

VULCANITE, A NEW COPPER TELLURIDE FROM
COLORADO, WITH NOTES ON CERTAIN
ASSOCIATED MINERALS

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ABSTRACT

A copper telluride found in specimens from the Good Hope Mine, Vulcan, Colorado, has been determined to be a new mineral. It is named vulcanite, from the locality of the mine.

Vulcanite forms light bronze to yellow-bronze aggregates of prismatic or bladelike to irregular grains of metallic luster. One prominent cleavage and one less prominent are probably pinacoidal. Twinning nearly at 45° to the prominent cleavage is shown. Hardness is between 1 and 2; specific gravity is indeterminate owing to impurities. In polished section, vulcanite is strongly birefractant (reflectivity in white light is *ca.* 36.0% to 58.5%), varying from bright yellow to yellow-white to medium blue-gray. Extinction is parallel to cleavage and the long axes of laths. Rotation sense is (-) relative to the prominent cleavage. Anisotropism is very strong; polarization colors are yellow-white, grayish yellow-white, yellow-orange, gray. Phase difference in white light is (-); elongation on the prominent cleavage is (-). Rotation angles (corrected A_r) range from $17.2^\circ \pm 0.6^\circ$ at $470 \text{ m}\mu$ to $24.7^\circ \pm 0.6^\circ$ at $650 \text{ m}\mu$. Phase differences (2θ) range from $58.0^\circ \pm 6.0^\circ$ at $470 \text{ m}\mu$ to $-9.0^\circ \pm 1.8^\circ$ at $650 \text{ m}\mu$. Microchemical tests show Cu and Te; etch tests are positive for 1:1 HNO₃, 1:1 HCl, FeCl₃, and KCN, negative for H₂Cl₂ and KOH.

X-ray powder diffraction data show that vulcanite is orthorhombic, with cell dimensions $a=4.09 \text{ \AA}$, $b=6.95 \text{ \AA}$, and $c=3.15 \text{ \AA}$. These values are in close agreement with those found for synthetic CuTe by Anderko and Schubert. The probable space group is *Pnmm*.

Twinning and intergrowths in rickardite associated with vulcanite are described briefly. A second telluride, also apparently new, is briefly described pending further investigation.

INTRODUCTION

During an investigation of the rotation properties of rickardite in U. S. National Museum Specimen R-933, from the Good Hope Mine, Vulcan, Gunnison County, Colorado, a mineral with even more remarkable optical properties was noted. The same mineral was subsequently found in United States National Museum Specimen 85136, from the same locality. Investigation indicates that it is a compound of copper and tellurium having unit cell constants essentially in agreement with those given by Anderko and Schubert for synthetic CuTe, a compound not heretofore reported as a mineral. The mineral therefore appears to be a new species. We propose to name it vulcanite, after the locality of the Good Hope Mine.

DESCRIPTION OF VULCANITE

Both specimens studied consist of fragments of mineralized rock cemented by rickardite, vulcanite, and native tellurium. Intergrown rickardite and vulcanite form a layer 0.5 to 3 mm. thick encrusting each

rock fragment. In general, rickardite predominates in the outer part of the layer, next to the rock fragments, whereas vulcanite predominates in the inner part. Tellurium fills the remainder of the spaces between fragments and forms scattered minute grains and small patches in the rickardite-vulcanite crusts as well.

In hand specimen, vulcanite is light bronze to yellow-bronze, with a metallic luster. No crystals are present, hence the morphology cannot be determined. Cleavage is visible on broken surfaces, but the number and

