, and calculated and measured values of d are given in Table 2. Identical patterns were obtained for both samples UC1649 and the principal material making up USNM, R7243. The pattern is the same as that given by Berry and Thompson (1962) for empressite II.

Single crystal x -ray measurements are reported for stuetzite by several investigators. The mineral is hexagonal and has cell constants as shown in Table 1. A measured powder pattern is compared with the published data for empressite I (stuetzite) of Berry and Thompson (1962) in Table 3. It is apparent that the measured values are similar, but a number of additional lines were measured by the writer. Several of these are doublets that are better resolved using a larger diameter camera, and several are lines of low intensity. The smaller cell dimensions obtained by the writer are perhaps attributable to correction of the film measurements for film shrinkage.

It would appear that the pattern cited by Thompson *et al.* (1951) and Berry and Thompson (1962) was obtained from the stuetzite associated with empressite in the U. S. National Museum specimen.

CHEMICAL COMPOSITION

A new analysis of empressite, presented in Column D of Table 4, reaffirms the originally proposed composition of $AgTe$ based on two analyses by Bradley (1914) and two by Dittus reported by Bradley (1915). The analysis of Thompson *et al.* (1951) on material having the same measured specific gravity as determined in the present study is presented in Column E. As mentioned previously, this material was found by the present writer to consist predominantly of empressite. This is perhaps to be expected in view of the specific gravity determinations. While there is no means of satisfactorily resolving the differences between this analysis and the others, it is worthy of note that were the analytical results inverted and the value reported for Ag given for Te and vice versa, the analysis would be in almost perfect agreement. Is it possible that the analyst inverted the determinations in his report? An error in the analysis is further suggested by the atomic ratios determined from the analysis. The analysis yields the formula $Ag_{4.29}Te_3$, departing considerably from the maximum value of $x=0.2$ reported by Markham (1960) for the formula $Ag_{5-x}Te_3$ in his study of the synthetic system. While some de-

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR EMPRESSITE (UC1649), EMPRESS JOSEPHINE MINE, KERBER CREEK DISTRICT, COLORADO. SPACE GROUP *Pmmn* OR *Pmn*, $a=8.90 \text{ \AA}$, $b=20.07$, $c=4.62$; Cu RADIATION, Ni FILTER, WAVELENGTH 1.5418 \AA . CORRECTED FOR FILM SHRINKAGE. CAMERA 114.6 mm DIAMETER

d_{meas}	I	hkl	d_{calc}	d_{meas}	I	hkl	d_{calc}	d_{meas}	I	hkl	d_{calc}
10.04	4	020	10.04	2.04	5	202	2.05	1.578	2b	422	1.583
4.37	1	140	4.37			142	2.04			192	1.579
4.02	4	111	4.02			212	2.04			541	1.577
		050	4.01			440	2.03			490	1.575
3.81	6	031	3.80	2.01	4	0.10.0	2.01			0.12.1	1.573
		121	3.80			091	2.01	1.562	1b	481	1.566
3.33	6	060	3.34			222	2.01			2.12.0	1.566
		240	3.33			052	2.00			3.10.1	1.564
3.18	5	141	3.18			361	2.00			432	1.558
3.04	1	221	3.05	1.962	1	421	1.966	1.516	1b	1.13.0	1.521
		051	3.03			232	1.960			103	1.517
2.97	$\frac{1}{2}$	250	2.98			1.10.0	1.958			0.12.2	1.515
2.89	4	151	2.90	1.920	3	431	1.920			113	1.513
		231	2.89			062	1.917			570	1.512
2.85	3	320	2.84			380	1.916	1.490	4	1.10.2	1.494
2.70	10	061	2.71	1.864	$\frac{1}{2}$	441	1.862			491	1.491
		330	2.71			162	1.859			4.10.0	1.490
		241	2.70	1.833	$\frac{1}{2}$	2.10.0	1.830			452	1.488
2.60	2	161	2.59			291	1.830			561	1.488
2.51	2	340	2.52			252	1.826	1.471	1b	382	1.474
		080	2.51	1.796	1	072	1.799			3.11.1	1.473
		301	2.50			3.12.1	1.793			043	1.472
		251	2.50			322	1.793			620	1.467
2.43	2b*	071	2.44			451	1.793	1.436	2	223	1.440
		321	2.42	1.771	1	510	1.773			053	1.438
2.32	4	261	2.31			381	1.770			571	1.437
2.29	1	012	2.29	1.757	2b	332	1.759			0.14.0	1.434
2.23	8	400	2.23			470	1.758			2.12.2	1.434
		090	2.23			520	1.753			0.11.2	1.432
		341	2.23	1.669	2	0.12.0	1.672	1.421	1	640	1.422
		360	2.22			182	1.669			233	1.422
		112	2.22			272	1.668			153	1.419
2.18	3	280	2.19			1.11.1	1.667			4.10.1	1.418
		032	2.18			480	1.665	1.403	1b	512	1.406
		122	2.18	1.650	1b	511	1.655			472	1.399
		420	2.17			1.12.0	1.644			621	1.399
2.14	5	181	2.14			471	1.643			243	1.398
		271	2.14	1.604	1b	092	1.604	1.363	3b	0.14.1	1.369
2.12	4	132	2.12			402	1.602			253	1.368
		351	2.12			362	1.600			303	1.367
		430	2.11							073	1.357

