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ČERNÝITE, A COPPER-CADMIUM-TIN SULFIDE WITH THE STANNITE STRUCTURE

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ABSTRACT

Černýite occurs as a rare constituent of two complex, zoned pegmatites in the Tanco mine, Bernic Lake, Manitoba, and the Hugo mine, Keystone, Pennington County, South Dakota. The mineral is tetragonal with space group $I\bar{4}2m$, $Z=2$; *a* 5.5330 and *c* 10.8266Å (Tanco) and *a* 5.4871 and *c* 10.8454Å (Hugo). $D_{calc.}$ are 4.776 and 4.618 gm/cm^3 for the Tanco and Hugo mine specimens respectively. Černýite has a Mohs hardness of 4 and is steel grey with a metallic lustre. Microhardness (VHN$_{50}$) are 210 (Tanco) and 189 (Hugo). Under reflected light (oil immersion), the mineral is distinctly anisotropic in shades of grey and bireflectant from light grey with a yellowish tint to a very light grey. Electron microprobe analyses gave the formulae: $(Cu_{1.99}Ag_{0.01})_{\Sigma 2.00}(Cd_{0.77}Zn_{0.14}Fe_{0.10})_{\Sigma 1.01}Sn_{1.00}S_{3.99}$ (Tanco) and $Cu_{1.99}(Cd_{0.37}Zn_{0.33}Fe_{0.29}Mn_{0.01})_{\Sigma 1.01}Sn_{1.00}S_{4.00}$ (Hugo) corresponding to the general formula $(Cu,Ag)_2(Cd,Zn,Fe,Mn)SnS_4$ (where $Cu \gg Ag$ and $Cd > Zn > Fe \gg Mn$) and approaching the end member Cu_2CdSnS_4. The strongest reflections in the X-ray powder pattern are: 3.167(10)(112), 1.954(4)(220), 1.939(7)(024), 1.662(5)(132) and 1.639(4)(116) for the Tanco mine specimen.

SOMMAIRE

La černýite est un minéral accessoire rare dans deux pegmatites complexes zonées, exploitées dans les mines Tanco au lac Bernic, Manitoba, et Hugo, à Keystone, comté de Pennington, Dakota du sud. Les groupes spatiaux possibles pour ce minéral tétragonal sont $I4/mmm$, $I422$, $I\bar{4}2m$ et $I\bar{4}m2$, $Z=2$. Les paramètres cristallins sont: *a* 5.5330, *c* 10.8266A (Tanco) et *a* 5.4871, *c* 10.845A (Hugo); les densités calculées, 4.776 et 4.618, respectivement. La černýite a une dureté de 4 et une microdureté VHN$_{50}$ de 210 et 189 pour les échantillons de Tanco et Hugo, respectivement. Le minéral gris d'acier, à éclat métallique, est dichroïque dans les teintes du gris, en lumière réfléchie dans l'huile; il est aussi biréflectant, d'un gris pâle légèrement jaunâtre à un gris très pâle. Les analyses ponctuelles à la microsonde donnent $(Cu_{1.99}Ag_{0.01})_{\Sigma 2.00}(Cd_{0.77}Zn_{0.14}Fe_{0.10})_{\Sigma 1.01}Sn_{1.00}S_{3.99}$ (Tanco) et $Cu_{1.99}(Cd_{0.37}Zn_{0.33}Fe_{0.29}Mn_{0.01})_{\Sigma 1.01}Sn_{1.00}S_{4.00}$ (Hugo), d'où la formule générale $(Cu,Ag)_2(Cd,Zn,Fe,Mn)SnS_4$ (avec $Cu \gg Ag$, $Cd > Zn > Fe \gg Mn$) tendant vers le pôle Cu_2CdSnS_4. Les raies les plus fortes du cliché de poudre de l'échantillon de Tanco sont 3.167(10)(112), 1.954(4)(220), 1.939(7)(024), 1.662(5)(132) et 1.639(4)(116).

