

## Stannite and kesterite from the Peerless pegmatite, Black Hills, South Dakota, USA

Stannin a kesterit z pegmatitu Peerless, Black Hills v Jižní Dakotě, USA (Czech summary)



(4 text-figs)

PETR ČERNÝ<sup>1</sup> – MORGAN MASAU<sup>1</sup> – T. SCOTT ERCIT<sup>2</sup> – RON CHAPMAN<sup>1</sup> – LEONARD E. CHACKOWSKY<sup>1\*</sup>

<sup>1</sup> Department of Geological Sciences, University of Manitoba, Winnipeg, MB, Canada R3T 2N2

<sup>2</sup> Mineral Sciences Section, Canadian Museum of Nature, Ottawa, ON, K1P 6P4

\* Present address: Manitoba Energy and Mines, Geological Services Branch, Winnipeg, MB

Stannite and kesterite occur as thumb-size nodules along the margins of the quartz core of the Peerless granitic pegmatite near Keystone in the Black Hills of South Dakota. Kesterite is associated with minor tetrahedrite and tennantite; rare chalcopyrite accompanies both stannite and kesterite. In individual nodules, stannite and kesterite are relatively homogeneous in chemical composition, but compositions are highly variable among different nodules. The main variables are Fe and Zn, whereas Cd is present in mere traces. Four samples examined in detail have average compositions of  $\text{Stn}_{75}\text{Kst}_{25}$ ,  $\text{Stn}_{72}\text{Kst}_{28}$  (zincian stannite) and  $\text{Stn}_{46}\text{Kst}_{54}$ ,  $\text{Stn}_{44}\text{Kst}_{56}$  (ferroan kesterite). Deviations from ideal stoichiometry are largely less than 1 % relative, and well within the limits of analytical error. The Cu:(Fe, Zn, Cd):Sn ratio is rather uniform and very close to 2:1:1, but it slightly favours (Fe,Zn,Cd) as in previously published analyses. The difference in unit-cell dimensions  $2a-c$  decreases with increasing  $(\text{Zn}+\text{Cd})/[(\text{Zn}+\text{Cd})+(\text{Fe}+\text{Mn})]$ , in accord with the data for quenched synthetic phases and some natural minerals. However,  $2a$  of kesterite is not equal to its  $c$ . Contents of the cadmian černýite component in the stannite-group minerals from granitic pegmatites are suspected to be only roughly correlated with other fractionation indicators in oxide and silicate minerals.

**Key words:** stannite, kesterite, černýite, granitic pegmatite, Black Hills, USA

### Introduction

Minerals of the stannite group are locally encountered in tin-bearing granitic pegmatites, although in very minor amounts as these rocks are notoriously poor in sulphides and sulphosalts of any kind. Considerable ranges in chemical composition of stannite  $\text{Cu}_2\text{FeSnS}_4$ , kesterite  $\text{Cu}_2\text{ZnSnO}_4$  and černýite  $\text{Cu}_2\text{CdSnO}_4$  were recognized in the past, as the Fe/Zn ratio and the content of Cd are highly variable among the different pegmatite localities. Here, we report on the occurrence, chemical composition and crystallographic data of minerals of the stannite – kesterite series from a new locality in the Black Hills of South Dakota, with a note on the geochemical relationships between the stannite-group minerals and other compositional variables in pegmatite minerals.

### The parent pegmatite

The Peerless pegmatite near Keystone, Pennington County, South Dakota is one of the more fractionated and internally complex pegmatites in the northern margin of the pegmatite field of the southern Black Hills. According to Sheridan et al. (1957), the pegmatite has an anticlinal shape, with a subhorizontal NW-trending crest flanked by SW- and NE-dipping limbs. The outcrop is about 185 by 110 m in size. Three major keels and several minor rolls complicate the apparently fracture-controlled underside of the pegmatite. In contrast, the crest is relatively simple, consisting essentially of two subparallel bulges.

Internally, the pegmatite consists of seven zones, two replacement units and two types of fracture-filling units (Sheridan et al. 1957). The pegmatite consists dominantly of microcline-perthite, microcline, plagioclase, amblygonite-montebrazite and muscovite, and it carries a diversified assemblage of accessory and secondary phases: columbite-tantalite, wodginite, microlite, ferrotapiolite, cassiterite, beryl, tourmaline, apatite, triphylite, garnet, biotite, zircon, spodumene, uraninite, chrysoberyl, tantalum rutile, triploidite (?), loellingite (?), pyrite, marcasite, stannite, kesterite, opal, pyrolusite, goethite, carbonate-apatite, vivianite, ferrisicklerite, heterosite, libethenite, pseudomalachite, goyazite, autunite, torbernite, siderite, malachite and azurite (Černý et al. 1985).

The pegmatite is a typical representative of the amblygonite subtype of complex rare-element granitic pegmatites, with all Li bound in primary phosphates (particularly in huge quantities of amblygonite-montebrazite) to the virtual exclusion of anhydrous Li-aluminosilicates (see London – Burt 1982 for the phase relationships, and Černý 1991 for classification criteria). The pegmatite is Na, P, F-rich, with Li, Be and subordinate Nb, Ta and Sn mineralization, and a modest enrichment in Rb and Cs. The K/Rb and K/Cs ratios are as low as 25.5 and 740, respectively, in K-feldspar of intermediate zones, 18 and 420 in muscovite of intermediate zones, and 13.2 and 385 in late slightly Li enriched muscovite of the central parts of the pegmatite.

