

Herzenbergite (SnS) in Proterozoic granite pegmatites in north-central Sweden

STEN-ANDERS SMEDS

Institute of Earth Sciences, Uppsala University, Norbyvägen 18 B, S-75236 Uppsala, Sweden

Abstract

Herzenbergite, SnS, was found in dykes in three granite pegmatite fields in north-central Sweden. It occurs as erratic replacements of cassiterite. The formation of herzenbergite was probably triggered by local interactions with fluids from sulphide-bearing graphitic schists located in the immediate vicinity of the pegmatite dykes.

KEYWORDS: herzenbergite, cassiterite, lithium pegmatites, Sweden.

Introduction

HERZENBERGITE, the Sn end-member of the solid-solution series herzenbergite-teallite (SnS–PbSnS₂) (Chang and Brice, 1971), has previously been described from only a few localities. In a sulphide-rich environment it occurs in Candalaria, Bolivia (Moh, 1969), at Björkskogsnäs, Sweden (Burke and Zakrzewski, 1990), and associated with cassiterite in the Maria Theresia mine in Bolivia (Ramdohr, 1935a) and Hoei mine, Japan (Miyahisa and Noda, 1964). Replacements of cassiterite by herzenbergite in sulphide deposits were described from Shinkiura, Japan (Aoki, 1971) and from Goluboye, Maritime region, Russia (Sirina *et al.*, 1982), whereas replacements of herzenbergite by cassiterite were found in Khoton Khay, Yakutia, Russia (Nekrasov *et al.*, 1971) and by a hydrostannate at Druzhba, Yakutia, Russia (Stolyarov *et al.*, 1988). The mineral was also noted from Dachang, China (Moh and Li, 1986). A replacement of nordenskiöldine by herzenbergite in veins associated with a pegmatite in marble was described by Ramdohr (1935b) from the Stiepelmann mine in Namibia.

The only report of herzenbergite from granitic pegmatites *sensu stricto* known to the author is Lahti's (1981) find of an unidentified tin sulphide, probably herzenbergite, which occurs as tiny inclusions in cassiterite and wodginite, and also as an identified mineral replacing cassiterite, in the Viitaniemi pegmatite in the Eräjärvi district in Finland. In the present paper, herzenbergite is described from pegmatites in north-central Sweden, and a mode of formation proposed.

Occurrence

In the years 1980–86 several subeconomic cassiterite-bearing lithium pegmatites were found in north-central Sweden. Herzenbergite associated with cassiterite has so far been identified from three of the pegmatite fields: Räggen, Järkvissle and Sidensjö-Hinnsjön (Fig. 1). All these pegmatite fields are associated with Härnö-type granites and typically carry schorl, garnet, beryl, columbite, triphylite, cassiterite and locally Li-aluminosilicates also, and are typically emplaced in andalusite-grade metagreywackes (Smeds, 1990).

Räggen. In Räggen, the pegmatite dykes with rare minerals occur in a 3 × 2 km area. The cassiterite-bearing dykes comprise the Räggen MOB Sn-deposit with 200 000 tonnes at 0.1% Sn (Fredrikson and Tuuri, 1986) and some minor dykes. Besides these, several glacial boulders of unknown provenance are found here. Herzenbergite was found in two of these boulders. Both boulders contain thin (3–4 dm) asymmetrically zoned dykes, which can be divided in two units, one composed of quartz–muscovite–cassiterite with minor albite, whereas the other half consists of K-feldspar–albite–muscovite–quartz. In one of the boulders ('GDB'), graftonite has also been found in the latter unit. The similarity of these boulders, and their positions along the main glacial boulder trend, suggest that they may have been torn out from the same dyke.