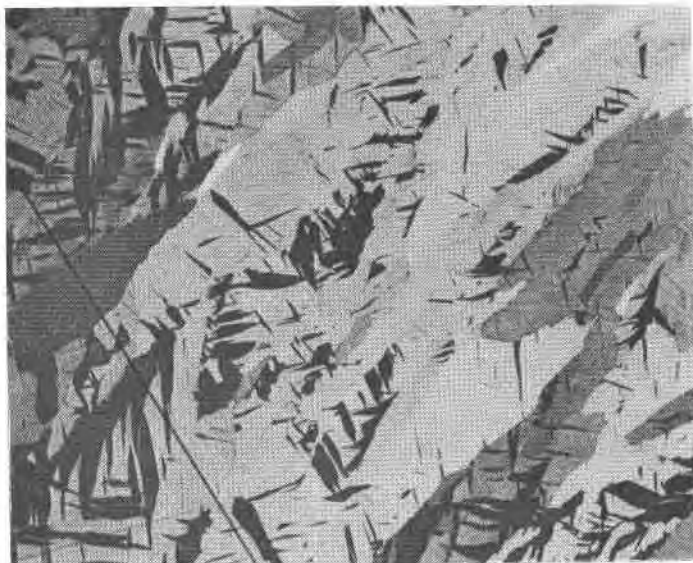


FIG. 1. Elongate irregular laths of vulcanite (pale gray to medium gray) partly replaced by rickardite (dark gray). Native tellurium (white) forms three minute northeast-trending grains and an irregular patch at the northeast corner of the photograph. Plain light, $\times 130$.

orientation of cleavages are indeterminate. Owing to intergrowth with rickardite, pure material for determining specific gravity is unobtainable. The material is extremely soft (1–2) and somewhat sectile.

Under the microscope, vulcanite grains range from lath-shaped to nearly equant to irregular (Fig. 1). Many grains fall in the range from 0.1 mm. to 1.1 mm. in length, but where partial replacement by rickardite is shown (see below) remnants of vulcanite crystals measurable in microns are abundant. A prismatic or blade-like habit is suggested. Some lath-shaped grains have a well-developed lengthwise cleavage, others show a poorly developed cleavage at right angles to the first, and still others show only the poorly developed cleavage. We judge that both cleavages are pinacoidal. Extremely thin twin lamellae along planes

nearly but not quite at 45° to the prominent cleavage occur in some grains.

The optical properties of vulcanite are so distinctive that identification of the mineral is a simple matter. They are as follows:

Color: bright yellow or yellow-white to medium blue-gray.

Reflectivity (photoelectric method in white light): maximum, 58.5%, minimum 36.0%.

These values are low, possibly by as much as 2-3%, because there are no grains entirely free of scratches, pits, and inclusions of rickardite.

Birefractance: very strong, as indicated by reflectivity values. Grains showing the well-developed cleavage are bright yellow when the cleavage is parallel to the polarizer vibration plane, blue-gray when the cleavage is at the perpendicular position. Elongate grains lacking the prominent cleavage are bright yellow when the long axis is parallel to the polarizer, bluish-gray at the perpendicular position.

Extinction: parallel to cleavage and elongation of laths.

Rotation properties (2):

Rotation sense: (-), relative to the well-developed cleavage and to long axes of plates showing this cleavage.

Anisotropism: very strong; polarization colors (nicols crossed) brilliant yellow-white, grayish yellow-white, yellow-orange, gray, depending on orientation.

Phase difference in white light: (+); the gypsum plate is strongly affected.

Elongation in white light: The principal cleavage direction is length fast. Plates lacking prominent cleavage are length slow.

Polarization figure: DR_r weak, DA_r strong. The field between the isogyres at the 45° position is orange; the areas outside the isogyres are blue.

Rotation angles and values of 2θ :

	A_r , observed, in degrees	A_r , corrected in degrees	2θ in degrees
470 μm	$20.7 \pm .7$	$17.2 \pm .6$	58.0 ± 6.0
520 μm	$24.5 \pm .5$	$20.4 \pm .4$	35.5 ± 3.0
546 μm	$26.2 \pm .5$	$21.8 \pm .4$	26.5 ± 2.5
589 μm	$28.2 \pm .6$	$23.5 \pm .5$	$6.1 \pm .8$
620 μm	$28.9 \pm .6$	$24.1 \pm .5$	$- 2.5 \pm 1.3$
650 μm	$29.6 \pm .7$	$24.7 \pm .6$	$- 9.0 \pm 1.8$

In the above, A_r , corrected, is the observed rotation angle corrected for the additional rotation produced by the reflecting plate (2). The value given for 2θ is the corrected value. Vulcanite in sodium light gives the highest values of A_r yet recorded for any mineral.