(Traduit par la Rédaction)

INTRODUCTION

The few mineralogical species having crystal structures similar to that of stannite, Cu_2FeSnS_4, can be represented by the general composition A_2BCS_4, where A = Cu or Ag, B = Fe or Zn and C = Sn, In or Ge. In contrast, Schäfer & Nitsche (1974) reported the synthesis of 40 compounds of the type Cu_2–II–IV–$S_4(Se_4)$ (II = Mn, Cd, Fe, Co, Ni, Zn or Hg; IV = Si, Ge, or Sn; tetrahedrally coordinated sulfur). The mineralogical representatives are restricted to stannite (Klaproth 1797), kesterite, Cu_2ZnSnS_4 (Orlova 1956), sakuraiite, $(Cu,Ag)_2(Zn,Fe)(In,Sn)S_4$ (Kato 1965), hocartite, Ag_2FeSnS_4 (Caye *et al.* 1968) and briartite, $Cu_2(Fe,Zn)GeS_4$ (Francotte *et al.* 1965). A new species analogous to synthetic Cu_2CdSnS_4 and possessing the structure of stannite has been discovered in two localities, the Tanco mine, Bernic Lake, Manitoba and the Hugo mine, Keystone, Pennington Co., South Dakota.

The new mineral species, cernýite, was discovered independently in the course of studies of the mineralogy of the Hugo pegmatite by the South Dakota School of Mines and Technology (SDSM&T) and of the Tanco pegmatite by the Canada Centre for Mineral and Energy Technology (CANMET). The Hugo Pegmatite occurrence was first noted by Dr. J. J. Norton of the U.S. Geological Survey in 1947; however,

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*Present address: Department of Geology, Lakehead University, Thunder Bay, Ontario P7B 5E1 samples were tentatively identified as stannite on the basis of X-ray powder diffraction measurements. Several kilograms of cernýite-bearing ore were recovered in 1973 by Mr. L. Judson, the mine owner, and given to Dr. J. A. Redden of the Department of Geology, SDSM&T. Dr. Redden supplied the samples to one of us (W.L.R.) for further study.

The mineral was found in the Tanco mine in 1969 in the course of extensive studies of the mineralogy of the pegmatite by Dr. P. Černý of the Department of Earth Sciences, University of Manitoba, who supplied material to Dr. D. C. Harris of the Mineral Science Laboratories, CANMET. Preliminary microprobe analyses by Dr. Harris indicated the presence of a cadmium-bearing sulfide mineral with a formula related to that of stannite. Investigation of the mineral was later undertaken by the first two authors.

Černýite (CHÄRNĪ•AIT) is named in honor of Dr. Petr Cerný, a prominent expert in the mineralogy of pegmatites, the characteristic host of the mineral .The mineral and name were approved by the Commission on New Minerals and Mineral Names, I.M.A. Type specimens from both the Tanco and Hugo mines are preserved in the collections of the Royal Ontario Museum (M34728, M34729 and M34730); National Reference Collection, Geological Survey of Canada (M5159 and M5160); Museum of Geology, South Dakota School of Mines and Technology (SDSM&T 5098 and 5099); National Museum of Natural History, Smithsonian Institution (136924); Crystallography Laboratory, Mineral Science Laboratories, CANMET and Department of Earth Sciences, University of Manitoba (M5159 and M5160).

Occurrence

Both occurrences of černýite consist of complex pegmatites in which sulfides are very minor or even rare constituents; however, local concentration of a number of rarer elements within the pegmatite, in particular Sn and Cd, seems to account for the presence of cernýite in such sulfide-poor environments.

The Hugo pegmatite, located 1.6 km south of Keystone, Pennington Co., South Dakota, has been described in detail by Norton *et al.* (1962). The pegmatite is economically important as one of the largest potash feldspar mines in the Black Hills; in addition, it has been a source of quartz, beryl, scrap and sheet mica, montebrasite, spodumene and columbite–tantalite. The pegmatite is an irregular body with a long dimension of about 215m and a maximum short dimension of 120m, occurring in quartz-mica schist and quartz-mica-staurolite schist country rock. Seven zones and two replacement bodies have been mapped in the pegmatite. In zone 4, quartz and albite (cleavelandite) are the dominant minerals; irregular masses of cernýite-kesterite intergrowths, ranging from microscopic size to 10×12cm, occur scattered at random in quartz throughout zone 4.

The cernyite – kesterite intergrowths are oriented in a manner that suggests crystallographic control during exsolution. The optical orientation of each mineral is constant throughout each mineral grain. The intergrowth is on such an intimate scale that the largest dimension of any černýite grain free of kesterite inclusions is on the order of 200μm.