Järkvissle. The rare-element pegmatite field of Järkvissle occupies about 4 × 7 km in the Indalsälven valley with several subparallel dykes and glacial boulders, some of them of unknown

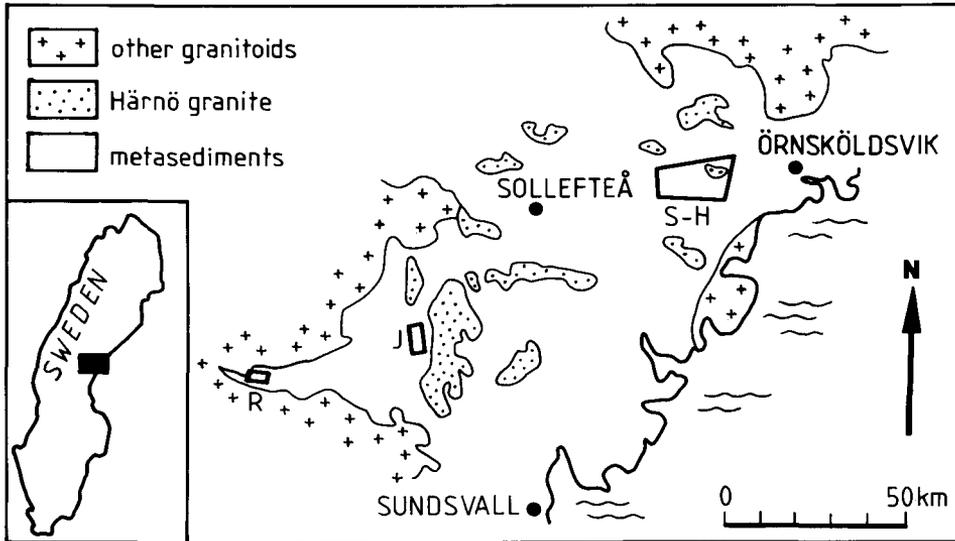


FIG. 1. Location map with pegmatite fields: R = Räggen, J = Järkvissle, S-H = Sidensjö-Hinnsjön. Geology modified after Loberg (1988).

source. Minor dykes (<1 m) are normally cassiterite- and triphylite-bearing, thicker dykes also spodumene-bearing, and in the thickest individual dykes (up to 4 m) an innermost core of petalite partly replaced by an intergrowth of spodumene and quartz is surrounded by an outer zone with primary spodumene. These spodumene-quartz intergrowth and spodumene dykes cluster into two swarms: the 380- and 700-systems. In almost every square metre of the dyke outcrops, at least some grains (2–20 mm) of cassiterite occur, also as rich disseminations locally. To date, herzenbergite has been found locally in both 380- and 700-systems, and also in two glacial boulders of unknown provenance.

Cassiterite associated with herzenbergite occurs in various mineral assemblages: in muscovite-quartz-cassiterite zones alternating with zones with additional albite (boulder A), in the groundmass of albite, muscovite, quartz, minor triphylite interstitial to 1–3 cm K-feldspar (boulder B and in the 380 dykes), and in a similar groundmass but adjacent to 1–10 cm K-feldspar, spodumene and spodumene-quartz intergrowth or petalite in the 700-system dykes.

Sidensjö-Hinnsjön. In the Sidensjö-Hinnsjön pegmatite field, the dykes bearing rare minerals occur in an area of approximately 20 × 5 km. To date, only the westernmost, the Rödmyrtjärnkullen ('RMT') dyke was found to contain herzenbergite. The RMT dyke is 1–3 dm in width with fine-grained quartz, muscovite and minor

albite, and with a rich dissemination of 1–3 mm cassiterite grains.

In all three pegmatite fields, the herzenbergite occurs exclusively on cassiterite as silvery grey coatings. The spatial distribution in outcrop is extremely spotty; cassiterite grains with and without herzenbergite have been noted within distances of 1 m from each other in the Järkvissle 700-dykes.

Paragenesis

Optical properties agree well with data given by Ramdohr (1975), the XRD powder pattern and structural parameters [orthorhombic with $a_o = 4.325(1)$, $b_o = 11.193(3)$, $c_o = 3.976(2)$ Å] with those of synthetic SnS and herzenbergite given by Mosburg *et al.* (1961); Miyahisa and Noda (1964); Aoki (1971); Nekrasov *et al.* (1971); Sirina *et al.* (1982), and the composition with that of synthetic SnS (Table 1).

In the samples from Järkvissle and RMT the herzenbergite replaces cassiterite, forming rims up to 0.5 mm thick penetrating into cassiterite along small fractures, cleavage and twin planes, and along contacts between cassiterite and inclusions of columbite-tantalite, forming a three-dimensional network with abundant remnants of cassiterite (Fig. 2A).