Microchemical: Tests for Cu and Te positive. Etch tests: 1:1 HNO_3 effervesces, staining dark gray; 1:7 HNO_3 effervesces after about 20 seconds, stains brownish-gray, and brings out cleavage; HCl bleaches grayish-white; FeCl_3 instantly darkens, staining light brown; KCN bleaches and then stains light brownish-gray; HgCl_2 and KOH negative.

X-RAY DATA FOR SYNTHETIC CuTe AND VULCANITE

In 1954, Anderko and Schubert (1) reported a study of the system Cu-Te in the region from about 34 to 67 at. % Te. They prepared mixtures in various proportions from electrolytic copper and tellurium of a purity of 99.7%. Samples weighing from 1 to 20 grams were fused in evacuated quartz tubes in a Tamman oven. Maximum weight loss due to volatiliza-

tion of Te in any experiment was 0.4%. Temperatures of fusion ranged upward of 600° C. X-ray and microscope studies of the products were supplemented by dilatometer studies. At compositions in the vicinity of 50 at. %, they obtained mixtures of Cu_4Te_3 * (synthetic rickardite) and a second phase of entirely different properties. In some preparations, small amounts of native tellurium were also present. From the phases

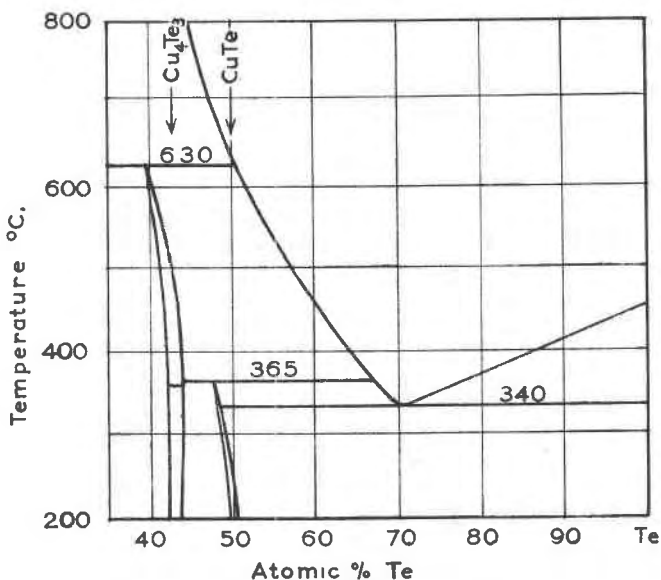


FIG. 2. Tellurium-rich portion of the system copper-tellurium, from Anderko and Schubert.

found at various temperatures and from x-ray studies, they concluded that the second phase had a composition very close to CuTe . Phase relations in the tellurium-rich portion of the system Cu-Te as interpreted by Anderko and Schubert are shown in Fig. 2. CuTe appears as a product of peritectic reaction of Cu_4Te_3 with liquid at about 365° and 67 at. % Te.

From x-ray powder and single crystal data, Anderko and Schubert concluded that CuTe is orthorhombic, with $a = 3.15 \pm 0.02$ kX units, $b = 4.07 \pm 0.02$ kX units, and $c = 6.92 \pm 0.02$ kX units. They calculated that the unit cell contains 2 Cu and 2 Te and that the space group is $Pmnm$.

X-RAY INVESTIGATION OF VULCANITE

X-ray powder diffraction data for vulcanite are given in Table I. The values obtained for interplanar spacings agree with values calculated

* According to Forman and Peacock (4), the formula of rickardite is $\text{Cu}_{4-x}\text{Te}_3$.

from values of $\sin^2\theta$ for CuTe given by Anderko and Schubert. The pattern is indexed on the basis of an orthorhombic unit cell with $a=4.09 \text{ \AA}$, $b=6.95 \text{ \AA}$, and $c=3.15 \text{ \AA}$. These values are in close agreement with those of Anderko and Schubert, except that we have transposed the axes to agree with the conventional form $b>a>c$. If the axes as reported by Anderko and Schubert for CuTe are similarly transposed, the space group for CuTe becomes $Pmnm$.