The stannite-kesterite minerals occur as thumb- to fist-size nodules in margins of the quartz core of the parent

pegmatite. Four samples of these phases were examined in this study, numbered PPK-1 to PPK-4. Each sample proved to consist of a single member of the stannite-kesterite series with somewhat variable but rather constrained composition.

## Experimental

Stannite and kesterite were initially analyzed on the Jeol 700 electron microprobe in the Mineral Sciences Division, Canada Museum of Nature in the wavelength dispersion mode, under the following conditions: voltage 15 kV, specimen current 25 nA, beam diameter 5  $\mu\text{m}$ , counting time 25 s (except 100 s for Cd) or 0.5 % precision, whichever was attained first. Standards were stibnite ( $\text{SbL}\alpha$ ,  $\text{SK}\alpha$ ), cassiterite ( $\text{SnL}\alpha$ ), arsenopyrite ( $\text{FeK}\alpha$ ), tephroite ( $\text{MnK}\alpha$ ), Cd-apatite ( $\text{CdL}\alpha$ ), sphalerite ( $\text{ZnL}\alpha$ ), and cuprite ( $\text{CuK}\alpha$ ). A second set of analyses was collected on the Cameca SX-50 instrument at the Department of Geological Sciences, University of Manitoba: voltage 15 kV, specimen current 20 nA, beam diameter 5  $\mu\text{m}$ , counting time 20 s for Cu, Fe, Zn, S and 50 s for Cd, Mn and Sb. Standards were  $\text{CuFeS}_2$  ( $\text{SK}\alpha$ ,  $\text{FeK}\alpha$ ,  $\text{CuK}\alpha$ ), spessartine ( $\text{MnK}\alpha$ ),  $\text{ZnS}$  ( $\text{ZnK}\alpha$ ), Cd ( $\text{CdL}\alpha$ ),  $\text{Sb}_2\text{Te}_3$  ( $\text{SbL}\alpha$ ) and  $\text{SnO}_2$  ( $\text{SnL}\alpha$ ). The data were reduced using the PAP routine of Pouchou – Pichoir (1984, 1985).

X-ray powder diffractograms were recorded on a Philips 1710 instrument, using Ni-filtered  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) and LiF as an internal standard ( $a = 4.0280[1] \text{ \AA}$ , calibrated against NBS Si batch 640a), scanning speed of  $1^\circ 2\theta$  per minute, and chart recording of  $1^\circ 2\theta$  per 1 cm. A second set of data was obtained for two specimens on the Siemens-Nicolet D 5000 instrument in transmission mode, using the same radiation and standard calibration as above, but  $\text{BaF}_2$  as an internal standard ( $a = 6.19901[5] \text{ \AA}$ ). Smear mounts were prepared by pulverization of several chips separated from different parts of each sample. In view of the slight to significant heterogeneity of stannite and kesterite, respectively, in each sample, the refined unit-cell dimensions should reasonably correspond to the average composition of each sample.

Unit-cell dimensions were refined using a modified version of the least-squares CELREF program of Appleman – Evans (1973). In view of the strongly pseudocubic nature of the tetragonal minerals examined, with  $2a$  almost equal to  $c$  in kesterite, only solitary diffractions with unique  $hkl$  indices were employed in the refinement. This reduced the number of diffractions applicable in individual cases to between 6 and 11, with consequent slight increase in standard error. However, we are satisfied that the potentially inferior accuracy of the results cannot substantially affect or reverse the values of  $2a-c$ . Repeated runs performed on two fundamentally different instruments yielded mutually consistent results, at testing to high precision.

## Stannite – kesterite

### Chemical composition

The compositions of the Peerless minerals correspond to formulas which conform to the stoichiometry of stannite and kesterite within the limits of analytical error. Contents of subordinate and trace elements are low, restricted to minor amounts of Sb, Mn and Cd. However, the values of  $(\text{Zn}+\text{Cd})/[(\text{Zn}+\text{Cd})+(\text{Fe}+\text{Mn})]$  are considerably variable among the four fragments investigated, although more stable within each of them. Samples PPK 1 and PPK 4 correspond to stannite, averaging at  $\text{Stn}_{75}\text{Kst}_{25}$  and  $\text{Stn}_{72}\text{Kst}_{28}$ , whereas PPK 2 and PPK 3 have the  $\text{Zn}>\text{Fe}$  composition of kesterite, with averages of  $\text{Stn}_{46}\text{Kst}_{54}$  and  $\text{Stn}_{44}\text{Kst}_{56}$ . The two stannite samples are much more homogeneous, the kesterite samples show a broader variability (Table 1). In general, the compositions of the Peerless minerals indicated by 31 spot analyses cover a range of at least  $\text{Stn}_{75}\text{Kst}_{25}$  to  $\text{Stn}_{28}\text{Kst}_{72}$ .

### Unit-cell dimensions

In accord with the variable chemical composition, the unit-cell dimensions of the four examined fragments also show considerable spread of values (Table 1). In contrast, the difference in the  $a/c$  ratio is mainly expressed between stannite on one hand and kesterite on the other. Owing to the patchy variable composition of each individual fragment, the unit-cell dimensions must be considered averages for the compositional ranges established

Table 1 Chemical composition and unit-cell dimensions of the Peerless stannite-kesterite minerals. \* data refined from P1720 diffractograms; \*\* data refined from D5000 diffractograms.