Within the rims, the herzenbergite forms anhedral 0.01–0.02 mm grains. They exhibit a platy euhedral shape apparently only in contact

Table 1. Chemical compositions of herzenbergite. Other elements not detected.

	1	2	3
Sn	78.73	78.98	78.80
S	21.27	21.10	21.07
Sum	100.00	100.08	99.87

1. Theoretical $\text{Sn}_{1.00}\text{S}_{1.00}$
2. Järkvissle 379V, mean of 4 analyses: $\text{Sn}_{1.01}\text{S}_{1.00}$
3. Räggen GDB, mean of 2 analyses: $\text{Sn}_{1.01}\text{S}_{1.00}$

with gangue minerals. It also commonly penetrates cleavage planes of muscovite, and appears to corrode boundaries between silicate grains up to 1–2 cm from the 'parent' cassiterite grains (Fig. 2B).

In one sample, JÄR 279V from the Järkvissle 380, cassiterite contains fractures filled with mainly Mn-apatite, but also with a light mica, quartz and a K-feldspar. The contacts between the minerals in the fractures and cassiterite are interpreted to have served as channelways for herzenbergite-generating fluids, as the cassiterite is typically corroded. The apatite-silicate veins are often boudinaged when totally surrounded by herzenbergite (Fig. 2A). Measurements of the length and orientation of the boudins in two polished thin-sections cut perpendicular to each other give similar extensions in all directions. The average extension, 10.2%, gives a volume increase of the herzenbergite relative to the cassiterite by approximately 34%; this corresponds to a theoretical volume increase of 35% in the conversion of SnO_2 to SnS , based on cell volume and number of atoms in the cells. Thus, it is plausible to suppose that the Sn-content of the herzenbergite is derived from the cassiterite in a sulphidation process.

In the same sample, patches of a fine grained, brownish, low-reflecting, transparent substance with low polishing hardness occurs with herzenbergite. Electron microprobe analyses suggest a varlamoffite-like composition (Table 2). The textural relationships may suggest coprecipitation; however, replacement after herzenbergite seems more likely (Fig. 2C). Also, a columbite crystal has been replaced by fersmite, i.e. (Fe, Mn) substituted by Ca, and a fracture filled with herzenbergite (Fig. 2C, Table 2).

In the Räggen boulders, the mutual herzenbergite-cassiterite textures do not unequivocally suggest replacement. Corrosion of the cassiterite occurs in limited amounts, but herzenbergite often forms rims, crystals and patches on flat cassiterite surfaces (Fig. 2D). Herzenbergite rims are not in contact with cassiterite locally but also

enclose gangue. One 30 μm euhedral grain of pyrrhotite was found in the herzenbergite mass. In addition to the intermediate columbite-tantalite compositions normally found in the cassiterite inclusions in the Räggen area (unpubl. data of the author), analyses of the 10–20 μm inclusions of Ta,Nb-bearing minerals in the cassiterite in this sample also yield wodginite- and Ca-microlite-like compositions.

Thus, much of the herzenbergite has formed by replacement of cassiterite. However, the rims overgrowing crystal faces of cassiterite and veinlets in silicates indicate that the process involved not only an introduction of sulphur but also mobilization and redeposition of tin over some distances.

Discussion and conclusions

The composition of herzenbergite and its physical properties agree well with those of virtually pure synthetic SnS. This is in agreement with other herzenbergites derived from cassiterite, as exemplified in Shinkuura, Japan and Goluboye, Russia (Aoki, 1971, and Sirina *et al.*, 1982, respectively).

The most likely cause of the scarcity of herzenbergite in nature is the rarity of the geological conditions necessary for its stability. In the occurrences described here, it is a very late mineral, if not the latest, and is locally associated with pyrrhotite.

The pegmatite deposits constitute very long narrow dykes with their longest:shortest dimension ratio up to 100:1. The herzenbergite occurs in a very sporadic and spotty manner, as exemplified in the Järkvissle dykes, which implies that the conditions required for its formation were of a very local character.