d_{meas}	I	d_{meas}	I	d_{meas}	I	d_{meas}	I	d_{meas}	I
1.333	1	1.224	1vb	1.134	1vb	1.059	$\frac{1}{2}$	0.952	1
1.312	2	1.205	1	1.112	1	1.032	1b	0.929	$\frac{1}{2}$ b
1.296	2b	1.191	$\frac{1}{2}$ b	1.099	$\frac{1}{2}$ b	1.007	1vb	0.918	$\frac{1}{2}$ b
1.257	1b	1.180	$\frac{1}{2}$	1.089	1b	0.974	1vb	0.905	1
1.245	1	1.172	$\frac{1}{2}$	1.074	1vb	0.970	$\frac{1}{2}$	0.896	$\frac{1}{2}$ b

* b=broad.

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR STUETZITE (UC4128), MAY DAY MINE, LA PLATA DISTRICT, COLORADO, COMPARED WITH DATA FROM BERRY AND THOMPSON (1962) FOR EMPRESSITE I (STUETZITE AS REDEFINED). SPACE GROUP $C6/mmm$, $a=13.38 \text{ \AA}$, $c=8.45$; Cu RADIATION, Ni FILTER, WAVELENGTH 1.5418 \AA CORRECTED FOR FILM SHRINKAGE. CAMERA DIAMETER 114.6 MM

