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Tin-bearing Minerals from Bolivian Polymetallic Deposits and Their Mineralization Stages

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Abstract: Various kinds of tin-bearing minerals, such as cassiterite, stannite, kesterite, franckeite, hocartite, teallite, cylindrite, rhodostannite, canfieldite, incaite and potosiite occur from polymetallic deposits in Eastern Cordillera of Bolivian Andes. These deposits, called Bolivian type polymetallic deposits, were formed by xenothermal mineralization related to Miocene igneous activities. The mineralization stages are generally divided into six as follows: I: quartz-tourmaline, II: quartz, III: quartz-pyrite, IV: sulfide, V: sulfosalt and VI: sulfate-phosphate stages. Cassiterite principally occurs in the quartz-tourmaline (I), quartz (II) and quartz-pyrite (III) veins. Stannite and kesterite appear in the sulfide (IV) and sulfosalt (V) veins. Meanwhile, tin-bearing sulfosalt minerals, such as franckeite, hocartite, teallite, cylindrite, rhodostannite and canfieldite are found commonly in the sulfosalt (V) vein in small amount. Homogenization temperature and NaCl equivalent concentration of fluid inclusions in quartz at each stage of the mineralization are I: 260° to 510° and 18.5 to 55.4 wt%, II: 250° to 405°C and 23.4 to 26.0 wt%, III: 250° to 400°C and 4.4 to 19.7 wt%, IV: 230° to 350°C and 1.5 to 10.6 wt%, and V: 190° to 300°C and 0.4 to 5.4 wt%, respectively. The homogenization temperatures, salinities and sulfur fugacities at each stage decrease as a whole with progressing the mineralization stages. Sulfur fugacity values at the III, IV and V stages are 10^{-13} to 10^{-7} atm., 10^{-15} to 10^{-9} atm., and 10^{-16} to 10^{-9} atm., respectively.

Introduction

The Bolivian tin belt extends from the northeast side of Lake Titicaca to the Argentinean border along the Eastern Cordillera of the Andean range, as shown in Fig. 1. Two distinct types of tin deposits are found in the belt (KELLY and TURNEAURE, 1970; TURNEAURE, 1971; CLARK and FARRAR, 1973; SUGAKI et al., 1981b, 1985). The first one is deep-seated hydrothermal (meso- and/or hypothermal) veins which were formed by mineralization closely related to the emplacement of Mesozoic granitic magma (AHLFELD and SCHNEIDER-SCHERBINA, 1964; SCHNEIDER and LEHMANN, 1977; MICHEL and REATTER, 1977; LEHMANN and SCHNEIDER, 1981; SUGAKI et al., 1985). The other is polymetallic ore deposits which contain tin, tungsten, silver, lead, zinc, antimony,

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Keywords: Bolivian-type tin deposits, Xenothermal deposits, Cassiterite, Stannite-kesterite, Tin sulfosalt minerals.

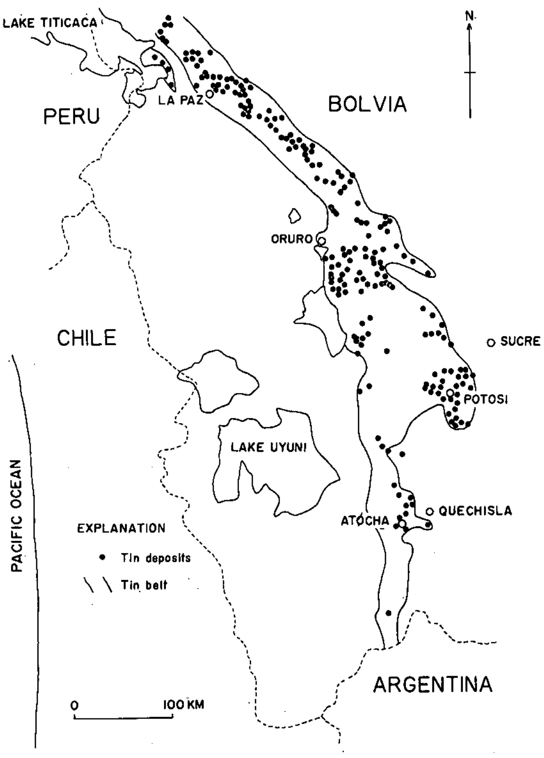

Fig. 1 Metallogenic belt in the Eastern Cordillera of Bolivia (After CLAURE and MINAYA, 1979).