The descriptions in the literature suggest that the mineral can be formed by primary crystallisation as well as by replacement of cassiterite or other Sn-minerals. In the present case, most of the herzenbergite clearly occurs as a replacement product. In the Räggen boulders the textures may suggest a primary origin. However, the unambiguous corrosion of cassiterite combined with herzenbergite deposited on flat, unreplaced surfaces of cassiterite, strongly suggest an extensive mobilisation and redeposition of Sn. Derivation of herzenbergite by breakdown of cassiterite is therefore most likely even in the Räggen boulders.

In pegmatites, and also in granitophile parageneses in general, cassiterite is the most common Sn-mineral. Sn(II)-species are comparatively rare. Apart from the present finds of herzenber-

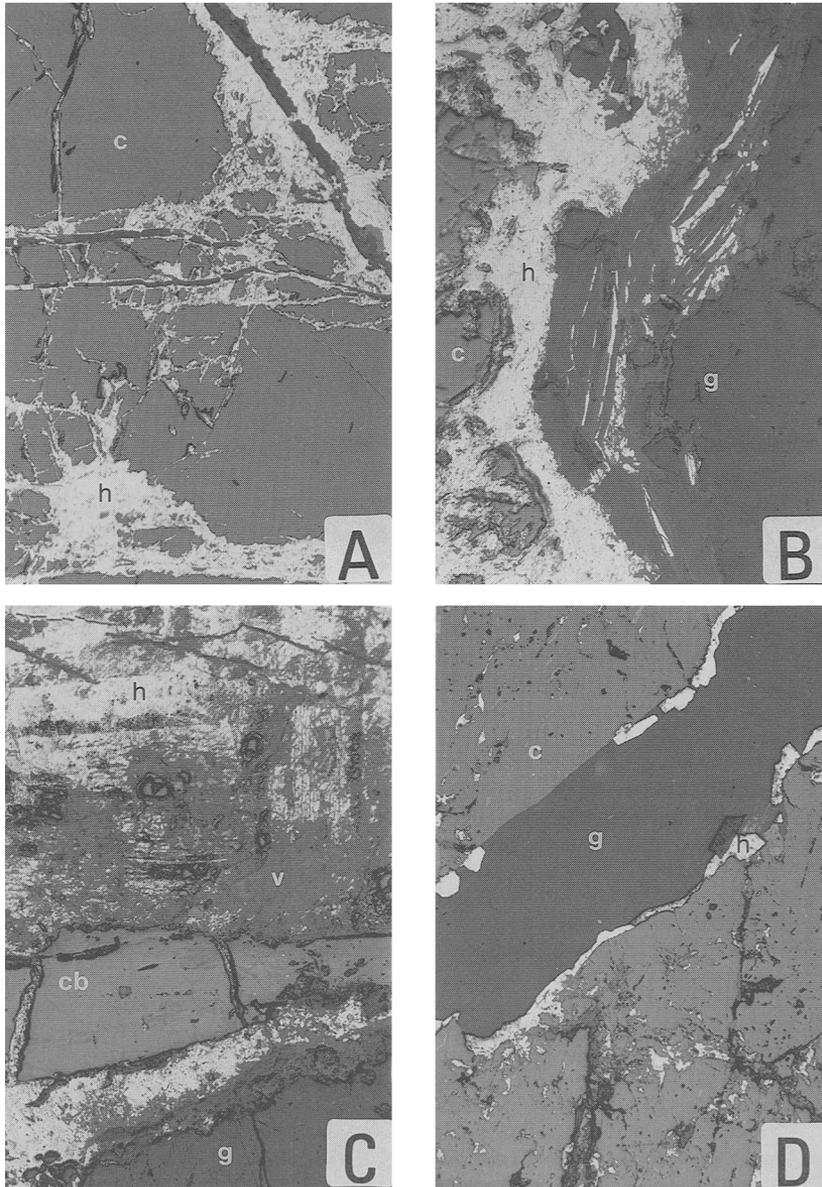


FIG. 2. Photomicrographs in reflected light: (A) Replacement by herzenbergite after cassiterite. Dark veinlets of apatite are boudinaged. (B) Herzenbergite penetrating into cleavage planes of muscovite. (C) Herzenbergite, with remnants of primary cassiterite, replaced(?) by 'varlamoffite'. Large columbite crystal replaced by low-reflecting fersmite. (D) Replacement of cassiterite by herzenbergite with euhedral herzenbergite crystals as probable redepositions. c = cassiterite, h = herzenbergite, cb = columbite, v = varlamoffite, g = gangue. 2A-2C from Järkvissle 380, 2D from Räggen GDB. Shorter dimension of photo equals 0.2 mm for A and B and 0.4 mm for C and D.