	PPK-1		PPK-2		PPK-3		PPK-4	
	ave.	2 $\sigma$ (6)	ave.	2 $\sigma$ (6)	ave.	2 $\sigma$ (10)	ave.	2 $\sigma$ (7)
Cu	29.46	0.11	29.48	0.22	29.19	0.15	29.32	0.14
Fe	9.17	0.25	5.80	1.08	5.91	1.08	9.49	0.09
Zn	4.33	0.11	8.74	1.38	8.38	1.40	3.86	0.04
Cd	0.47	0.04	0.40	0.11	0.37	0.11	0.40	0.04
Mn	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01
Sn	27.18	0.25	26.86	0.11	26.98	0.15	27.32	0.24
S	29.03	0.14	29.30	0.14	29.21	0.15	29.32	0.14
Total	99.64	0.27	100.59	0.25	100.05	0.28	99.72	0.39
atomic contents normalized to 8 atoms								
Cu	2.024	0.003	2.012	0.014	2.003	0.010	2.007	0.006
Fe	0.717	0.018	0.450	0.083	0.461	0.084	0.740	0.006
Zn	0.289	0.007	0.580	0.092	0.559	0.094	0.257	0.002
Cd	0.018	0.002	0.015	0.004	0.014	0.004	0.015	0.001
Mn	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Sn	0.999	0.011	0.981	0.005	0.991	0.005	1.001	0.009
S	3.953	0.007	3.961	0.014	3.971	0.012	3.979	0.010
unit-cell dimension								
a*	5.444(1)		5.431(1)		5.434(3)		5.450(2)	
c	10.782(3)		10.843(9)		10.828(8)		10.768(6)	
V	319.55		319.82		319.73		319.84	
c/a	1.981		1.997		1.993		1.976	
a**	–		–		5.437(2)		5.450(1)	
c	–		–		10.827(9)		10.773(8)	
V	–		–		320.06		319.99	
c/a	–		–		1.991		1.977	

by electron-microprobe analysis, which are representative of the full extent of variability in each of the four fragments.

As mentioned in "Experimental methods", two X-ray diffraction instruments in two configurations with two different internal standards were used for one stannite and one kesterite sample. The results shown in Table 1 are in part literally, and in all cases statistically identical.

### Associated minerals

Stannite and kesterite are largely free of inclusions or intergrown primary phases, but some additional minerals were identified in intimate association. Also, most of the sulphides are very fresh, but all samples are sporadically crisscrossed by brownish fracture coatings, and two fragments (PPK-3 and PPK-4) are penetrated by very fine veinlets of a soft green material.

In reflected-light microscope and in back-scattered electron images, the stannite-kesterite minerals are homogeneous and largely free of inclusions. However, sample PPK-2 contains a few irregular grains of tetrahedrite, and tennantite is present in PPK-4 (Table 2) with rare chalcopyrite and probable covellite. Chalcopyrite and an Ag-bearing Pb, Bi-sulfide were found in PPK-1.

As to the alteration products, the above-mentioned green veinlets possibly belong to an unknown phosphosilicate of Cu, Fe and Sn. The highly variable composition suggests, however, an extremely intimate mixture of two or more phases (Table 3); finely layered ( $\leq 3 \mu\text{m}$ ) tex-

ture of this material revealed by BSE images also suggests a heterogeneous aggregate. Cassiterite and an unidentified mineral of Cu, possibly a carbonate, decorate the interior of the phosphosilicate veinlets (Fig. 1). Another probable intergrowth of alteration products yields prominently Sb-rich but Sn- "free" compositions (Table 3). In contrast, a plumbogummite-like phase shows good stoichiometry but excessive remainder to 100 wt. %; poor polish suggests microporous aggregation which could affect the analytical results. Besides cassiterite, the only secondary phase that was reliably identified is scorodite.



Fig. 1 Alteration products of the Peerless stannite (sample PPK-1). Grey veinlets – unknown Cu, Fe, Zn-phosphosilicate (or a multiphase mixture); black – carbonate of Cu; white in black – cassiterite.

Table 2 Chemical composition of tetrahedrite (average of 5) and tennantite (average of 2) enclosed in the Peerless kesterite.

	Tetrahedrite PPK-2	Tennantite PPK-3
Cu	38.19	42.85
Fe	2.85	5.32
Zn	4.47	2.84
Cd	0.17	0.03
Mn	0.02	0.01
Ag	0.52	0.00
Sb	26.03	1.55
As	1.67	18.63
Bi	0.91	0.20
Sn	0.15	0.00
S	24.99	28.08
Total	99.97	99.52
atomic contents normalized to 13 sulfur atoms		
Cu	10.028	10.013
Fe	0.853	1.415
Zn	1.141	0.645
Cd	0.025	0.004
Mn	0.005	0.004
Ag	0.081	0.000
$\Sigma$	12.132	12.081
Sb	3.566	0.190
As	0.372	3.691
Bi	0.072	0.014
Sn	0.022	0.000
$\Sigma$	4.032	3.895
S	13.000	13.000

## Discussion

### Crystal chemistry

Stannite  $I-42m$  and kesterite  $I-4$  were well-defined in terms of structure (Hall et al. 1978, Kissin et al. 1978, Kissin – Owens 1979, 1989), but the relationship between structure and chemical composition is not unambiguous. Bernardini et al. (1990) place the boundary between the two phases at 60 to 70 mole % of the Zn component, whereas Kissin (1989) finds evidence for 40 mole % at 500 °C and probably even less at lower temperatures. Thus we term the samples at hand strictly on the basis of chemical composition, as the correlation with cation distribution and space group requires refinements of the structures (see below).