Table 1 Tin-bearing minerals from Bolivian type polymetallic deposits

Minerals	Chemical formula	Crystal system	Cell parameters a (α)	b (β)	c (γ)
Cassiterite	SnO_2	Tet	4.73	-	3.18
Herzenbergite	SnS	Orth	4.33	11.19	3.98
Ottemannite	Sn_2S_3	Orth	8.82	14.04	3.75
Berndtite	SnS_2	Hex	3.65	-	5.90
Stannite	Cu_2FeSnS_4	Tet	5.45	-	10.75
Kesterite	Cu_2ZnSnS_4	Tet	5.43	-	10.87
Rhodostannite	$Cu_2FeSn_3S_8$	Tet	7.29	-	10.31
Hocartite	Ag_2FeSnS_4	Tet	5.74	-	10.96
Canfieldite	Ag_8SnS_6	Orth	15.31	7.55	10.70
Teallite	$PbSnS_2$	Orth	4.29	11.35	4.05
Franckeite	$FePb_6Sb_2Sn_2S_{14}$	Tri	46.9 (90.0°)	5.82 (94.6°)	17.30 (90.0°)
Cylindrite	$FePb_3Sb_2Sn_4S_{15}$	Tri	11.73 (90.0°)	5.79 (92.4°)	5.81 (93.9°)
		Tri	11.71 (90.0°)	3.67 (92.6°)	6.32 (90.8°)
Incaite	$FePb_4Sb_2Sn_4S_{14}$	Tri	17.29 (90.0°)	5.79 (94.1°)	5.83 (90.0°)
Potosiite	$Fe_7Pb_8Sb_{16}Sn_{18}S_{115}$	Tri	188.06 (90.0°)	70.10 (92.2°)	17.28 (90.0°)

and bismuth (Turneaure, 1935, 1960, 1971; Ahlfeld, 1936, 1967; Turneaure and Welter, 1947; Ahlfeld and Schneider-Scherbina, 1964; Sillitoe et al., 1975; Sillitoe, 1976; Hanus, 1977, 1982; Grant et al., 1980; Sugaki et al., 1981b, c, 1983, 1984, 1986b) and were produced by mineralization related to volcano-plutonic igneous activities in the Miocene age, such as granite, quartz porphyry and dacite (Evernden et al., 1977; Grant et al., 1979). The latter is called as Bolivian type (polymetallic) tin deposits which are thought to belong to a typical xenothermal type.

A large number of tin-bearing minerals have been reported from the Bolivian type tin deposits and are listed in Table 1. In general, cassiterite, stannite and kesterite are the common constituents in tin ores and the others are accessory or rare. Franckeite and cylindrite, however, sometimes occur as the principal ore minerals in the San Jose and Trinacria mines, respectively. In this paper, mineral paragenesis and mineralogical data of the tin minerals from Bolivian type (polymetallic) deposits will be described in relation to their mode of occurrence.

Geologic Setting

Many tin deposits of the polymetallic type occur in the Eastern Cordillera of the Bolivian Andes (Fig. 2). The geology of the area is composed mainly of a Paleozoic system which is partly covered by Mesozoic and Tertiary sediments. The Paleozoic basement consists of intensely folded and faulted quartzite, sandstone and slate of the Ordovician and Silurian ages. The Mesozoic sediment exposed in a limited area of the Potosi and Quechisla districts is composed of red or green colored sandstone and mudstone, conglomerate, limestone and other sediments of the Cretaceous age. Meanwhile, conglomerate, sandstone, dacitic tuff, tuff breccia and volcanic complex of the Miocene age are distributed in the Potosi, Quechisla and Sur Lipez districts. The Paleozoic system was intruded and metamorphosed by Mesozoic batholiths near La Paz. Granitic rocks of the late Oligocene to the Miocene age (Illimani, Tres Cruces, Chualla Grande

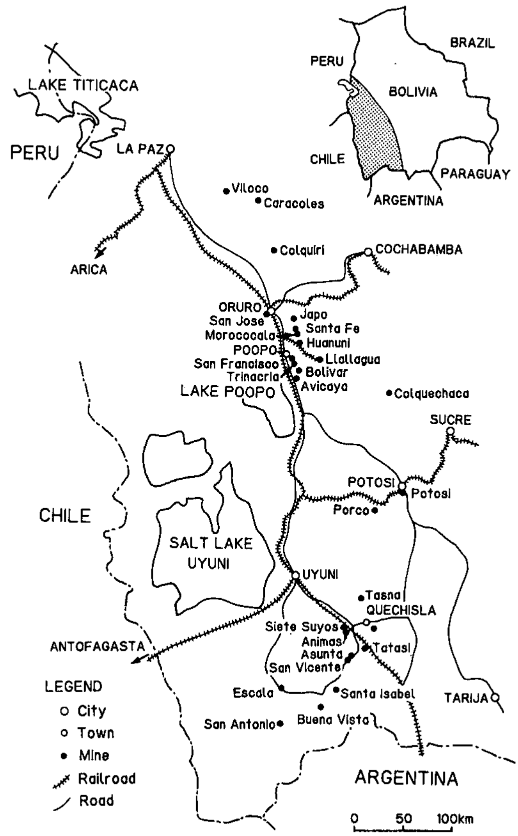

Fig. 2 Location of Bolivian tin mines producing polymetallic ores.