gite, they seem to be restricted to oxide phases such as the thoreaulite-foordite series $\text{Sn}(\text{Ta}, \text{Nb})_2\text{O}_6$ (Černý *et al.*, 1988) and stannomicrolite $\text{Sn}_2^{2+}\text{Ta}_2\text{O}_7$ (Vorma and Siivola, 1967;

Ercit *et al.*, 1987). These are very rare minerals, restricted to only a few localities. This indicates that exotic conditions atypical of pegmatites (and other granitophile parageneses) are required (as

Table 2. Chemical composition of ferrocolumbite, fersmite, and "varlamoffite" from sample JÄR 379V, Järkvissele.

	1	2	3
FeO	12.99	0.45	3.3 - 4.5
MnO	5.14	0.20	n.d.
Ta ₂ O ₅	36.82	35.71	1.4 - 4.0
Nb ₂ O ₅	43.73	44.62	0.6 - 2.5
CaO	n.d.	15.84	0.1 - 0.5
SnO ₂	0.40	1.69	74.3 - 77.8
TiO ₂	0.94	1.61	0.2 - 0.4
Sum	100.02	100.12	

1. Ferrocolumbite:

(Fe_{0.71}Mn_{0.29})_{1.00}(Nb_{1.30}Ta_{0.66}Ti_{0.05}Sn_{0.01})_{2.02}O₆

2. Fersmite:

(Ca_{1.06}Fe_{0.02}Mn_{0.01})_{1.09}(Nb_{1.26}Ta_{0.61}Ti_{0.08}Sn_{0.04})_{1.99}O₆

3. "Varlamoffite", range of 8 analyses.

discussed by Eadington, 1985, and Černý *et al.*, 1988).

The conditions of formation of the herzenbergite occurrences examined here, can be delineated as follows:

1. Magmatic crystallisation of lithium-rich pegmatites with primary spodumene and with primary petalite were found by London (1984, 1986) to be within the ranges 3–4 kbar and 2–3 kbar respectively at *c.* 600–400 °C. The breakdown of petalite to the spodumene–quartz intergrowth, observed at Järkvissele, was established experimentally by London (*op. cit.*) at 400–520 °C for the 2–3 kbar range. All these *P, T* conditions are, however, undoubtedly too high for crystallisation of herzenbergite, as it represents a late replacement product.

2. Herzenbergite may coexist with cassiterite in the whole range of geologically realistic conditions of *T* (Drábek and Štemprok, 1974). Also, at *T* between 200–500 °C SnS has been found to precipitate under acid to slightly alkaline solutions (pH 2–9) (Nekrasov *et al.*, 1971).

3. The varlamoffite-like substance in the JÄR379V sample suggests even more alkaline conditions of pH 8–10 as Diman and Nekrasov (1966) noted coprecipitation of amorphous cassiterite with herzenbergite in experiments under such conditions. However, despite the ambiguous textural relationships discussed earlier; the varlamoffite found in the JÄR379V sample may be a weathering product, in agreement with observations by Stolyarov *et al.* (1988). Experiments by Moh and Hutchison (1977) showed that alteration of SnS yields, together with SnS₂, metastannic acid which is converted into supergene cassiterite,

i.e. 'varlamoffite'. Thus, the genetic history of the varlamoffite substance occurring in the JÄR379V sample remains unresolved at present.

4. The *f*_{O₂} and *f*_{S₂} control the precipitation of herzenbergite or the conversion of cassiterite to herzenbergite. Diman and Nekrasov (1966) noted that SnS precipitates under reducing conditions from solutions relatively low in S. In terms of *f*_{S₂} vs. *T* the stability field of SnS corresponds roughly to that of FeS *sensu lato* (Drábek and Štemprok, 1974, and references therein). As noted earlier, pyrrhotite formed with herzenbergite in one of the Räggen boulders.