Table 3 Chemical composition of alteration products of the Peerless stannite, kesterite and associated minerals.

	"Sn, Fe, Cu-phosphosilicate" after stannite						"Cu, Fe-antimonate"			probable plumbogummite
	1	2	3	4	5	6	A	B	C	
SO <sub>3</sub>	0.48	0.36	0.64	0.57	0.20	0.27	0.36	5.82	0.03	0.91
P <sub>2</sub> O <sub>5</sub>	1.29	2.97	1.88	0.48	1.95	2.16	2.44	2.12	1.88	20.21
SiO <sub>2</sub>	5.21	4.30	4.99	2.11	6.15	7.29	0.86	0.60	0.76	0.04
Al <sub>2</sub> O <sub>3</sub>	0.03	0.05	0.16	0.03	–	–	0.04	0.06	0.04	22.67
SnO <sub>2</sub>	48.66	45.09	53.65	62.42	55.05	50.42	0.11	0.18	0.19	0.63
As <sub>2</sub> O	0.11	0.23	1.50	0.12	–	–	3.38	4.88	6.15	0.11
Sb <sub>2</sub> O	0.03	0.05	0.07	0.34	–	–	12.53	4.78	35.10	0.09
Bi <sub>2</sub> O <sub>3</sub>	0.05	0.00	0.01	0.00	–	–	3.66	0.63	17.12	0.00
FeO	17.91	16.25	19.36	20.77	17.22	18.70	7.79	14.42	14.36	1.48
MnO	0.03	0.01	0.04	0.00	–	–	0.00	0.00	0.01	0.02
PbO	0.00	0.00	0.00	0.00	–	–	0.05	0.00	0.00	28.70
CuO	13.64	16.66	7.92	5.72	9.36	13.74	58.51	60.46	12.36	1.04
ZnO	1.99	2.01	0.38	0.29	0.97	0.56	0.47	0.26	0.38	0.83
CdO	0.05	0.00	0.03	0.00	–	–	0.64	0.04	1.61	0.00
Ag <sub>2</sub> O	0.00	0.00	0.00	0.00	–	–	0.20	0.00	0.01	0.00
Total	89.49	87.98	90.64	92.85	90.90	93.14	91.04	94.25	90.03	76.75

The slight deviations of the atomic contents from the ideal integral formula are insignificant, as most of them amount to less than 1 % relative (Table 1). All of them are well within the limits of experimental error.

The Cu:(Fe,Zn,Cd):Sn ratio is of interest, as it was claimed in the literature to apparently deviate from the ideal 2:1:1 stoichiometry. Figure 2A shows plots of previously published data, with identification of sources for those which distinctly deviate from the main cluster centered only slightly off the theoretical value. Our data (Fig. 2B) show a much lesser spread; the significance of the very slight drift of a considerable proportion of the data to higher-than-ideal (Fe,Zn,Cd), analogous to that shown in Fig. 2A, cannot be evaluated at present.

Figure 3A shows the average compositions and unit-cell dimensions of the samples examined in good accord with the trends established for synthetic phases (Bernardini et al. 1990) and natural minerals (Corazza et al.

1986, Kissin 1989, Kissin – Owens 1989). The  $2c$ – $a$  versus  $(Zn+Cd)/[(Zn+Cd)+(Fe+Mn)]$  diagram in Figure 3B also shows good agreement of our data with the trend of synthetic and natural phases. The only noticeable difference rests in the fact that Kissin (e. g., 1989) treated all kesterite samples as totally pseudocubic with  $2a=c$ . He suggested several reasons why the data of Corazza et al. (1986) and Bernardini et al. (1990), which indicate  $2a \neq c$ , could be distorted. None of Kissin's argu-

ments (such as mixtures of two phases, lack of splitting of structurally related diffractions) apply to our data. Unfortunately, Cu radiation was the only one available in our laboratory at the time of this study, which limited the resolution of closely spaced doublets. However, we are confident that  $2a \neq c$  shown by our data is meaningful, as explained in the experimental section.

We must emphasize that the problem of overlaps versus splits of X-ray powder diffractions from structurally analogous interplanar spacings is not a question of these two easily identifiable extremes alone, but an affair complicated by transition through broadening and partial overlaps which are difficult to assess on X-ray powder records in general, and on Debye-Scherrer and Guinier films in particular. The controversy of  $2a=c$  versus  $2a \neq c$  (and of  $2a >$  or  $< c$ ) can be approached only by the exclusive use of uniquely indexed diffractions in cell refinement, despite of the low numbers of useful data and consequently larger standard errors.