Several fragments of vulcanite were removed from our specimens for single crystal photographs, but all photographs taken are too indistinct to be usable, apparently because the fragments were deformed during removal. Extreme care in removal of fragments from the polished surfaces failed to resolve the difficulty.

TABLE I. X-RAY POWDER DATA FOR VULCANITE (CuTe)
 $Pmnm$; $a_0=4.09 \text{ \AA}$, $b_0=6.95 \text{ \AA}$, $c_0=3.15 \text{ \AA}$
 Cu/Ni radiation, $K_\alpha=1.5418 \text{ \AA}$; Camera diameter 114.6 mm.

I (Est.)	d (Obs.) \ddagger	d (Calc.)	hkl	I (Est.)	d (Obs.) \ddagger	d (Calc.)	hkl
4	6.94	6.95	010	2	1.521	1.522	041
0.2	3.88*			1.5	1.439	{1.438	112
6	3.52	3.52	110			{1.435	022
3	3.47	3.48	020	1	1.425	1.426	141
0.2	3.34 \ddagger			1	1.391	1.390	050
0.2	3.23*			0.5	1.376	1.378	231
0.2	3.18	3.25	?(001)	0.5	1.353	1.354	122
7	2.86	2.87	011	0.5	1.337	1.338	310
3	2.65	2.65	120	1	1.324	1.324	240
1.5	2.49	2.50	101	0.5	1.301	1.302	032
3	2.35*	{2.34	021	2	1.271	{1.272	051
		{2.35	111			{1.269	320
3	2.32	2.32	030			{1.251	301
0.5	2.24*			0.5	1.249	{1.248	202
2	2.05 \ddagger	2.05	200	2	1.241	1.241	132
10	2.03	{2.03	121	2	{1.225	1.228	212
		{2.02	130		{1.214	1.214	151
1.5	1.866	1.866	031	2.5	1.177	1.175	{330
2.5	1.762	1.762	220				{222
0	1.738	1.738	040	0.2	1.158	n.d.	
0.2	1.701	1.698	131	0.2	1.150	n.d.	
2	1.665	1.665	211	2	1.115	n.d.	
0.2	1.597	1.599	140	0.5	1.100	n.d.	
1.5	1.576	1.575	002	1	1.081	n.d.	
1	1.532	{1.533	230				
		{1.536	012				

* Lines due entirely or in part to native tellurium.

\ddagger Lines due entirely or in part to rickardite.

\ddagger Corrected for film shrinkage.

In our powder photographs, there are a number of weak lines that cannot be indexed. These are probably due to impurities of rickardite and native tellurium. One line at 3.18, not accounted for by these contaminants, is near the calculated value of the (001) reflection of vulcanite. However, if the space group of vulcanite is $Pmnm$, indicated by Anderko and Schubert for synthetic $CuTe$, this reflection is prohibited. It is quite possibly due to some unidentified impurity, particularly since the difference between observed and calculated values is 0.03. Except for the line at 3.18, the indices for other lines are consistent with space group $Pmnm$; however, there are insufficient reflections of the type ($h0l$) to prove conclusively that vulcanite belongs to this space group.

So far as the optical and physical properties of $CuTe$ are given by Anderko and Schubert, they agree with those observed for vulcanite.

TEXTURAL FEATURES OF VULCANITE AND ITS RELATIONS TO RICKARDITE AND TELLURIUM

The outstanding textural features of the specimens studied are the variety and complexity of intergrowths of vulcanite and rickardite and the relationships of these two minerals to native tellurium. The simplest intergrowths are of the type shown in the central part of Fig. 3, in which thin blades of rickardite occur in two sets oriented at a high angle to one another and roughly at 45° to the length of the vulcanite host grain. Vulcanite grains showing the prominent cleavage may show two sets of inclusions, like the grain figured, and a third set parallel to the cleavage. These intergrowths are of the kind commonly produced by exsolution. Anderko and Schubert found identical intergrowths in synthetic $CuTe$ and concluded that with cooling, excess Cu in $CuTe$ was exsolved as rickardite. The similarity of intergrowths in the synthetic and natural materials is so remarkable that one would infer that vulcanite, as initially deposited, was likewise a solid solution.