The Tanco pegmatite is located at Bernic Lake in southeastern Manitoba in the Superior Province of the Canadian Shield. The regional geology has been summarized by Černý & Turnock (1971); the pegmatite has been interpreted as intruding amphibolites (meta-andesites) that were deformed in the Kenoran orogeny. The undeformed pegmatite may have been intruded during a final, dilational period of the orogeny. Both metamorphic and plutonic rocks of the region yield ages of 2600 m.y. The Tanco pegmatite, described in detail by Crouse & Černý (1972), is mined for its tantalum-bearing minerals. The pegmatite also contains potentially economic deposits of pollucite and refractory-grade spodumene.

The pegmatite is a tabular body from 18 to 85m thick striking east-west with a shallow dip to the north. The body has been found to extend 1200m along strike and 450m down dip, as proven by drilling; however, the total extent of the pegmatite is as yet unknown. Nine zones have been distinguished within the pegmatite body. Cernýite occurs in the central intermediate zone 6, one of the latest zones to form. This zone consists largely of microcline perthite, albite, and quartz with subordinate lithian muscovite. Numerous accessory minerals include beryl, wodginite, spodumene and cassiterite, along with many others listed by Crouse & Černý (1972). Sulfides occur as small nodules and fillings of miarolitic cavities and late fractures; they are among the last minerals to form in this zone. According to Harris & Cerný (1977), early-formed sulfide assemblages consist of pyrrhotite, sphalerite, hawleyite, chalcopyrite, bismuth, stannite, kesterite and černýite replaced or cemented by later gladite-pekoite, gustavite, tetrahedrite, cosalite, galena, bournonite, pyrargyrite, miargyrite and bismuthian antimony. Grains containing černýite never exceed 100μm in maximum dimension. They commonly contain černýite at the centre surrounded by stannite, rimmed locally by kesterite (Fig. 1).

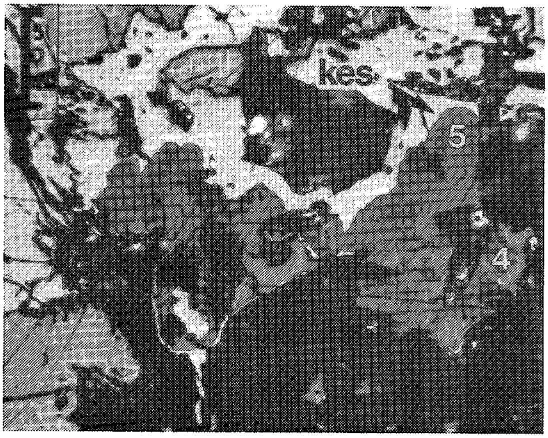

FIG. 1. A complex grain of černýite, stannite and kesterite (all grey) lying in quartz (black) and chalcopyrite (white) and surrounded by bismuthinite (white, high relief), from the Tanco mine. A rim of kesterite is faintly visible (lighter grey) surrounding a core of polycrystalline stannite and minor černýite. The minor rim of kesterite (kes) was analyzed semiquantitatively, and the areas of stannite labelled 4 and 5 correspond to the analyses with the same numbers in Table I. Černýite, consisting of small areas intergrown with stannite, was too small for analysis (oil immersion, crossed polarizers, 8° from extinction).

CHEMICAL DATA

Analyses in this study were performed on a Materials Analysis Company (MAC) Model 400 electron microprobe analyzer operated at 25kV and 0.03μA specimen current. Specimens were tested for homogeneity by shifting the electron beam and collecting 10 sec. counts from five to ten points on a grain. The data were reduced by means of the EMPADR VII program of Rucklidge & Gasparrini (1970). The standards and X-ray lines used in the analyses were as follows: Zn*Kα* from synthetic Cu_2ZnSnS_4; Fe*Kα*, Cu*Kα*, Sn*Lα* and S*Kα* from synthetic Cu_2FeSnS_4; Cd*Lα* from synthetic CdS and Mn*Kα*, Ag*Lα* and Sb*Lα* from the pure metals. The results of the analyses are given in Table 1. Structural formulae were calculated on the basis of eight atoms, based on similarity to the stannite formula. On the basis of these analyses and calculations, no significant non-stoichiometry seems to be present, implying order among the atomic sites.

Černýite from the Hugo mine coexists with kesterite in an intimate, lamellar intergrowth.