Stuetzite				Empressite I				Stuetzite				Empressite I			
d _{meas}	I	hkl	d _{calc}	d _{meas}	I	hkl	d _{calc}	d _{meas}	I	hkl	d _{calc}	d _{meas}	I	hkl	d _{calc}
11.59	5	10 $\bar{1}$ 0	11.59							5382	1.541			1891	1.350
4.77	1	0221	4.78					1.536	1b	0772	1.541			55.10.0	1.349
4.37	4	2130	4.38	4.40	$\frac{1}{2}$	12 $\bar{2}$ 0	4.41			5382	1.541			1236	1.346
3.88	3	2131	3.89	3.97	$\frac{1}{2}$	0112	3.98			7180	1.535			2465	1.345
3.56	6	1122	3.57			12 $\bar{2}$ 1	3.92			3364	1.534	1.318	$\frac{1}{2}$	4593	1.322
3.52	6	0331	3.52	3.56	1	1122	3.59	1.484	1	5490	1.484			4484	1.320
3.35	5	2240	3.35			0331	3.54			5164	1.483			1565	1.319
3.21	2	3140	3.21	3.40	$\frac{1}{2}$	0222	3.43	1.464	2	5491	1.461			37.10.0	1.314
3.11	5	2241	3.11			2240	3.37			6390	1.460	1.293	$\frac{1}{2}$	0990	1.298
3.03	7	2132	3.04	3.23	$\frac{1}{2}$	1340	3.24			0445	1.460			0883	1.297
2.82	3	0003	2.82	3.04	2	1232	3.06	1.441	$\frac{1}{2}$	7182	1.442			1346	1.296
2.62	7	2242	2.62			1341	3.03			6391	1.439			2684	1.287
2.55	8b*	1342	2.56	2.83	$\frac{1}{2}$	0003	2.83			4483	1.438	1.281	$\frac{1}{2}$	0991	1.283
		3251	2.54	2.64	1	2242	2.64	1.424	4	0881	1.428			0665	1.278
2.39	$\frac{1}{2}$	0442	2.39	2.55	5	2351	2.55			0773	1.427				
2.37	$\frac{1}{2}$	2133	2.37			1450	2.55			5383	1.427				
2.32	3	5050	2.32			0223	2.54			3255	1.426				
2.27	2	0333	2.28	2.24	1	0551	2.25			0664	1.425				
2.24	4	3252	2.25			3360	2.25	1.346	6	7183	1.348				
		0551	2.24	2.17	10	1452	2.18			3365	1.347				
		3360	2.23			3361	2.17			7292	1.342				
2.16	10b	4152	2.17			2243	2.16			2136	1.341				
		3361	2.16	2.12	2	2461	2.14	1.314	2	64.10.1	1.313				
		2243	2.15			1343	2.13			5493	1.313				
2.11	6	4261	2.12	2.04	1	0004	2.12			5165	1.312				
		1343	2.12			0552	2.05			4484	1.311				
		0004	2.11			1561	2.04	1.290	1b	6393	1.296				
2.03	4	0552	2.03			0443	2.03			8192	1.291				
		5161	2.02			1124	2.02			3146	1.290				
		0443	2.02	1.933	1	0660	1.947			0883	1.288				
1.931	5	3253	1.933			2353	1.944			73.10.1	1.288				
		6060	1.931			3470	1.920			9090	1.287				
1.900	3	3470	1.905	1.910	$\frac{1}{2}$	1254	1.911	1.276	2	6284	1.279				
		2134	1.903	1.873	$\frac{1}{2}$	3471	1.873			55.10.2	1.276				
1.865	3	5162	1.867			2570	1.871			0991	1.273				
		4371	1.858	1.664	$\frac{1}{2}$	0770	1.668			0665	1.272				
		5270	1.855			3580	1.668	1.246	$\frac{1}{2}$	82.10.1	1.250				
1.816	$\frac{1}{2}$	5271	1.812			2354	1.662			5275	1.249				
1.790	$\frac{1}{2}$	0553	1.790			4481	1.653			73.10.2	1.246				
		2244	1.780	1.546	$\frac{1}{2}$	0772	1.552			3256	1.245				
1.757	$\frac{1}{2}$ b	3144	1.765			3582	1.552			7184	1.242				
		0662	1.756			1780	1.547	1.230	$\frac{1}{2}$	0992	1.232				
1.699	$\frac{1}{2}$	0444	1.707			3364	1.542			4156	1.230				
		5272	1.699	1.463	$\frac{1}{2}$	0445	1.466	1.205	1	55.10.3	1.209				
1.674	2	5163	1.674			0850	1.460			0007	1.207				
		4480	1.673	1.445	$\frac{1}{2}$	3601	1.450			0556	1.204				
		0115	1.672			4483	1.448			64.10.3	1.202				
1.657	2	7070	1.656			0851	1.439			6394	1.201				
		5380	1.655	1.429	$\frac{1}{2}$	0664	1.434			0117	1.201				
		3254	1.654			2355	1.433	1.169	$\frac{1}{2}$ b						
1.579	1	6281	1.579			2790	1.427	1.158	$\frac{1}{2}$						
		4373	1.578			3474	1.423	1.135	1						
		2135	1.577	1.351	2	1783	1.357	1.117	$\frac{1}{2}$						
1.547	1b	5273	1.549			3365	1.354	1.106	$\frac{1}{2}$ b						
		0335	1.548			2792	1.353	1.087	$\frac{1}{2}$						

* b=broad.

parture of natural material from synthetic is to be expected, it is unlikely that the discrepancy would be this great.

In Columns G and H is reported an analysis for stuetzite. Unfortunately the analysis sample contained approximately 20 per cent of

TABLE 4. CHEMICAL COMPOSITION OF EMPRESSITE AND STUETZITE.