and Kumurana batholiths) intrude into the Silurian and Ordovician formations in the central part (near Viloco, Caracoles, Avicaya and Potosi) of the Eastern Cordillera. In addition, Miocene quartz porphyry and dacite are often found as stocks, dykes, domes and sub-volcanic complexes at the Oruro, Llallagua, Potosi, Tasna and Chorolque mines in the central and southern parts of the Cordillera. Such porphyry and dacite generally suffer intensely hydrothermal alterations such as silicification, sericitization and chloritization.

Bolivian type polymetallic ore deposits are mostly vein type which fills fissures developed in the quartzite, sandstone and slate of the Silurian or Ordovician formation, and dacitic tuff, tuff breccia, pyroclastics etc. of the Miocene formation. Bolivian type tin deposits such as the Viloco and Caracoles mines occur in Miocene granitic rocks. They also fill fractures in or around stocks of quartz porphyry and dacite such as those in the San Jose, Llallagua, Potosi, and Chorolque mines. Tin deposits which develop as veinlets, stockwork and impregnation in altered dacitic porphyry stocks and sub-volcanic complexes are called "porphyry tin" by SILLITOE et al. (1975) and GRANT et al. (1980).

Occurrence and Mineral Paragenesis of Tin-bearing Minerals

Based on the data obtained by our investigation on thirty-five Bolivian polymetallic deposits (Fig. 2) in entire tin belt, the mineralizations that formed the Bolivian tin deposits can be divided into the following six stages: I) quartz-tourmaline, II) quartz, III) quartz-pyrite, IV) sulfide, V) sulfosalt and VI) sulfate-phosphate.

Thirteen tin-bearing minerals will be comprehensively described according their mode of occurrence and mineral paragenesis in relation to these mineralization stages.

Cassiterite: Cassiterite is the principal tin mineral in Bolivian deposits, and occurs in a) quartz-tourmaline (I) veins (Avicaya, Viloco and Chorolque mines), b) quartz (II) veins (Huanuni, Avicaya), c) quartz and pyrite (III) veins (Potosi, Tasna and Siete Suyos), d) sulfide (IV) veins (San Jose, Santa Fe, Morococala, Japo, Bolivar, Potosi, Siete Suyos, Animas and Tatasi), and e) sulfosalt (V) veins (San Jose, Bolivar, San Francisco, Trinacria, Potosi and Tatasi). Among the tin bearing ores, a), b) and c) are principal, and d) and e) are subordinate. Cassiterite is found in various kinds of ores, and its deposition extends over a long range of mineralization from stage I to stage V.

In a quartz-tourmaline vein, cassiterite appears as euhedral or subhedral crystals, usually 0.5 to 7 mm long and sometimes 1 to 5 cm in size. It shows close association with quartz and tourmaline, and sometimes with wolframite, arsenopyrite and bismuthinite. The beautiful crystals of euhedral cassiterite (Fig. 3-A) in the quartz-tourmaline veins of the Principal section of the Viloco mine are famous all over the world. The crystals take short prismatic form up to 8 cm in size and are semitransparent dark brown to dark yellowish brown in color. Cassiterite in the quartz vein at the Huanuni and Avicaya mines occurs as aggregates of euhedral and subhedral crystals (0.5 to 3.0 cm in size). Its aggregate is assembled mostly with quartz (Figs. 3-B, 4-A) and occasionally with pyrite and apatite. The crystals often show growth zoning (Fig. 4-B). Cassiterite in the quartz-pyrite vein is found as aggregates of euhedral and subhedral crystals (0.05 to 2.0 mm in size), commonly accompanied by small amounts of sphalerite, arsenopyrite, stannite, pyrrhotite, bismuthinite and wolframite. Cassiterite found in sulfide veins appears as aggregates of fine-grained subhedral and anhedral crystals, 5 to 300 μm in size, assembling mainly with pyrite, arsenopyrite, sphalerite, stannite, chalcopyrite, wurtzite and marcasite, and small amounts of jamesonite, franckeite and wolframite (Fig. 4-C, D). Aggregates of fine-grained cassiterite are occasionally found in sulfosalt veins, which consist of sphalerite, stannite, wurtzite, jamesonite, franckeite and sometimes of cylindrite, zinckenite, andorite, rhodostannite and berthierite. Cassiterite occasionally appears as an euhedral crystal, 0.1 to 0.2 mm in size, in druse consisting of zinckenite, andorite and