TABLE 1. ELECTRON MICROPROBE ANALYSES OF ČERNÝITE AND ASSOCIATED MINERALS

Wt %	1	2	3	4	5
Cu	28.1	29.0	26.5	28.9	29.1
Ag	---*	---*	0.20	n.d.	n.d.
Fe	3.6	2.3	1.1	6.5	10.2
Zn	4.9	10.9	2.0	5.5	1.6
Cd	9.3	1.7	18.2	4.9	2.0
Mn	0.06	0.03	n.d.**	---	---
Sn	26.3	27.1	24.9	26.5	26.0
Sb	---	---	n.d.	0.11	0.46
S	28.5	29.7	26.9	29.3	30.1
total	100.8	100.7	99.8	101.7	99.5

Structural formula (eight atoms)

1. Černýite from the Hugo Mine
   $Cu_{1.99}(Cd_{0.37}Zn_{0.33}Fe_{0.29}Mn_{0.01})_{\Sigma 1.01}Sn_{1.00}S_{4.00}$
2. Kesterite from the Hugo Mine
   $Cu_{1.99}(Zn_{0.73}Fe_{0.18}Cd_{0.07})_{\Sigma 0.98}Sn_{1.00}S_{4.04}$
3. Černýite from the Tanco Mine
   $(Cu_{1.99}Ag_{0.01})_{\Sigma 2.00}(Cd_{0.77}Zn_{0.14}Fe_{0.10})_{\Sigma 1.01}Sn_{1.01}S_{3.99}$
4. Stannite from the Tanco Mine
   $Cu_{1.98}(Fe_{0.51}Zn_{0.37}Cd_{0.19})_{\Sigma 1.07}Sn_{0.97}S_{3.98}$
5. Stannite from the Tanco Mine
   $Cu_{1.99}(Fe_{0.79}Zn_{0.11}Cd_{0.07})_{\Sigma 0.97}(Sn_{0.95}Sb_{0.02})_{\Sigma 0.97}S_{4.07}$

* Silver could not be analyzed due to secondary fluorescence from small inclusions of an unidentified silver-bearing phase. A dash otherwise denotes that the element was not sought.

** "n.d." denotes not detected at a detection limit of $\leq$ 0.02 wt %.

The composition of the černýite (analysis 1, Table 1) is quite far removed from the idealized end-member composition Cu_2CdSnS_4 in that only a slight majority of cadmium atoms populate the cadmium site. The coexisting kesterite (analysis 2) is reasonably close to end-member kesterite composition, with surprisingly low cadmium content.

In the Tanco mine, coexisting černýite–stannite assemblages are fairly common and in one case, a černýite–stannite–kesterite assemblage was found. Unfortunately, due to the small domain size, it was not possible to analyze compositions of coexisting černýite and stannite nor to determine the composition of kesterite. Column 3, Table 1 shows the analysis of a grain of černýite coexisting with unanalyzable stannite; X-ray diffraction data pertain to this grain. Columns 4 and 5 provide the analyses of two areas of stannite from a complex grain with cores of černýite too small for analysis and rims of stannite with a very narrow outer rim of kesterite pictured in Figure 1. The kesterite was found to contain approximately 11.5 wt% Zn and 2.6 wt% Fe, or 79.1 atomic % Zn and 20.9 atomic % Fe in the zinc site of ideal Cu_2ZnSnS_4. The stannites are fairly zinc-rich, although they have surprisingly low cadmium contents.

The foregoing data illustrate that, on a compositional basis alone, černýite is a species distinct from a cadmium-bearing stannite or kesterite, even though the Hugo-mine specimen is far removed from the end-member composition. In fact, appreciable substitution of zinc and iron for cadmium is possible in černýite, to the extent that cadmium atoms may be outnumbered by zinc and iron atoms in the cadmium site. The limits of solid solution remain to be determined experimentally. On the other hand, cadmium was found to enter the *B* sites of coexisting stannite to a maximum of approximately 19 at.% (7 at. % in coexisting kesterite).

CRYSTALLOGRAPHY

X-ray data for černýite from both localities (Table 2) may be compared with data for synthetic Cu_2CdSnS_4 (Schäfer & Nitsche 1974). The data reported here were obtained on a 114.6mm Gandolfi camera, the only practical means of collecting powder data in view of the small size of the grains available for study. Filtered Co*Kα* radiation (λ=1.7902Å) was employed, and *d* spacings were also calculated for resolved $CoK\alpha_1$ λ=1.78890Å) and $CoK\alpha_2$ (λ=1.79278Å) reflections. Relative intensities were estimated visually.