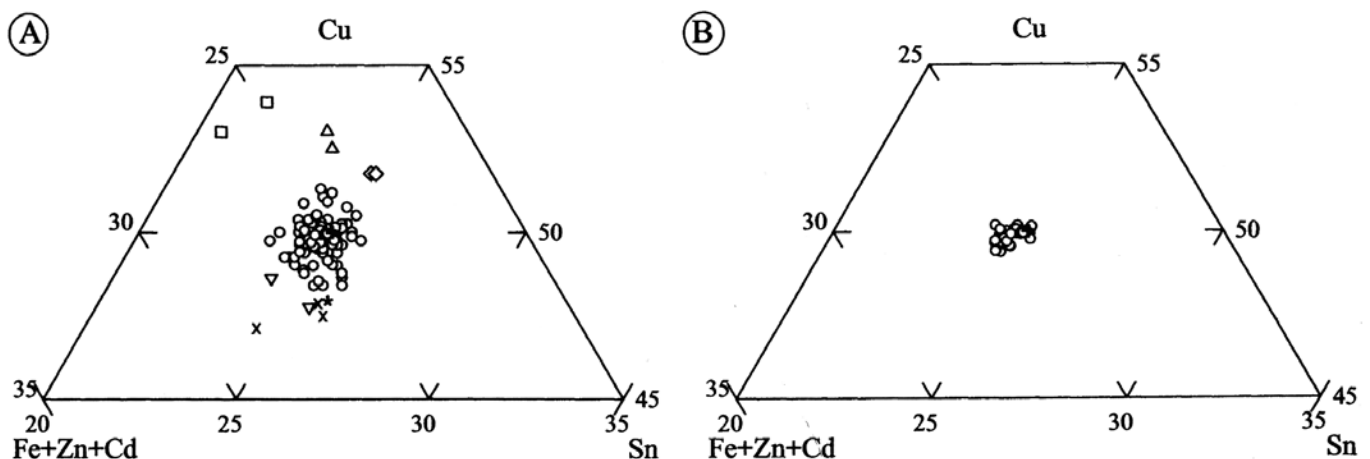


Fig. 2 A: The cation proportions (Fe+Zn+Cd) – Cu – Sn in stannite and kesterite from the literature and from the present work. Compositions most deviating from the ideal 1:2:1 ratio (+) are some of those reported by Oen (1970; squares), Springer (1968; triangles), Springer (1972; diamonds), Černý – Harris (1978; inverted triangles), Corazza et al. (1986; x's), and Čech – Hak (1982; \*). B: Same as A for the Peerless stannite and kesterite alone, showing a systematic trend toward enrichment in (Fe+Zn+Cd), but well within the analytical error.