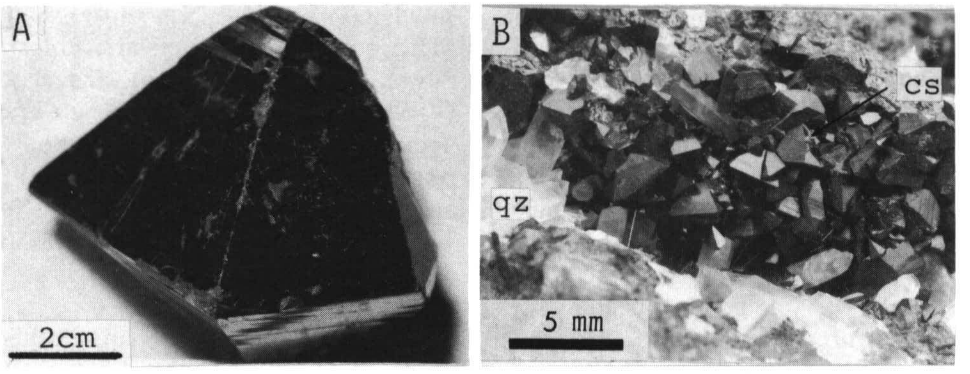

Fig. 3 Cassiterite samples.
A: Typical euhedral crystals of cassiterite from the Viloco mine. B: Cassiterite(cs) and quartz(qz) from the Huanuni mine.

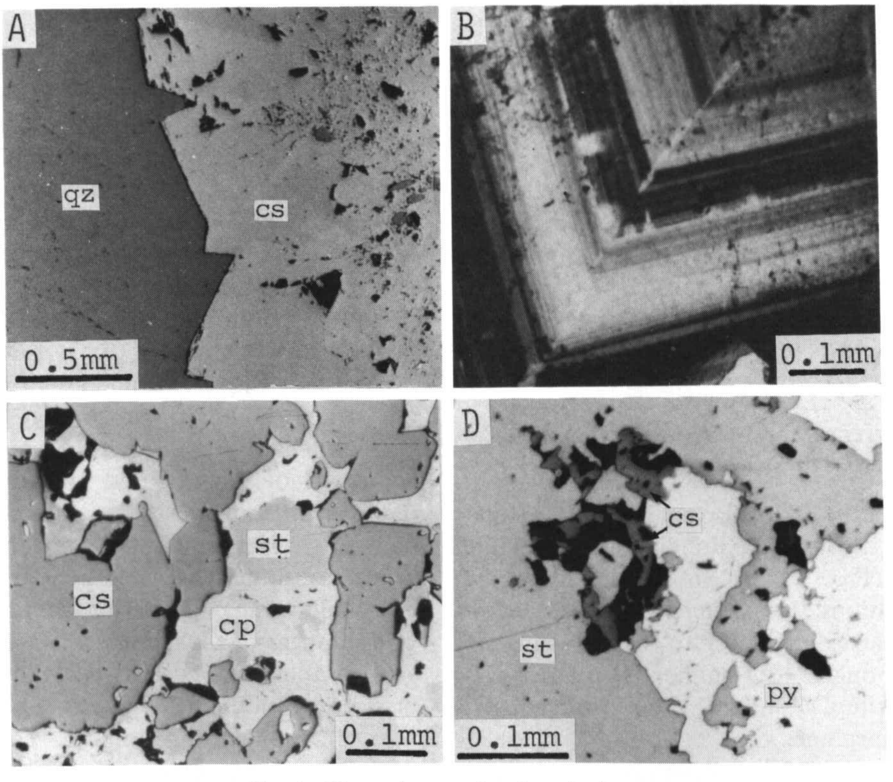

Fig. 4 Photomicrographs of cassiterite.
A: Subhedral cassiterite(cs) aggregate with quartz(qz) from the Chorolque mine. B: Growth zoning of cassiterite from quartz vein, Avicaya mine. C: Euhedral cassiterite(cs) embedded by stannite(st) and chalcopyrite(cp) from sulfide vein, Avicaya mine. D: Aggregate of fine grained cassiterite(cs) assembled with stannite(st) and pyrite(py) from sulfide vein, Siete Suyos mine.

stannite in the central portion of the vein.