The data were indexed on tetragonal cells, the lattice parameters of which were obtained by means of the PARAM least-squares refinement program of Stewart *et al.* (1972). All reflections were consistent with a tetragonal cell except one at *d*=2.977Å in the Tanco mine specimen, attributed to the (222) reflection of a tetrahedrite impurity. The observed condition for a possible reflection was *hkl* with *h*+*k*+*l*= 2*n*.

The černýite grain from the Hugo mine proved to be a single crystal and was subsequently examined by precession camera at three levels along

TABLE 2. X-RAY DIFFRACTION POWDER DATA

	Synthetic Cu_2CdSnS_4 (Schäfer&Nitsche 1974) Guinier, CuKα $\underline{a}$=5.586,$\underline{c}$=10.834 Å			Černýite Tanco Mine, Manitoba 114.6mm Gandolfi,CoKα $\underline{a}$=5.5330(27)*,$\underline{c}$=10.8266(79)Å			Černýite Hugo Mine, South Dakota 114.6mm Gandolfi,CoKα $\underline{a}$=5.4871(15),$\underline{c}$=10.8454(55)Å			
hkℓ	$d_{obs.}$	$d_{calc.}$	I/I_{100}	$d_{obs.}$	$d_{calc.}$	I/I_{10}	$d_{obs.}$	$d_{calc.}$	I/I_{10}	
002	5.438	5.417	9	—	—	—	5.39	5.42	3	
011	4.969	4.965	1	—	—	—	4.88	4.90	2	
110	3.951	3.950	5	3.95	3.91	1	3.87	3.88	2	
112	3.192	3.191	100	3.167	3.171	10	3.151	3.155	10	
—	—	—	—	2.977	?	½	—	—	—	
020	2.791	2.793	7	2.770	2.767	3	2.734	2.744	3	
004	2.710	2.708	20	2.706	2.707	2	2.712	2.711	2	
022	2.481	2.482	5	2.470	2.464	2	2.433	2.448	½	
121	—	—	—	—	—	—	2.364	2.393	½	
114	2.234	2.234	6	2.221	2.226	1	2.225	2.223	3	
220	1.975	1.975	22	1.954	1.956	4	1.937	1.940	5B**	
024	1.945	1.944	61	1.939	1.935	7	1.927	1.929	5B	
222	1.855	1.855	2	—	—	—	—	—	—	
031	—	—	—	1.825	1.818	½	—	—	—	
006	1.806	1.806	9	—	—	—	—	—	—	
130	1.766	1.766	1	—	—	—	—	—	—	
132	1.679	1.679	28	1.662	1.665	5	1.649	1.653	4	
116	1.641	1.642	12	1.639	1.639	4	1.638	1.639	4	
224	1.595	1.596	3	—	—	—	1.576	1.578	2	
134	1.479	1.480	2	—	—	—	—	—	—	
040	1.397	1.396	2	1.384	1.383	1	1.371	1.372	2	
008	1.354	1.354	1	—	—	—	1.356	1.356	2	
226	1.333	1.333	1	—	—	—	—	—	—	
332	1.279	1.279	1	1.265	1.268	1	1.259	1.258	3	
136	1.263	1.263	1	1.257	1.256	3	1.248	1.252	3	
240		.		—	—	—	1.224	1.227	1	
028		.		—	—	—	1.213	1.215	1	
244		.		1.127	1.125	3	1.117	1.118	5	
228		.		1.114	1.113	2	1.110	1.111	3	
152		.		1.063	1.064	1	1.055	1.056	2	
336		.		1.055	1.057	½	1.052	1.052	2	
1.1.10		.		1.043	1.043	1	1.046	1.045	2	
440		.		—	—	—	0.9703	0.9700	1	
048		.		—	—	—	0.9649	0.9642	1	
352		.		—	—	—	0.9270	0.9272	1	α_1
							0.9267	0.9272	1	α_2
156		.		—	—	—	0.9238	0.9246	1	
1.3.10		.		—	—	—	0.9200	0.9197	1	

* Figures in parentheses represent the standard deviation, in terms of least units cited to their immediate left, as determined by least squares refinement.