	A	B	C	D	E	F	G	H
Ag	45.81	45.17	43.70	44.9	54.77	58.49	47.3	58.5
Pb	—	—	—	0.05	—	—	9.18	—
Cu	—	—	—	0.35	—	—	0.03	—
Zn	—	—	—	—	—	—	0.78	—
Fe	—	0.22	2.16	0.20	—	—	1.70	—
Te	54.19	54.75	53.84	53.6	45.26	41.51	33.6	41.5
S	—	—	—	0.10	—	—	3.47	—
Rem.	—	0.39	0.34	0.70	—	—	3.50	—
Total	100.00	100.53	100.04	99.90	100.03	100.00	99.56	100.0
SG		7.51		7.61	7.61		8.00	

- A. Theoretical weight percentages for empressite, AgTe .
- B. Empressite, Empress Josephine mine, Kerber Creek district, Colorado. Average of two analyses. Remainder is insoluble—0.39. Analyst Bradley (1914).
- C. Empressite, type locality. Average of two analyses. Remainder is insoluble—0.34, trace CaO present. Analyst Dittus in Bradley (1915).
- D. Empressite, type locality. Remainder includes SiO_2 —0.40, Al_2O_3 —0.3. Contains very minor pyrite, chalcopyrite, and sericite. Analyst Jun Ito.
- E. Empressite, "type material," USNM, R7243. Analyst R. N. Williams in Thompson *et al.* (1951).
- F. Theoretical weight percentages for stuetzite, Ag_5Te_3 .
- G. Stuetzite, May Day mine, La Plata district, Colorado (UC4128). Remainder includes Au —0.1; As —0.10; SiO_2 —2.19; Al_2O_3 —0.60; TiO_2 —0.01; V_2O_5 —0.3; $\text{MgO} + \text{MnO}$ 0.2; Ca , Sr , Ba trace. Contains known impurities of galena (major), silicates (major), and minor amounts of tetrahedrite-tennantite, pyrite, and sphalerite. Analyst Jun Ito.
- H. Stuetzite, analysis G recalculated after deducting impurities.

intimately intergrown impurities that could not be separated by physical means, and it was necessary to identify the impurities and deduct them from the total. The recalculated analysis yields precisely the formula Ag_5Te_3 , and supports Markham's (1960) conclusion that there is only slight deviation from this ratio. Perfect agreement of the recalculated analysis with the theoretical weight percentages is somewhat fortuitous since a small but undetermined amount of silver is probably present in the galena and tetrahedrite-tennantite known to be present as impurities.

SYNTHESIS

The synthesis of a silver telluride with higher tellurium content than hessite (Ag_2Te) has been reported by several investigators (Pelabon, 1906; Pellini and Quercigh, 1910; Chickashige and Saito, 1916; Koern, 1939; Kracek and Ksanda, 1940; Thompson *et al.*, 1951; and Markham, 1960). Various formulae have been assigned to the phase, but that most recently shown to apply is Ag_5Te_3 or $\text{Ag}_{5-x}\text{Te}_3$. This material, corresponding to stuetzite as here redefined, is readily prepared from fusions of the elements and by reaction in the solid state between the elements in either dry or hydrothermal runs.

Attempts by the writer to synthesize the phase AgTe were not successful. The low temperature range of stability of empressite makes preparation from fusions impossible. Both dry and hydrothermal runs containing stoichiometric amounts of Ag and Te gave as products hessite plus tellurium, stuetzite plus tellurium, or hessite plus stuetzite plus tellurium. Silver apparently reacts early to form hessite and is thus depleted. Reaction with the remaining tellurium metal is slow, and the hessite may become armored with stuetzite.

A third phase, having the composition $\text{Ag}_{1.9}\text{Te}$, is reported by Kiukula and Wagner (1957), who determined free energies of formation for hessite (Ag_2Te), $\text{Ag}_{1.9}\text{Te}$, and stuetzite ($\text{Ag}_{1.64}\text{Te}$) at temperatures of 250° C. and 300° C. This phase was not encountered in the present study.

THERMAL BEHAVIOR

A differential thermal analysis curve was obtained for empressite from the type locality (UC1649) using a Deltatherm unit with a constant heating rate of 10° C. per minute. The curve is reproduced below as Fig. 1 and shows a series of endothermic reactions, all but one of which is readily accounted for by referring to the phase diagram for the system Ag-Te (Fig. 2). X-ray powder diffraction photographs were prepared from material heated in stages in evacuated silica tubes and quenched in water to aid in interpretation of the reactions.