Stannite-kesterite system mineral: This is also one of the principal tin minerals from Bolivian polymetallic deposits, and often occurs in the quartz-pyrite (III), sulfide (IV) and sulfosalt (V) veins described above. Among these veins, the sulfide (IV) vein, principally consisting of pyrite and/or sphalerite, is important for a

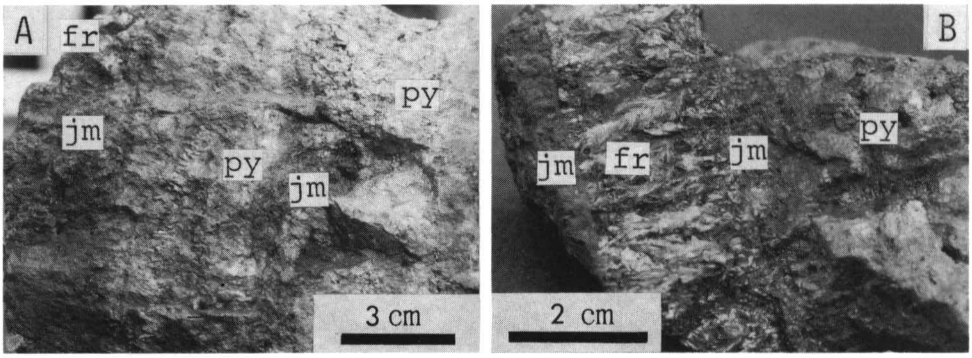

Fig. 5 Occurrence of franckeite and jamesonite.
A: Pyrite(py), jamesonite(jm) and franckeite(fr) from the San Jose mine. B: Foliated crystal aggregate of franckeite(fr) with jamesonite(jm) and pyrite(py), San Jose mine.

high concentration of stannite. In the sulfide veins at the San Jose, Santa Fe, Morococala, Viloco, Potosi, Chorolque, Siete Suyos, Animas and Tatasi mines, the stannite-kesterite system mineral commonly occurs as granular crystals (5 to 500 μm in size) and massive or irregularly shaped aggregates, and assembles closely with pyrite, sphalerite, arsenopyrite, chalcopyrite, cassiterite and quartz. It is sometimes found as thin bands, 1 to 3 mm side, alternately crustified with pyrite in the sulfide vein, and occasionally appears as an euhedral crystal, 1 to 5 mm in size, in druse composed of pyrite in the central portion of the sulfide vein.

Stannite in the quartz-pyrite (III) veins at the Avicaya and Siete Suyos mines usually appears as a patch-like and massive aggregate of granular crystals (0.05 to 1.0 mm in size) and is closely associated with cassiterite, arsenopyrite and sphalerite, in addition to quartz and pyrite. Stannite also occurs as irregularly formed aggregates of granular crystals (5 to 200 μm in size) in the sulfosalt (V) veins at the San Francisco, Trinacria, Bolivar, Potosi and Animas mines. It is usually accompanied by sphalerite, pyrite, franckeite, jamesonite, tetrahedrite, bournonite, wurtzite, quartz and occasionally zinckenite, andorite, hocartite, cylindrite, canfieldite, berthierite, semseyite, and electrum in sulfosalt ores.

Franckeite: Franckeite is one of the diagnostic minerals found in the Bolivian tin deposits. It occurs in sulfosalt band consisting mainly of jamesonite in pyritic sulfide (IV) veins at the San Jose, Huanuni, Llallagua, Carguaicollo, Animas, Siete Suyos and San Francisco mines. At San Jose, franckeite is the principal ore mineral and often appears as the central band (1 to 10 cm width) in the pyrite (sulfide) vein. The franckeite band sometimes has symmetrical jamesonite rims (1 to 2 cm width) at the boundaries of the pyrite vein (Fig. 5-A, B). Franckeite is usually found as aggregates of foliated crystals, 0.1 to 1.9 mm in size, closely associating with jamesonite, pyrite, stannite, arsenopyrite, sphalerite, galena, wurtzite, marcasite and cassiterite (Fig. 6-A).

Hocartite: Hocartite occurs in sulfosalt band or veinlet, 1 to 5 cm wide, consisting mainly of franckeite at the Animas, Siete Suyos, Tatasi and Asunta mines, but its amount is slight. The bands usually appear at the central portion of pyritic sulfide (IV) veins. Hocartite occurs in granular form, 10 to 300 μm in size, in close association with franckeite, stannite, sphalerite, pyrite, marcasite, canfieldite, quartz and others. Picot and Johan (1982) described hocartite from the Tacama and Colquechaca mines.