** B = Broad

each axis. The condition for diffraction of $h+k+l = 2n$ was confirmed and the diffraction symbol *4/mmI-/—* was determined, corresponding to the possible space groups $I4/mmm$, $I422$, $I4mm$, $I\bar{4}2m$ and $I\bar{4}m2$. A structural refinement by Szymański (1978) has subsequently confirmed the space group $I\bar{4}2m$, *i.e.*, identical with that of stannite (Brockway 1932; Hall *et al.* 1978).

The lattice parameters of černýite, as determined by powder diffraction, provide further convincing proof of its uniqueness. Figures 2 and 3 are isometric projections of triangular prisms which illustrate the variation of lattice parameters and *c*/*a* ratio, respectively, as a function of the composition of the *B* position in compounds of formula A_2BCS_4. The compo-

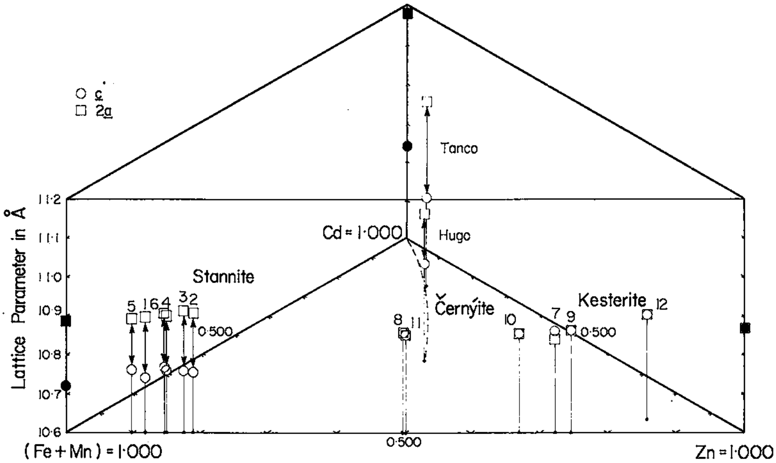

FIG. 2. The base of the figure, the compositional triangle Fe-Zn-Cd, illustrates the composition of the *B* position in the general formula A_2BCS_4; lattice parameters 2*a* and *c* are plotted in the vertical direction. The data of Kissin & Owens (in prep.) on stannite and kesterite are compared to 2*a* and *c* of the two černýite specimens and synthetic Cu_2CdSnS_4 (Schäfer & Nitsche 1974). The triangular prism is viewed orthographically in a direction perpendicular to the Zn-Fe join. The dashed line represents the projection of the černýite compositions onto the composition triangle. Solid symbols are synthetic minerals.

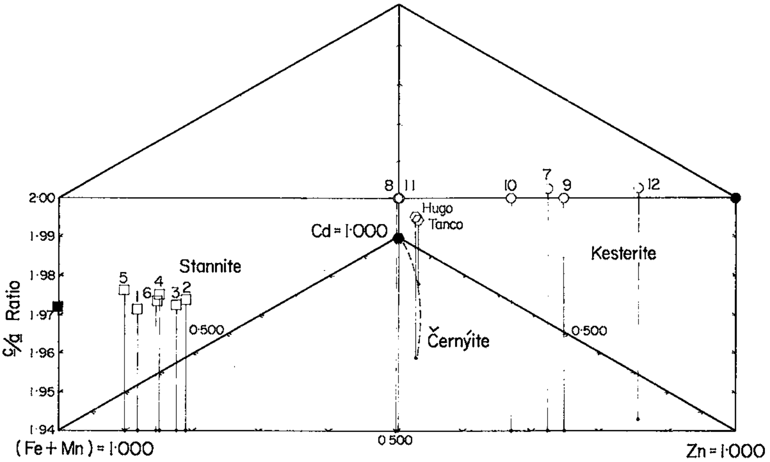

FIG. 3. The same composition plane as in Fig. 2 with *c*/*a* ratio for the same specimens plotted in the vertical direction.

sition triangle has apices of Cd, Zn and Fe+Mn, although Mn is always less than 1% for the data considered here. For comparison, data obtained from six natural and one synthetic stannite and six natural and one synthetic kesterite, as described in detail by Kissin & Owens (in prep.), are plotted with data for the two černýite specimens and synthetic Cu_2CdSnS_4.