The first endothermic peak at 210° C. marks the thermal decomposition of empressite to stuetzite plus tellurium. This decomposition is not reversible on the down-temperature gradient, at least at the experimental cooling rate used. The rather broad endothermic peak at 294° C. marks the inversion of the low temperature or alpha polymorph of stuetzite to the beta form (see Koern, 1939; and Kracek and Rowland, 1955). The peak present at 335° C. could not be accounted for by either the phase diagram or x-ray photographs, and may represent a reaction of the thermocouple. This conclusion is supported by the greater variance in

temperature recorded for the higher temperature reactions as compared with those shown in Figure 2. The major endothermic reaction at 356° C. results from the beginning of melting at the eutectic between beta stuetzite and tellurium. The sharp endothermic peak at 433° C. has a temperature somewhat higher than would be indicated from the phase diagram (419° C.), and marks the temperature of the peritectic reaction by which beta stuetzite plus liquid is converted to gamma stuetzite plus liquid. The endothermic trough culminating at 456° C. results from the peritectic

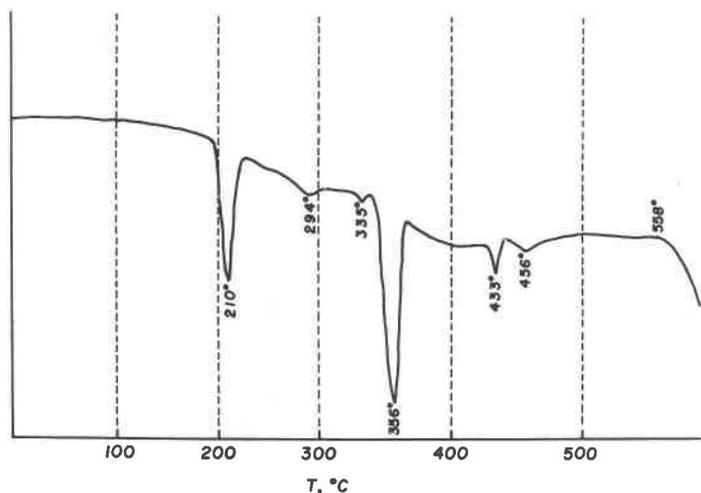


FIG. 1. Differential thermal analysis curve for empressite.

tic reaction of gamma stuetzite plus liquid to form the cubic (beta) modification of hessite plus liquid. The final reaction, beginning at 558° C., results from total melting to form one homogeneous liquid, and is somewhat higher in temperature than is indicated by the solidus curve of the phase study.

The only previous mention of the thermal behavior of empressite is by Thompson *et al.* (1951) who state that when fused in vacuum the product gives powder lines of "empressite" (stuetzite) and strong lines of clausthalite. There is no elaboration as to a source for selenium to form clausthalite.

OCCURRENCE AND ASSOCIATIONS

Empressite has been reported only at the Empress Josephine mine, Kerber Creek district, Saguache County, Colorado. Burbank (1932) and Patton (1915) describe the occurrence of a lens-shaped body of tellurides

between faces of lead-zinc ore. Telluride minerals include empressite, native tellurium, sylvanite, petzite, hessite, rickardite and altaite. Telluride mineralization is later than deposition of the enclosing sulfides, and a reaction rim of altaite often separates other tellurides from the abundant galena. Hessite is described (Burbank, 1932) as irregular intergrowths with empressite, suggesting contemporaneity. Colinear relations