Teallite: Ahlfled and Munoz (1955) reported occurrences of teallite in the San Jose, Huanuni, Monserrat, Carguaicollo, Candelaria, Vicunita and Colquechaca mines. Teallite is also found in the Colquiri mine. Teallite from the Colquiri mine occurs as a band (5 cm wide) with gearksutite in the sulfide vein (San Carlos Ramo No. 4), which consists of

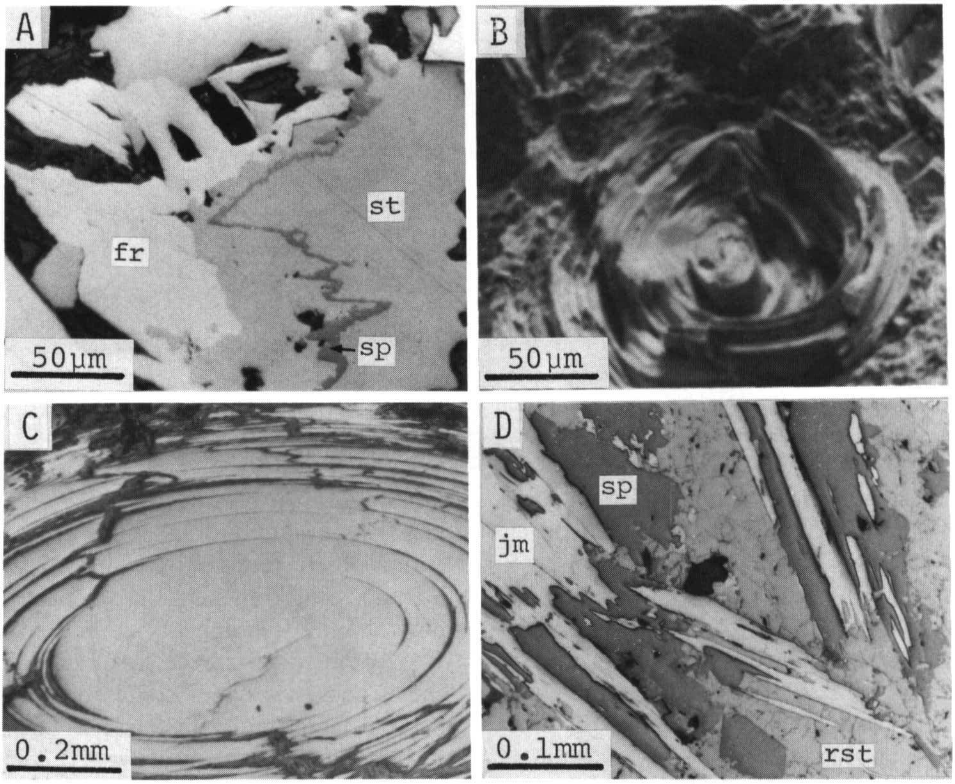

Fig. 6 Photomicrographs of cylindrite, franckeite and rhodostannite.
A: Association of franckeite(fr), stannite(st) and sphalerite(sp), Trinacria mine. B, C: Cylinder formed crystal of cylindrite from the Trinacria mine. D: Intergrowth of rhodostannite(rst), jamesonite(jm) and sphalerite(sp), Trinacria mine.

sphalerite, pyrrhotite, pyrite and vivianite. The teallite band is principally composed of franckeite, cassiterite, sphalerite, pyrite, fluorite, apatite and alunite in addition to teallite and gearksutite. Teallite in the band appears as a thin veinlet or stringer, 5 to 10 mm wide, consisting of aggregates of its lath-like crystal, 1 to 10 mm long.

Cylindrite: Cylindrite is the most famous mineral among the many interesting sulfosalts found in Bolivian tin deposits and its occurrence is restricted to a few mines in the Poopo area of the Oruro district. It is found in the Trinacria mine and is small amounts in the San Francisco and Pampa Rosario mines. Cylindrite from Trinacria occurs as a band, 2 to 5 cm wide, along with sphalerite at a central part of the pyritic sulfide vein (Bolivia Ramo A). It appears as a cylindrical form, 0.3 to 5.0 mm in diameter and 5 to 15 mm in length (Fig. 6-B, C), associating with franckeite, jamesonite, pyrite and marcasite besides sphalerite.

Rhodostannite: SPRINGER (1968) described rhodostannite from the Poopo area and the Carguaicollo mine. Rhodostannite from the Falla Poopo vein of the San Francisco mine occurs as aggregates of fine-grained crystals less than 10 μm in size, closely assembled with pyrite, sphalerite, stannite, stibnite, jamesonite, franckeite and wurtzite. Rhodostannite from the Trinacria mine is also found in gaps of aggregates of pyrite, sphalerite, jamesonite, wurtzite, stannite and cassiterite (Fig. 6-D).

Canfieldite: Canfieldite is found under the microscope in franckeite-andorite rich sulfosalt ores from the Colquechaca and Asunta mines. It occurs as an irregular form, 20 to 50 μm in size, closely assembled with hocartite, stannite and franckeite.

Incaite: Incaite was described by MAKOVICKY

(1974) as a cylindrite-like mineral in ores from the Poopo area. It occurs as a cylindrical form similar to cylindrite, and associates closely with cylindrite, stannite, miargyrite and sphalerite.