In Figure 2, the *a* parameter has been doubled for convenience in plotting against *c*. Stannite shows a rather limited range of solid solution, to about 20% Zn+Cd in the *B* positions, and a very slight variation in lattice parameters. Significantly, 2*a* is greater than *c* in a constant ratio. On the other hand, kesterite is strongly pseudo-cubic so that 2*a* cannot be distinguished from *c* by powder X-ray methods. Point 7, obtained by means of single-crystal diffractometer measurements, shows that *c* is very slightly greater than 2*a*. The lattice parameters of kesterite decrease slightly with increasing substitution in the *B* position. Černýite shows some affinities with the stannite structure in that 2*a* is also greater than *c*, but there is considerable solid solution of Fe+Zn+Mn in the *B* position. The *c* parameter of černýite shows no variation with composition of the *B* position, but the 2*a* parameter decreases markedly. Within the limits set by sparse data, the černýite 2*a* parameter can be seen to vary linearly with solid solution of Fe+Zn+Mn, in spite of the fact that the Tanco mine specimen contains very little zinc and the Hugo mine specimen contains more zinc than iron. This observation can be reconciled by the great similarity in cell volumes of synthetic stannite and kesterite (317.92Å^3 and 320.91Å^3, respectively), apparently due to the very similar ionic radii of Fe^{2+} and Zn^{2+} (Kissin & Owens, in prep.).

The plot of *c*/*a* ratio *vs.* composition of the *B* position shown in Figure 3 clearly contrasts the three species. Stannite and kesterite have constant ratios of 1.97 and 2.00, respectively, whereas the axial ratio of černýite varies markedly from 1.94 for the end-member Cu_2CdSnS_4 to about 1.975 for the Hugo mine specimen.

PHYSICAL PROPERTIES

The appearance of černýite in hand specimen was discernible only in the Hugo mine specimen, where it is intimately intergrown with kesterite. The physical properties given here apply equally to kesterite; however, the two minerals could not be distinguished in hand specimen. The color of černýite is steel grey with a metallic lustre. Weathered surfaces are greenish grey to iron-black. The mineral has a black streak and a Mohs hardness of about 4. No crystal forms or cleavages were discernible.

Due to the small size of the Tanco mine specimens and the difficulty in obtaining a pure sample from the Hugo mine specimen, the density of černýite could not be measured. The calculated density for synthetic Cu_2CdSnS_4 based on lattice parameters of Schäfer & Nitsche (1974) is 4.779 gm/cm^3, whereas calculated densities for the Tanco and Hugo mine specimens are 4.776 and 4.618 gm/cm^3, respectively. Micro-indentation hardness was determined on a Leitz Durimet hardness tester using 50g for 15 sec. Results for černýite from the Tanco and Hugo mines and for accompanying kesterite from the Hugo mine are presented in Table 3.

TABLE 3. REFLECTANCE AND MICROINDENTATION HARDNESS OF ČERNÝITE AND KESTERITE

	Černýite Tanco mine	Černýite Hugo mine	Kesterite Hugo mine
Reflectance: wavelength			
470 nm	24.6	25.5	25.4
546	23.4	25.6	24.6
589	22.3	25.0	24.0
650	22.7	24.3	24.0
Microidentation hardness			
VHN_{50}	189	210	334

OPTICAL PROPERTIES

Under reflected light in air, černýite is medium grey and cannot be readily distinguished from kesterite. Bireflectance is imperceptible, and anisotropy is very weak, in shades of grey. Under oil immersion, černýite is distinctly bireflectant from creamy grey with a yellowish tint to very light grey and anisotropic in shades of grey. In contrast, kesterite under oil is weakly bireflectant from light grey to pale whitish grey and more weakly anisotropic. As an overall effect, černýite appears brighter and slightly darker than kesterite. Černýite is readily distinguished from stannite, which typically has brown to greenish bireflectance and much stronger anisotropy.

Coexisting černýite and kesterite can be distinguished by etching with 1:1 HNO_3. Kesterite is more readily stained by the etchant (Fig. 4).