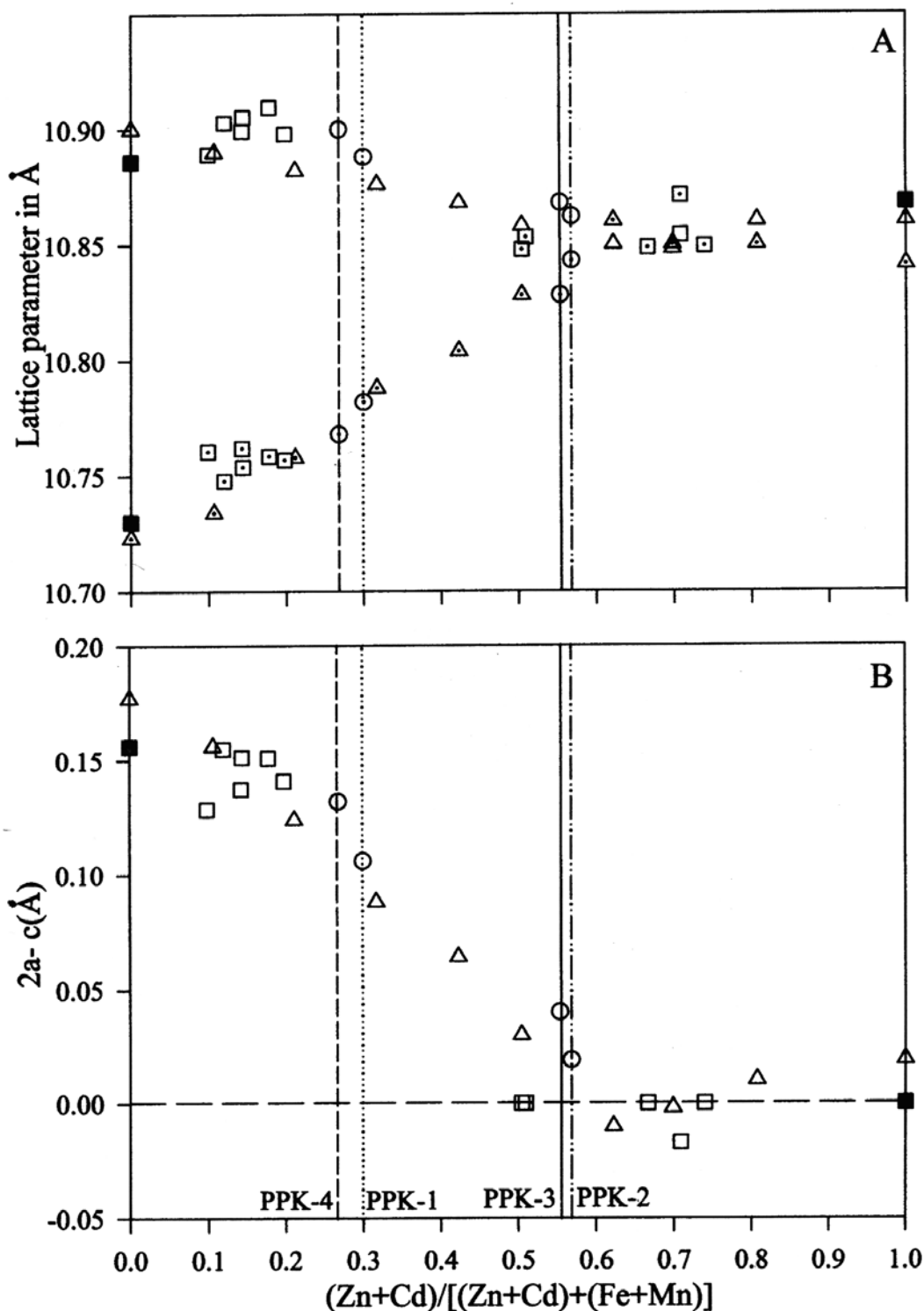


Fig. 3 A: unit-cell dimensions ( $2a$  as open symbols,  $c$  as open symbols with dots) of the Peerless stannite and kesterite (circles, labelled), of the synthetic 750 °C phases of Bernardini et al. (1990, X-ray powder diffraction data; triangles), and of the samples examined by Kissin – Owens (1989) and Kissin (1989) (squares; unpublished numeric data supplied by S. A. Kissin, pers. comm. 2000, except for kesterite from the Hugo pegmatite) versus  $(Zn+Cd)/[(Zn+Cd)+(Fe+Mn)]$ . B:  $2a-c$  versus  $(Zn+Cd)/[(Zn+Cd)+(Fe+Mn)]$  of the same sets of samples as in A.

### Petrologic aspects

Stability fields proposed by Kissin (1989) show stannite (including probable high stannite above ~700 °C) and kesterite separated by a miscibility gap. However, the study of synthetic phases of intermediate compositions, quenched at high temperatures (750 and 550 °C) suggested the existence of metastable compositional transitions between stannite and kesterite fields (Kissin 1989, Bernardini et al. 1990), which correspond to some natural minerals examined by Corazza et al. (1986). Breakdown of these phases into kesterite and stannite is observed in

some cases (Harris – Owens 1972, Petruk 1973, Kissin 1989, Kissin – Owens 1979, 1989). In other instances, metastable survival of such transitional, compositionally intermediate phases from their crystallization to ambient temperatures can be expected.

The average compositions of the Peerless stannite-kesterite phases fall within the intermediate range of  $Stn_{74}Kst_{26}$  to  $Stn_{44}Kst_{56}$ . At the temperature of crystallization in the quartz core of the parent pegmatite, which can be estimated at ~450 to 350 °C (London 1986, Morgan – London 1987, Chakoumakos – Lumpkin 1990), the Zn-poor compositions fall within the two-phase region of

Kissin's (1989, Fig. 2) phase diagram. The considerable variability of composition within the individual examined fragments suggests rapid crystallization, which would promote formation of a metastable phase. A low temperature of such metastable precipitation, and the even lower thermal regime during a relatively rapid cooling, typical of small pegmatite bodies, would hinder exsolution into a pair of stable phases.

#### Paragenesis and geochemistry

The low content of Cd in the Peerless stannite-kesterite is in sharp contrast with elevated up to dominant Cd proportions in stannite-kesterite-černýite phases from other granitic pegmatites (Fig. 4). This raises a question about a possible correlation of fractionation of Cd from Zn in minerals of the stannite group with other pairs of elements which characterize the progress of differentiation in granitic pegmatites, such as K-Rb, K-Cs, Nb-Ta, Zr-Hf or Al-Ga in oxide and silicate minerals. Unfortunately, data available for such correlations are scarce and non-systematic, which makes numeric comparisons vague and potentially misleading. This is not particularly surprising, as the fractionation of base metals is controlled by mechanisms different from those affecting, e. g., rare alkalis. The partitioning of Cd between stannite minerals, sphalerite and greenockite or hawleyite is another complicating factor, although probably signifi-

cant only in the most fractionated and Cd-enriched pegmatites (cf. Černý – Harris 1978).

Concerning the Peerless minerals, however, some additional observations should be mentioned. The association of tetrahedrite and tennantite with kesterite could be fortuitous and cannot be considered significant without checking a statistically significant number of samples of both stannite and kesterite from different parts of the Hugo quartz core. Secondary alteration products, however, show close dependence on the composition of primary phases. Scorodite is restricted to the tennantite-bearing sample, whereas the Sb-rich alteration product is associated with tetrahedrite-bearing kesterite. The ubiquitous presence of phosphorus in the alteration products of sulphide minerals should not be surprising, as late, low-temperature generations of phosphates listed in the introductory description of the pegmatite are relatively widespread throughout the pegmatite.

*Acknowledgements.* This work was supported by the Natural Sciences and Engineering Research Council of Canada Equipment and Research Grants to P. Černý and F. C. Hawthorne. The authors are indebted to the late W. L. Roberts for the examined specimens, and to S. A. Kissin and M. F. Márquez-Zavala for critical reviews of the manuscript.