Potosiite: Potosiite, a mineral which has recently been discovered (WOLF et al., 1981) appears as a microscopic crystal, 5 to 10 μm in size, in ore from the Andacabe mine in the Potosi district, and closely assembles with quartz, galena and cerussite.

Herzenbergite: Herzenbergite occurs in the Maria Teresa mine, and closely associates with pyrite, cassiterite, stannite, sphalerite, arsenopyrite and chalcopyrite (RAMDOHR, 1935).

Berndtite: This occurs as a fine hexagonal crystal of a secondary mineral as an inclusion in pyrite in the oxidation zone which corresponds to the upper part of the ore deposits in Cerro Rico de Potosi (MOH and BERNDT, 1964; MOH, 1966).

Ottemannite: Ottemannite is also a secondary mineral, and appears as a fine, lath-like crystal in the oxidation zone of Cerro Rico de Potosi. It often shows twin and strong anisotropism (MOH and BERNDT, 1964; MOH, 1966).

Chemical Compositions and Crystal Data of Tin Minerals

Cassiterite: Analytical data obtained by EPMA for cassiterite from principal Bolivian tin deposits were given by SUGAKI et al. (1981a, 1986a). The iron content of cassiterite in the five type veins described above is shown in Fig. 7. The FeO mol% in cassiterite from the quartz-tourmaline vein (I) is 0 to 2.1 (Viloco), 0 to 2.7 (Avicaya), and 2.7 to 5.9 (Chorolque). In the quartz (II) vein, it is 0.1 to 1.9 at Huanuni. Cassiterite from the quartz-pyrite (III) vein of Siete Suyos has 1.4 to 8.8 mole% FeO. The iron content of cassiterite from the sulfide (IV) and sulfosalt (V) veins is less than 2.6 mole% FeO, except at Potosi, where it is 4.3 to 9.4 mole% FeO, which is the highest among cassiterites from the Bolivian tin deposits. Cassiterite from the Japo, Santa Fe and Morococala mines (sulfide veins) and Trinacria (sulfosalt vein) has less than 0.2 mole% FeO.

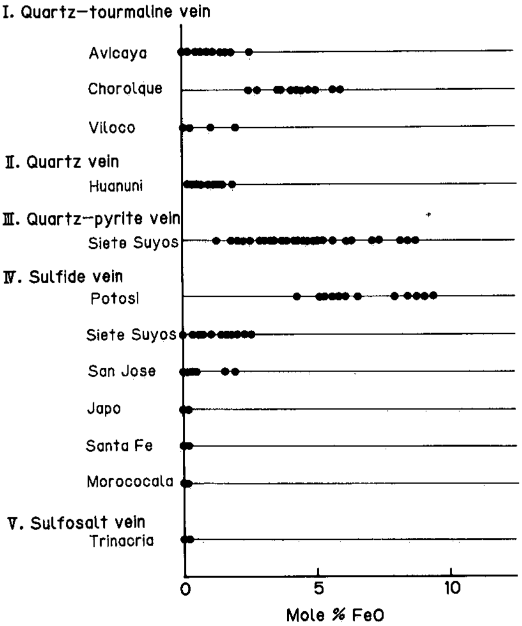

Fig. 7 FeO contents of cassiterite crystallized at stages from I to V of the mineralization.

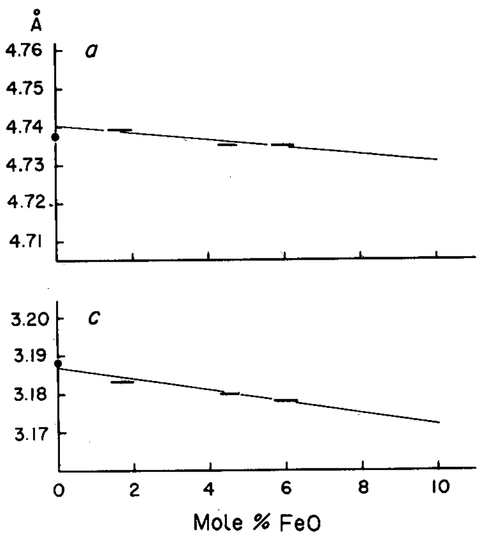

Fig. 8 Relation between cell parameters and iron contents of cassiterite.

On the other hand, cassiterite from Siete Suyos (quartz-pyrite vein) contains 0.0 to 0.3 mole% In_2O_3 in addition to FeO.