In the natural material, however, a variety of intergrowths due to partial replacement of vulcanite by rickardite is present. In the rickardite-vulcanite crusts, vulcanite is most abundant in a zone bordering native tellurium. In this zone, only incipient replacement by rickardite is shown. Away from the native tellurium, the grains of vulcanite show progressive replacement by rickardite, and adjacent to the rock fragments there is a zone in which only remnants of vulcanite are present. Replacement is guided by the same sets of planes in vulcanite as those along which rickardite inclusions occur in Fig. 3. The relationships are shown in Fig. 4. In the central part of the figure irregular laths of vulcanite extend nearly across the full length of the photograph. At the bottom, where vulcanite borders a body of native tellurium, replacement of vulcanite by rickardite has not progressed far, but in the upper part of

the photograph replacement is nearly complete, and only remnants of the laths remain. In the incipient stage, however, oriented inclusions of rickardite in vulcanite are produced. Every gradation between intergrowths of the type of Fig. 3 and those of Fig. 4 is shown in polished sections. The replacement intergrowths are also illustrated in Fig. 1.

In view of the complexity of relationships, the origin of individual intergrowths is not always clear. We judge, however, that intergrowths such as those of Fig. 3 are due to exsolution of rickardite from vulcanite.

Textural relationships of native tellurium to the other minerals are likewise varied. Boundaries of tellurium with vulcanite and rickardite are in general complex and interpenetrating. Tellurium has formed by replacement of the other two minerals, along grain boundaries, along

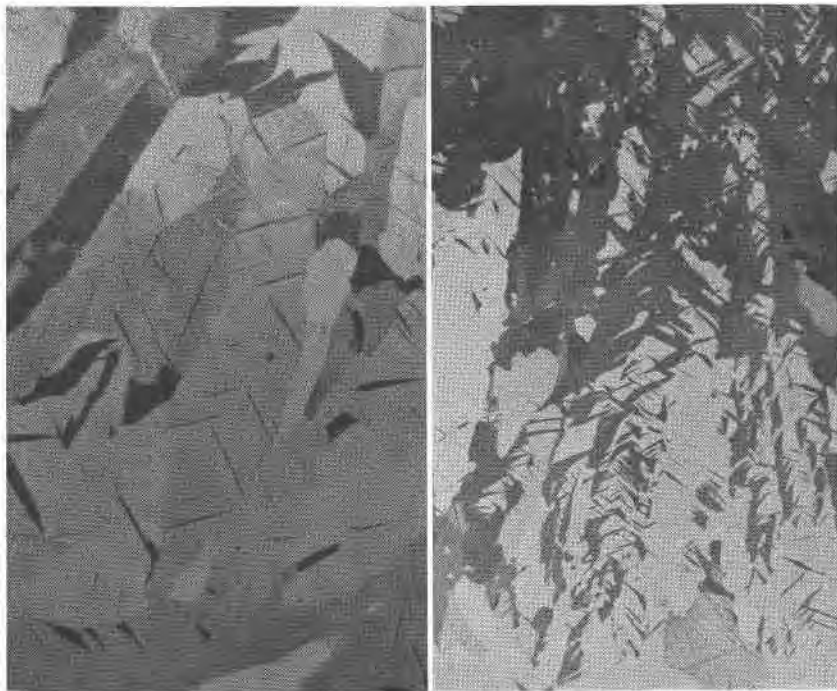


FIG. 3 (left). Vulcanite (pale to medium gray) and rickardite (dark gray), with a patch of native tellurium (white, bottom margin). The oriented intergrowth in the vulcanite grain in the central part of the field, and similar intergrowths elsewhere in the field, have the characteristics of exsolution intergrowths. The coarser intergrowths at the top and lower left are of the type produced by partial replacement of vulcanite by rickardite, as illustrated in Fig. 4. Plain light, $\times 190$.