Submitted January 4, 2000

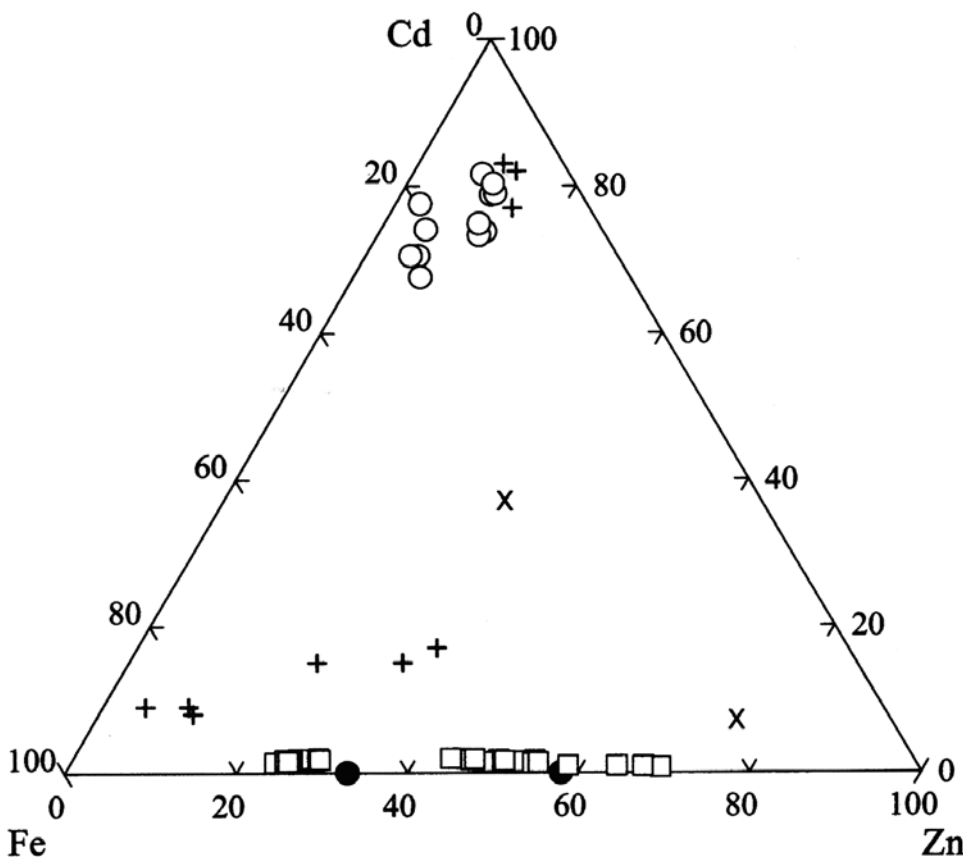


Fig. 4 The Fe - Zn - Cd ratio in stannite, kesterite and černýite from granitic pegmatites: Tanco (Kissin et al. 1978, +), Černý – Harris 1978, +), Hugo (Kissin et al. 1978, x), Mangualde (Oen 1970, solid circles), Barquilla (Murciego et al. 1991, open circles) and Peerless (this paper, open squares).