5. Barsukov *et al.* (1987) noted that tin in fluids in equilibrium with cassiterite below the *f*_{O₂} conditions defined by the Ni–NiO buffer is preferentially bivalent and that the solubility of cassiterite in a reducing medium is greater than under oxidising conditions. Holland (1959) stated that SnS is stable at a *f*_{O₂} of *c.* 10^{–40} at 327 °C. Thus exceptionally low *f*_{O₂} conditions are apparently required for the formation of herzenbergite.

These conditions cannot be expected near the end of pristine pegmatite consolidation. Pore fluids from the enclosing metamorphic suite may have an effect, after the consolidating pegmatite attained thermal equilibration with the host rocks.

6. Pyrrhotite-bearing graphitic schists which are prominent in the immediate vicinity of all the three herzenbergite-bearing localities may be proposed as factors promoting reducing conditions: the RMT dyke in the Sidensjö–Hinnnsjön pegmatite field is located in metagraywackes only a few metres from intercalations of graphitic schists; the Räggen boulders probably originate from a metagraywacke area where ground geophysical surveys have revealed unusually abundant high-conducting layers (Esa Tuuri, Stockholm, pers. comm., 1981); and the Järkvissele dykes are also emplaced in metagraywackes with graphitic schists cropping out in close vicinity to them.

Thus, it may be concluded that late, reducing, sulphuric pore fluids equilibrated with the graphitic schists may have interacted locally with cassiterite after thermal equilibration of the pegmatites with country rocks. As tin is, by far, the dominant cation in cassiterite, a very 'pure' SnS formed during the resulting sulphidation process.

Acknowledgements

Thanks are due to Mr. Olle Wallner and Mr. Claes Åhlinder, Uppsala, for preparing the thin sections, to Claes Åhlinder for performing the microprobe analyses,

and to Ms Christina Wernström, Uppsala, for redrawing the figures. The manuscript benefitted from reviews by Drs Örjan Amcoff, Uppsala, and Petr Cerny, Winnipeg, which are greatly appreciated.