FIG. 4 (right). Progressive replacement of irregular laths of vulcanite (pale gray to medium gray) by rickardite (darker shades of gray), guided by crystallographic directions of vulcanite. At the bottom, rickardite occurs as thin discs and incipient networks in vulcanite. At the top, only remnants of vulcanite in rickardite are present. Plain light, $\times 70$.

cleavages and other crystallographic planes, and locally along fractures. Despite the gross crustification shown by the ore specimens, the three minerals have clearly not formed by simple cavity filling.

The paragenetic sequence indicated is therefore vulcanite (earliest), rickardite, and tellurium (latest). This means a change, in successive phases deposited, from $\text{Cu}:\text{Te}=1:1$ to $\text{Cu}:\text{Te}$ ca 4:3, and then to $\text{Cu}:\text{Te}=0$. This is a puzzling sequence—a simple sequence tellurium-vulcanite-rickardite, involving a progressive increase in $\text{Cu}:\text{Te}$ ratio, or a sequence rickardite-vulcanite-tellurium, involving a decrease in $\text{Cu}:\text{Te}$ ratio, would be easier to understand. The experiments of Anderko and Schubert are of interest here. They found that in alloys with compositions in the neighborhood of 50 at. % Te, the phases present and their fabric depend on the conditions of cooling. A melt of 50 at. % Te at 800°C ., when quenched in water (their Fig. 3) gave a mixture of Cu_4Te_3 , CuTe with exsolution discs of Cu_4Te_3 , and a eutectic of CuTe and Te . This is a disequilibrium assemblage, for the stable phases at this composition (Fig. 2) should be Cu_4Te_3 and CuTe . The ore here described would appear likewise to be a disequilibrium assemblage, but in all probability was formed in an open system rather than a closed one.

As an alternative, it may be that in the ore body as a whole vulcanite was replaced by rickardite, in open system, and that the excess tellurium was taken into solution but later deposited at certain points in the ore body, partly by replacement of both the earlier minerals. Without knowledge of mineral relations throughout the ore bodies of the Good Hope Mine, including the three-dimensional mineral distribution and proportions therein, the interpretation is purely speculative. However, from the work of others on ores of the Good Hope Mine, it seems evident that the ores varied in mineral composition from place to place, and that vulcanite was not everywhere present. So distinctive a mineral could have scarcely have been overlooked.

In the synthetic system (Fig. 2), CuTe is deposited at a temperature between 340°C . and 365°C . The direct applicability of the phase diagram to natural systems, however, is open to the usual questions.

WATANABE'S WORK ON WEISSITE

So far as we can determine, CuTe has not previously been recognized as a mineral. However, in 1938 (5), and again in 1950 (6), Ramdohr referred to a work in Japanese by M. Watanabe, in which both natural and synthetic copper tellurides were apparently discussed. Ramdohr stated that according to Watanabe's findings, weissite corresponds to artificially prepared Cu_2Te , which can hold about 5% Te in excess and then agrees fully with analyzed natural weissite. Watanabe described weissite, however, as cream-white to dark blue, whereas Ramdohr and other

investigators (7, p. 113; 8, p. 357) describe weissite as light gray, similar to chalcocite, weakly bireflectant, and moderately anisotropic in pink, bluish gray, and blue. Weissite as thus described has been definitely established as a mineral species (8), but it is clearly not vulcanite. Yet from Watanabe's description of bireflectance as quoted by Ramdohr, it is conceivable that the substance described by Watanabe as weissite may actually have been that described here as vulcanite. Unfortunately, Watanabe's work is not available to us.