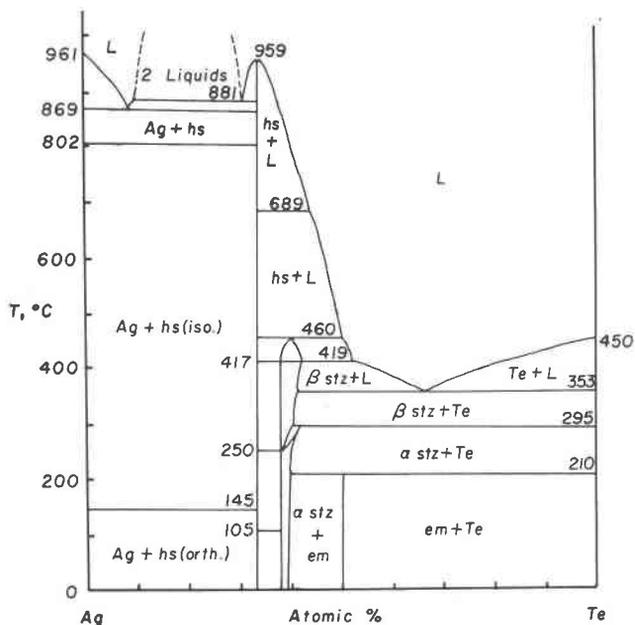


FIG. 2. The binary system silver-tellurium modified from Kracek and Ksanda (1940), Kracek and Rowland (1955), and Markham (1960) to show the presence of empressite (AgTe). Abbreviations used: hs=hessite, stz=stuetzite, em=empressite, Ag=silver, Te=tellurium, L=liquid.

of hessite, stuetzite and empressite (Fig. 3), combined with polished section similarities between hessite and stuetzite, suggest that the association is probably that of empressite—stuetzite observed in the present study. Petzite and sylvanite were not observed by the writer, but are described by Burbank (1932) as present in veinlets in quartz with sphalerite, galena and altaite. Native tellurium and rickardite are closely associated with each other but were not observed in contact with empressite in the present study. Bradley (1914) mentions native tellurium as present with empressite on the type specimen. Thus, both of the described direct associations empressite—stuetzite and empressite—tellurium lie on the Ag-Te binary join.

Stuetzite has been described from several localities, and is noted from two new occurrences in the present study. Previously described is the association with empressite which led to redefinition of the species by Thompson *et al.* (1951) from study of the U. S. National Museum specimen from the type locality. This association was also noted by the present writer. Thompson *et al.* (1951) also describe the occurrence of stuetzite with associated altaite from the Red Cloud mine, Gold Hill district,

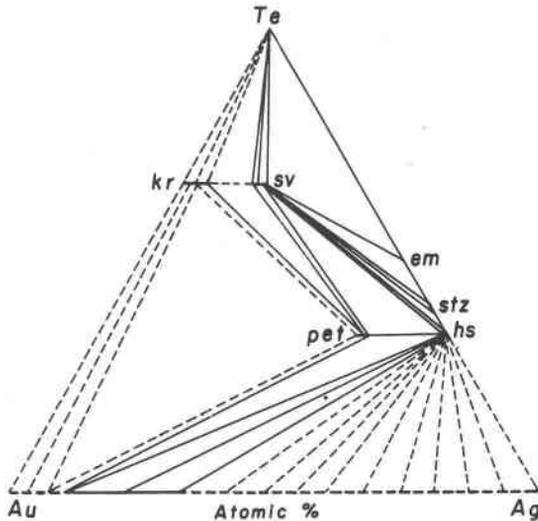


FIG. 3. Observed (—) and inferred (---) tie lines in the system Au-Ag-Te based on associations of empressite and stuetzite from Colorado localities. Tie lines to empressite valid only to 210° C., above which temperature empressite decomposes to stuetzite plus tellurium. (Modified from Markham, 1960).

Boulder County, Colorado. Other tellurides from this mine identified in the present study include hessite, petzite and sylvanite.

Markham (1960) describes stuetzite associated with sylvanite in a single specimen from the Kalgoorlie district, Western Australia; and from Vatukoula, island of Viti Levu, Fijian group. For the second locality the observed associations are listed as stuetzite—sylvanite, stuetzite—tellurium, stuetzite—tellurium—sylvanite, and stuetzite—tellurium—coloradoite

In the present investigation new occurrences of stuetzite were noted at the May Day mine, La Plata district, La Plata County, Colorado, and the Golden Fleece mine, Lake City, Hinsdale County, Colorado. In the May Day ores stuetzite (mis-labeled hessite) is an abundant constituent of telluride replacement masses, and was observed in the associations

stuetzite—sylvanite, stuetzite—hessite—sylvanite, and stuetzite—altaite. Sulfide minerals are commonly intergrown with the tellurides and include galena, sphalerite, tetrahedrite—tennantite. It is believed that x-ray examination of "hessite" specimens from the May Day mine may prove stuetzite to be the most common telluride mineral from the deposit. More complete data concerning the mineralogy of telluride deposits in the La Plata district are given by F. W. Galbraith in Eckel (1949). Specimens from the Golden Fleece mine show the associations stuetzite—petzite and stuetzite—hessite—petzite.