The reflectance of černýite was measured in air using a Leitz MPE microscope photometer with a silicon reference standard (*N* 2538.42, issued by the IMA Commission on Ore Microscopy). The data for the two černýite specimens and the accompanying kesterite are presented

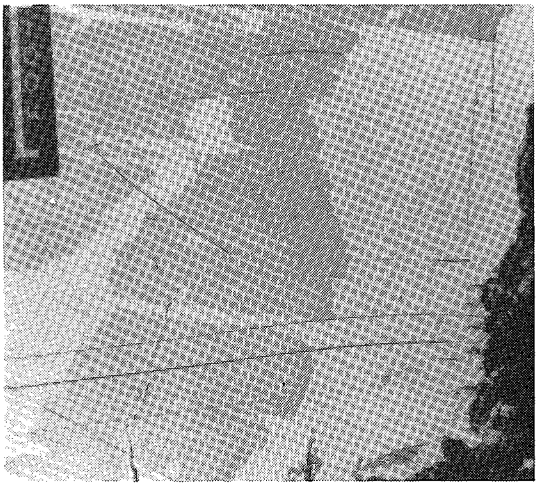

FIG. 4. A lamellar intergrowth of černýite (light) and kesterite (dark) with contrast enhanced by etching with 1:1 HNO_3. The minute white specks in the large grain of černýite are an unidentified silver-bearing mineral (oil immersion).

in Table 3. Bireflectance was not measurable in černýite.

STABILITY RELATIONS

Cu_2CdSnS_4, synthetic end-member černýite, was produced under unspecified conditions by Moh & Ottemann (1962). The compound was also synthesized from binary starting materials by Hahn & Schulze (1965) by annealing at 650-900°C. Nitsche *et al.* (1967) employed iodine vapor transport of the elements in an evacuated silica tube across a thermal gradient of 1100°C to 800-750°C to produce single crystals of Cu_2CdSnS_4. Moh (1976) reported the synthesis of Cu_2CdSnS_4 by H. Mayer under unspecified conditions. The compound was found to melt incongruently at 914±5° to (Zn,Cd)S and a melt of composition Cu_2SnS_3 with no intervening high-temperature inversions. Mayer's D.T.A. studies of the pseudobinary system Cu_2ZnSnS_4 (kesterite) –Cu_2CdSnS_4 (černýite) revealed the existence of complete solid solution between the two end-members from their incongruent melting points down to 492±3°C, where a miscibility gap appeared at about 80 wt. % Cu_2CdSnS_4 and 20 wt % Cu_2ZnSnS_4.

Based on evidence given earlier, černýite seems to possess a considerable range of solid solution with kesterite and stannite. The extent of solid solution may be such that less than 50% of the *B* site is occupied by Cd atoms; Zn seems to predominate over Fe in the remainder. The oriented, lamellar intergrowths within the Hugo mine specimen, however, suggest that černýite and kesterite have formed by unmixing of a high-temperature, homogeneous phase, in agreement with the results reported by Moh (1976). Immiscibility between černýite and kesterite is to be expected in the light of the recent structural work of Hall *et al.* (1978) and Szymański (1978); the two minerals possess the space groups $I\bar{4}2m$ and $I\bar{4}$, respectively.

Relationships between černýite and stannite observed in the Tanco mine specimens are less clear. Although optical and compositional boundaries between the two minerals are quite sharp in aggregates with černýite cores and stannite rims, the structural work cited above has shown them to be isostructural. Complete solid solution between the two is thus to be expected. The apparent lack of convergence of lattice parameters in the composition triangle, however, raises doubts about miscibility between černýite and stannite, although the data are admittedly scanty.

Harris & Černý (1977) have recently presented data showing the mineralogical diversity and textural evidence of rapid, late-stage quenching and incomplete replacement reactions in the sulfide-rich assemblages of the Tanco mine. In particular, early-formed cassiterite appears to have reacted with somewhat later chalcopyrite, sphalerite and hawleyite to form final-stage stannite, kesterite and černýite. The assemblages found in the Tanco mine may thus be disequilibrium products of arrested reactions.

DISCUSSION

Ramdohr (1960) described a poorly characterized but optically distinctive species which he called "brown stannite". Ramdohr believed "brown stannite" to be a tin-rich member of the fahlore group, but investigations by Moh & Ottemann (1962) subdivided "brown stannites" into several quite different species. One of these, characteristic of high-temperature, pegmatitic occurrences, has a stannite-like composition and crystal structure, but contains cadmium instead of iron. Moh & Ottemann did not provide quantitative data, but an X-ray fluorescence chart for a specimen from a pegmatite at Cáceres, Spain, in their Figure 1A, indicates a composition similar to that of the Hugo mine specimen in this study (by comparison of intensities of the $K\alpha$ lines of Cd, Zn and Fe). The optical properties reported by Moh & Ottemann for this type of "brown stannite" agree closely with those of cernýite. Thus, some "brown stannites" are probably identical to cernýite.

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