## References

- Appleman, D. E. – Evans, H. T., Jr. (1973): Job 9214: indexing and least-squares refinement of powder diffraction data. – U. S. Geol. Survey, Comp. Contrib. 20 (NTIS doc. PB2–16188).
- Bernardini, G. P. – Bonazzi, P. – Corazza, M. – Corsini, F. – Mazzetti, G. – Poggi, L. – Tanelli, G. (1990): New data on the  $\text{Cu}_2\text{FeSnS}_4$ – $\text{Cu}_2\text{ZnSnS}_4$  pseudobinary system at 750 ° and 550 °C. – Eur. Jour. Mineral., 2: 219–225.
- Čech, F. – Hak, S. (1982): Ferroan kesterite from Vernéřov, near Aš, western Bohemia, Czechoslovakia. – Acta Univ. Carolinae, Geol., (1): 45–51.
- Černý, P. – Harris, D. C. (1978): The Tanco pegmatite at Bernic Lake. XI. Native elements, alloys, sulfides and sulfosalts. – Canad. Mineral., 16: 625–640.
- Černý, P. – Roberts, W. L. – Ercit, T. S. – Chapman, R. (1985): Wodginite and associated oxide minerals from the Peerless pegmatite, Pennington County, South Dakota. – Amer. Mineral., 70: 1044–1049.
- Černý, P. (1991): Rare-element granitic pegmatites. Part I: Anatomy and internal evolution of pegmatite deposits. – Geoscience Canada, 18: 49–67.
- Chakoumakos, B. C. – Lumpkin, G. R. (1990): Pressure-temperature constraints on the crystallization of the Harding pegmatite, Taos County, New Mexico. – Canad. Mineral., 28: 287–298.
- Corazza, M. – Corsini, F. – Tanelli, G. (1986): Stannite group minerals: investigations on stannite and kesterite. – Rend. Soc. Italiana Mineral. Petrol., 41: 217–222.
- Hall, S. R. – Szymanski, J. T. – Stewart, J. M. (1978): Kesterite,  $\text{Cu}_2(\text{Zn},\text{Fe})\text{SnS}_4$ , and stannite,  $\text{Cu}_2(\text{Fe},\text{Zn})\text{SnS}_4$ , structurally similar but distinct minerals. – Canad. Mineral., 16: 131–137.
- Harris, D. C. – Owens, D. R. (1972): A stannite-kesterite exsolution from British Columbia. – Canad. Mineral., 11: 531–534.
- Kissin, S. A. (1989): A reinvestigation of the stannite ( $\text{Cu}_2\text{FeSnS}_4$ )–kesterite ( $\text{Cu}_2\text{ZnSnS}_4$ ) pseudobinary system. – Canad. Mineral., 27: 689–697.
- Kissin, S. A. – Owens, D. R. (1979): New data on stannite and related tin sulfide minerals. – Canad. Mineral., 17: 125–135.
- (1989): The relatives of stannite in the light of new data. – Canad. Mineral., 27: 673–688.
- Kissin, S. A. – Owens, D. R. – Roberts, W. (1978): Černýite, a copper-cadmium-tin sulfide with the stannite structure. – Canad. Mineral., 16: 139–146.
- London, D. (1986): The magmatic-hydrothermal transition in the Tanco rare-element pegmatite: evidence from fluid inclusions and phase equilibrium experiments. – Amer. Mineral., 71: 376–395.
- London, D. – Burt, D. M. (1982): Lithium minerals in pegmatites. In: Černý, P. (Ed.), Granitic pegmatites in science and industry – Mineral. Assoc. Canada Short Course Hbk. 8: 99–133.
- Morgan, G. B., VI. – London, D. (1987): Alteration of amphibolitic wallrocks around the Tanco rare-element pegmatite, Bernic Lake, Manitoba. – Amer. Mineral., 72: 1097–1121.
- Murciego Murciego, A. – Gonzalo Corral, J. F. – Babkine, J. – Dusausoy, Y. – Suares Barrios, M. (1991): Primera aparición de cernýita ( $\text{Cu}_2\text{CdSnS}_4$ ), un análogo cadmífero de la estannina en España. – Bol. Soc. Esp. Mineral., 14(1): 112–113.
- Oen, I. S. (1970): Paragenetic relations of some Cu-Fe-Sn sulfides in the Mangualde pegmatite, north Portugal. – Mineral. Deposita, 5: 59–84.
- Petruk, W. (1973): Tin sulphides from the deposit of Brunswick Tin Mines Limited. – Canad. Mineral., 12: 46–54.
- Pouchou, J. L. – Pichoir, F. (1984): A new model for quantitative analysis. I. Application to the analysis of homogeneous samples. – La Recherche Aerosp., 3: 13–38.
- (1985): “PAP” (ppZ) procedure for improved quantitative microanalysis. In: Microbeam Anal. – 1985, San Francisco Press, San Francisco, California, 104–106.
- Sheridan, D. M. – Stephens, H. G. – Staatz, M. H. – Norton, J. J. (1957): Geology and beryl deposits of the Peerless pegmatite, Pennington County, South Dakota. – U. S. Geol. Survey Prof. Paper 297-A.
- Springer, G. (1968): Electronprobe analyses of stannite and related tin minerals. – Mineral. Mag., 36, 1045–1051.
- (1972): The pseudobinary system  $\text{Cu}_2\text{FeSnS}_4$ – $\text{Cu}_2\text{ZnSnS}_4$  and its mineralogical significance. – Canad. Mineral., 11: 535–541.

## Stannin a kesterit z pegmatitu Peerless, Black Hills v Jižní Dakotě, USA

Stannin a kesterit se vyskytují jako několikacentimetrové agregáty podél okrajů křemenného jádra granitického pegmatitu Peerless u Keystone, v Black Hills v Jižní Dakotě. Kesterit je doprovázen akcesorickým tetradritem a tennantitem; vzácný chalkopyrit doprovází kesterit i stannin. Stannin a kesterit jsou relativně homogenní v jednotlivých agregátech, ale oba minerály jsou značně variabilní v různých slucích. Kolísají hlavně obsahy Fe a Zn, zatímco Cd je přítomno pouze ve stopách. Čtyři detailně zkoumané vzorky mají průměrné složení  $\text{Stn}_{75}\text{Kst}_{25}$ ,  $\text{Stn}_{72}\text{Kst}_{28}$  (zinečnatý stannin) a  $\text{Stn}_{46}\text{Kst}_{54}$ ,  $\text{Stn}_{44}\text{Kst}_{56}$  (železnatý kesterit). Stechiometrie je téměř ideální, s odchylkami většinou menšími než 1 % a nepřesahujícími meze analytických chyb. Poměr  $\text{Cu}:(\text{Fe}, \text{Zn}, \text{Cd}):\text{Sn}$  je téměř konstantní a blízký k hodnotě 2:1:1, ale suma (Fe, Zn, Cd) je k dalším dvěma komponentám poněkud vyšší, stejně jako ve spolehlivých údajích citovaných v literatuře. Rozdíl v mřížkových konstantách  $2a - c$  klesá se stoupajícími hodnotami  $(\text{Zn}+\text{Cd})/[(\text{Zn}+\text{Cd})+(\text{Fe}+\text{Mn})]$ , v souladu s údaji pro syntetické fáze a některé přírodní minerály. Hodnota  $2a$  pro kesterit však není totožná s hodnotou  $c$ , jak předpokládá Kissin (1989). Pokud jde o výskyty stanninu, kesteritu a černýitu v granitických pegmatitech, obsahy Cd jsou pravděpodobně jen velmi zhruba korelovatelné s jinými indexy frakcionace v oxydech a silikátech.