The associations of stuetzite observed in the present study are compatible with Markham's (1960) 300° C. isothermal section of the system Au-Ag-Te and with his equilibrium diagrams assembled from associations in the Kalgoorlie and Vatukoula deposits. The presence of empressite as a lower temperature phase requires modification of the tie lines on a lower temperature isothermal section as shown in Fig. 3. This tie line configuration is based on associations observed or inferred from the present study. Decomposition of empressite at temperatures exceeding 210° C. would yield precisely the same configuration as shown by Markham (1960).

ACKNOWLEDGMENTS

The writer gratefully acknowledges financial assistance from the George and Anna Garrey Fund for defraying the cost of chemical analyses. Specimens for the study were made available through the courtesy of Mr. P. E. Desautels of the U. S. National Museum; Prof. J. R. Hayes of the Colorado School of Mines; Mr. John Murphy of the Denver Museum of Natural History; and by Mr. H. E. Miller, a Boulder, Colorado, mineral collector.

REFERENCES

- BERRY, L. G. AND R. M. THOMPSON (1962) X-ray powder data for ore minerals: The Peacock atlas. *Geol. Soc. Am. Memoir* 85.
- BURBANK, W. S. (1932) Geology and ore deposits of the Bonanza mining district, Colorado. *U. S. Geol. Survey Prof. Paper* 169.
- BRADLEY, W. M. (1914) Empressite, a new tellurium mineral from Colorado. *Am. Jour. Sci.* 38, 163-165.
- (1915) On the mineral empressite. *Am. Jour. Sci.* 39, 223.
- CHICKASHIGE, M. AND I. SAITO (1916) Metallographische Untersuchung über das System von Silber and Tellur. *Mem. Coll. Sci. Univ. Kyoto*, 1, 361-368.
- DONNAY, G., F. C. KRACEK AND W. R. ROWLAND (1956). The chemical formula of empressite. *Am. Mineral.* 41, 722-723.
- ECKEL, E. B. (1949) Geology and ore deposits of the La Plata district, Colorado. *U. S. Geol. Survey Prof. Paper* 219.
- KIUKKULA, K. AND C. WAGNER (1957) Measurements on galvanic cells involving solid electrolytes. *Jour. Electrochem. Soc.* 104, 385-386.

- KOERN, V. (1939) Das binare Legierungssystem Ag-Te. *Naturwissenschaften*, **27**, 432.
- KRACEK, F. C. AND C. J. KSANDA (1940) Phase relations in the system silver-tellurium (abs.). *Trans. Am. Geophys. Union*, **21**, 363.
- AND W. R. ROWLAND (1955) The system silver-tellurium. *Ann. Rept. Geophys. Lab., Carnegie Inst. Washington Yearbook* **54**, 135-136.
- MARKHAM, N. L. (1960) Synthetic and natural phases in the system Au-Ag-Te. *Econ. Geol.* **55**, 1148-1178, 1460-1477.
- PATTON, H. B. (1915) Geology and ore deposits of the Bonanza district, Saguache County, Colorado. *Colo. State Geol. Survey Bull.* **15**, 105-111.
- PELABON, M. H. (1906) Sur le sulfre, le seleniure, et le tellure d'argent. *Compte Rendus Acad. Sci.* **143**, 294-296.
- PELLINI, G. AND E. QUERCIGH (1910) I tellururi d'argento. *Rend. Accad. Lincei (Roma)* (5), **19**, 415-421.
- SCHRAUF, A. (1878) Ueber die Tellurerze Siebenburgens. *Zeit. Krist.* **2**, 209-252.
- THOMPSON, R. M. (1949) The telluride minerals and their occurrence in Canada. *Am. Mineral.* **34**, 342-382.
- M. A. PEACOCK, J. F. ROWLAND AND L. G. BERRY (1951) Empressite and stuetzite. *Am. Mineral.* **36**, 458-470.

Manuscript received, August 30, 1963; accepted for publication, November 4, 1963.