References

- Aoki, Y. (1971) Herzenbergite from the Shinkiura mine, Oita prefecture, Japan. *J. Japan. Assoc. Mineral. Petrol. Mining Geol.*, **65**, 221–9 (Japanese with English Abstract).
- Burke, E. A. J. and Zakrzewski, M. A. (1990) Herzenbergite and associated antimony minerals from Björkskogsnäs, Hällefors, Sweden. *Geol. Fören. Stockh. Förh.*, **112**, 85–6.
- Barsukov, V. L., Durasova, N. A., Kovalenko, N. I., Ryabchikov, I. D., and Ryzhenko, B. N. (1987) Oxygen fugacity and tin behaviour in melts and fluids. *Geol. Zbornik—Geol. Carpatica*, **38**, 723–33.
- Černý, P., Fransolet, A.-M., Ercit, T. S., and Chapman, R. (1988) Foordite, SnNb_2O_6 , a new mineral species, and the foordite–thoreaulite series. *Can. Mineral.*, **26**, 889–98.
- Chang, L. L. Y. and Brice, W. R. (1971) The herzenbergite–teallite series. *Mineral. Mag.*, **38**, 186–9.
- Diman, Ye. N. and Nekrasov, Y. Ya. (1966) Formation conditions for simple sulfides of tin, as indicated by experiments. *Dokl. Acad. Sci. U.S.S.R., Earth Sci. Sect.*, **170**, 193–6.
- Drábek, M. and Štemprok, M. (1974) The system Sn-S-O and its geological application. *Neues Jahrb. Mineral., Abh.*, **122**, 90–118.
- Eadington, P. J. (1985) The solubility of cassiterite in hydrothermal solutions in relation to some lithological and mineralogical associations in tin ores. In *Granite-related mineral deposits, geology, petrology and tectonic setting* (R. P. Taylor and D. F. Strong, eds.). Canadian Institute of Mining and Metallurgy, Conference, Halifax 1985. Extended Abstracts, 110–15.
- Ercit, T. S., Černý, P., and Siivola, J. (1987) The composition of stannomicrolite. *Neues Jahrb. Mineral., Mh.*, 249–52.
- Fredrikson, G. and Turri, E. (1986) Rare-element pegmatite prospects in Västernorrland and Jämtland. *Abstracts, 17e Nordiska Geologmötet, Helsingfors*, **38**.
- Holland, H. D. (1959) Some applications of thermochemical data to problems of ore deposits. I. Stability relations among the oxides, sulfides, sulfates and carbonates of ore and gangue metals. *Econ. Geol.*, **54**, 184–223.
- Lahti, S. I. (1981) On the granitic pegmatites of the Eräjärvi area in Orivesi, southern Finland. *Bull. Geol. Surv. Finland*, **314**, 1–63.
- Loberg, B. E. H. (1988) *Geologi. Material, processer och Sveriges berggrund*. 4th ed., Norstedts, Stockholm, 469 pp.
- London, D. (1984) Experimental phase equilibria in the system $\text{LiAlSiO}_4\text{-SiO}_2\text{-H}_2\text{O}$: a petrogenetic grid for lithium-rich pegmatites. *Am. Mineral.*, **69**, 995–1004.
- (1986) Magmatic-hydrothermal transition in the Tanco rare-element pegmatite: Evidence from fluid inclusions and phase-equilibrium experiments. *Ibid.*, **71**, 376–95.
- Miyahisa, M. and Noda, M. (1964) Herzenbergite and associated minerals from the Hoei mine, Kyushu, Japan. *J. Min. Soc. Japan*, **6**, 349–60. (In Japanese.)
- Moh, G. H. (1969) The tin-sulphur system and related minerals. *Neues Jahrb. Mineral., Abh.*, **111**, 227–63.
- and Hutchison, C. S. (1977) Hydrocassiterites. *Ibid.*, **131**, 13–7.
- and Li, J.-L. (1986) Paragenesis and genesis of the tin-bearing sulfide ores in Dachang/China. *Ibid.*, **153**, 267–72.
- Mosburg, S., Ross, D. R., Bethke, P. M., and Toulmin, P. (1961) X-ray powder data for herzenbergite, teallite and tin trisulfide. *U.S. Geol. Surv. Prof. Paper*, **424C**, 347.
- Nekrasov, I. Ya., Sipavina, L. S., and Kupriyanov, V. N. (1971) Hydrothermal synthesis of simple tin sulfides. *Dokl. Acad. Sci. U.S.S.R., Earth Sci. Sect.*, **200**, 153–6.
- Ramdohr, P. (1935a) Vorkommen und Eigenschaften des Herzenbergits. *Zeits. Kristallogr.*, **92**, 186–9.
- (1935b) Ein Zinnvorkommen im Marmor bei Arandis, Deutsch-Südwestafrika. *Neues Jahrb. Mineral. Geol. Paläont.*, **70A**, 1–48.
- (1975) *Die Erzminerale und ihre Verwachsungen*, 4th ed. Akademie-Verlag, Berlin, 1277 pp.
- Sirina, T. N., Ryabeva, Ye. G., and Chistyakova, N. I. (1982) New data on herzenbergite. *Dokl. Acad. Sci. U.S.S.R., Earth Sci. Sect.*, **264**, 126–30.
- Smets, S.-A. (1990) Regional trends in mineral assemblages of Swedish Proterozoic granitic pegmatites and their geological significance. *Geol. Fören. Stockh. Förh.*, **112**, 227–42.
- Stolyarov, I. S., Silenko, T. M., Dorokhova, G. I., Yurkina, K. V., and Ryabeva, Ye. G. (1988) Herzenbergite from Yakutia. *Dokl. Acad. Sci. U.S.S.R., Earth Sci. Sect.*, **239**: 156–60.
- Vorma, A. and Siivola, J. (1967) Sukulaite— $\text{Ta}_2\text{Sn}_2\text{O}_7$ —and wodginitite as inclusions in cassiterite in the granite pegmatite in Sukula, Tammela in SW Finland. *C.R. Soc. Géol. Finlande*, **39**, 173–87.

[Manuscript received 17 August 1992;
revised 23 October 1992]