NOTES ON RICKARDITE

Rickardite in the specimens studied exhibits a complex pattern of polysynthetic twinning along two sets of planes that are probably at right angles to one another (Fig. 5). This type of twinning is strongly suggestive of inversion from a high-temperature form to a low-temperature form. In 1907, from a study of the system CuTe , Chikashige (3) recognized an inversion at or near 365° , and this temperature has been confirmed by Wassermann, Wallbaum, and Keymling (private communication to Anderko and Schubert) and by Anderko and Schubert (1). The latter authors (their Fig. 1) show twinning in synthetic Cu_4Te_3 that appears identical with that of our Fig. 5. Ramdohr (6) noted inversion



FIG. 5. Rickardite (medium to dark gray), showing complex twinning. In the large crystal in the upper half of the field a thin blade of vulcanite (white) is oriented at about 45° to the twinning, but other blades show variation in orientation. White to light gray grains are vulcanite. Crossed nicols, $\times 140$.

twinning in rickardite from the Good Hope Mine and suggested that the high temperature form might be cubic. Anderko and Schubert obtained a diffraction pattern from the high-temperature form, but the vagueness of the lines at high reflection angles prevented definite indexing. They state that a cubic indexing appeared excluded, but a relationship to the structure of CuS appeared to be shown.

The orthogonal pattern of twinning shown by rickardite in the material studied here suggests that the high-temperature form has either a cubic symmetry as suggested by Ramdohr, or a higher order of tetragonal symmetry, but further investigation of this matter is necessary.

Just as vulcanite contains inclusions of rickardite, rickardite in many places contains oriented inclusions of vulcanite that appear to be of the same origin and suggest that rickardite, as first deposited, contained excess Te. The inclusions are commonly oriented at about 45° to the complex twinning, more rarely parallel to it, but there is some variation in orientation.

UNKNOWN MINERAL

An unknown mineral occurs in the polished sections studied as patches of anhedral grains with the following properties:

Color: medium brownish-gray (liverwurst gray).

Reflectivity: 32% in white light, by photoelectric method.

Bireflectance: weak but perceptible, more grayish to more brownish as the stage is rotated.

Specific gravity: not determinable from material at hand.

Hardness: not greater than 2.

Cleavage and twinning: none observed.

Polishing characteristics: polishes smoothly. Polishing hardness < vulcanite and rickardite.

Anisotropism: distinct; polarization colors (nicols exactly crossed) medium gray, slate-gray, gray with brownish tint. With analyzer slightly uncrossed, a golden-brown color is seen.

Polarization figure: at 45° position isogyres are black, with an orange tint on concave sides.

Center of field is bluish gray.

Sign of phase difference in white light: (—), effect on gypsum plate is distinct.

Rotation angles and 2θ:

Wavelength	Observed A_r in degrees	Corrected A_r in degrees	2θ in degrees
470 mμ	2.2 ± .1	1.8 ± .1	-1.7 ± .1
520 mμ	1.5 ± .1	1.2 ± .1	-2.7 ± .1
546 mμ	1.3 ± .1	1.0 ± .1	-2.2 ± .1
589 mμ	0.8 ± .1	0.6 ± .1	-2.4 ± .1
620 mμ	0.4 ± .1	0.3 ± .1	+2.9 ± .1
650 mμ	0.0 ± .2	0.0 ± .2	+3.1 ± .1
589 mμ	0.9 ± .1	0.7 ± .2	-3.7 ± .1

(oil n 1.515)

The corrected values are the observed values corrected for the effect of the reflecting plate. Values for 2θ are corrected values. It will be noted that the mineral is essentially isotropic at 650 mμ and that the sign of 2θ passes through zero between 589 mμ and 620 mμ.

Qualitative microchemical tests indicate that the mineral contains Cu and Te, but material sufficient for quantitative chemical analysis or for spectrographic analysis with equipment available to us cannot be obtained from the specimens.

The X-ray powder pattern of the mineral cannot be identified with that of any known mineral species. Incomplete single crystal studies indicate that the mineral is hexagonal. Further studies are in progress and additional material is being sought with the aim of characterizing the mineral properly.

ACKNOWLEDGMENTS

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Note: On the eve of transmittal of the manuscript of this paper, the authors received a communication from Dr. Paul Ramdohr, saying that he has been studying a mineral, in an ore from a Japanese locality, which he concludes is also $CuTe$. This indicates a second occurrence of vulcanite. Like the authors, Dr. Ramdohr infers that the pleochroism reported by M. Watanabe for weissite was that of natural $CuTe$.