The relation between cell constant (SUGAKI et al., 1981a, 1986a) and the iron content of cassiterite from the Bolivian tin deposits is shown in Fig. 8. The cell parameters *a* and *c*

Table 2 Analytical data obtained by EPMA for stannite-kesterite system mineral and rhodostannite

	Weight percent							Atomic percent					
	Cu	Fe	Zn	Sn	In	S	Total	Cu	Fe	Zn	Sn	In	S
Stannite	Tatasi mine, Santo Domingo vein, -70mL												
	25.3	13.7	4.2	22.4	4.6	29.8	100.0	21.4	13.1	3.4	10.1	2.1	49.9
	25.4	14.4	3.2	22.6	4.7	29.9	100.2	21.4	13.7	2.6	10.2	2.2	50.0
	25.6	14.5	2.4	21.9	5.2	29.8	99.4	21.6	14.0	2.0	10.0	2.4	50.0
	Tatasi mine, Angeles vein, -70mlL												
	27.8	11.7	2.7	25.4	1.6	30.0	99.2	23.6	11.3	2.3	11.5	0.7	50.5
	27.2	12.0	3.3	25.5	2.9	29.5	100.4	23.1	11.6	2.7	11.6	1.4	49.7
	27.5	12.4	3.6	25.3	1.2	30.1	100.1	23.2	11.8	2.9	11.4	0.6	50.2
	Tatasi mine, Angeles vein, -70mL												
	27.4	1.2	14.1	26.5	1.9	29.1	100.2	23.7	1.2	11.9	12.3	0.9	50.0
	27.5	2.8	11.9	26.5	2.2	29.1	100.0	23.8	2.8	10.0	12.3	1.1	50.0
	28.4	7.9	7.0	26.0	2.0	29.0	100.3	24.3	7.7	5.8	12.0	0.9	49.3
	Animas mine, Inca Ramo 6 vein, 617L												
	28.5	12.7	1.4	26.8	0.7	29.7	99.9	24.2	12.3	1.2	12.2	0.3	49.9
	28.2	13.5	1.2	26.7	0.3	29.8	99.8	23.9	13.0	1.0	12.1	0.1	50.0
	27.7	13.9	1.4	25.6	1.1	29.7	99.4	23.5	13.4	1.2	11.6	0.5	49.9
	Animas mine, Colorada Ramo A vein, 545L												
	29.1	12.2	0.8	27.2	0.1	29.7	99.1	24.8	11.9	0.7	12.4	0.0	50.2
	28.8	12.6	0.6	27.7	0.0	29.6	99.2	24.6	12.2	0.5	12.7	0.0	50.1
	29.4	12.8	0.5	27.3	0.1	30.1	100.2	24.7	12.3	0.4	12.3	0.1	50.3
	Siete Suyos mine, Nueva vein, 14L												
	28.2	11.6	2.8	27.6	0.1	29.7	99.9	23.9	11.2	2.3	12.6	0.0	50.0
	28.4	11.9	1.6	27.8	0.0	29.8	99.4	24.2	11.5	1.3	12.7	0.0	50.3
	28.1	12.2	1.9	27.8	0.6	29.6	100.1	23.9	11.8	1.6	12.7	0.3	49.9
Rhodostannite	San Francisco mine, Falla Poopo vein												
	18.7	7.8	0.0	43.2	0.0	30.7	100.3	16.8	8.0	0.0	20.8	0.0	54.5
	18.6	8.0	0.0	42.4	0.0	30.6	99.6	16.8	8.1	0.0	20.4	0.0	54.6
	18.7	7.9	0.0	43.0	0.0	29.9	99.5	17.0	8.1	0.0	20.9	0.0	53.9
	18.8	7.9	0.0	42.9	0.0	29.9	99.5	17.1	8.2	0.0	20.9	0.0	53.8
	18.3	8.0	0.0	42.3	0.0	30.8	99.4	16.4	8.2	0.0	20.4	0.0	54.9

decrease slightly in proportion to an increase in FeO content.

Stannite-kesterite system mineral: Stannite from the Bolivian tin deposits contains some zinc, and forms a solid solution with kesterite. Analytical data obtained by EPMA for the stannite-kesterite system minerals from the San Jose, Huanuni and Avicaya mines were given by SUGAKI et al. (1981a). Chemical compositions of the stannite-kesterite system minerals from the Tatasi, Animas and Siete Suyos mines are given in Table 2. The zinc content of stannite and kesterite in mole% Cu_2ZnSnS_4 is shown in Fig. 9. Stannite from the quartz-pyrite (III) veins (Avicaya and Siete Suyos) has 0.5 to 19.5 mole% Cu_2ZnSnS_4. However, stannite from sulfide (IV) veins at all mines (San Jose, Siete Suyos, Huanuni and Tatasi) except the one at Viloco, contains more zinc than that from quartz-pyrite (III) veins, as seen in Fig. 9. Stannite from the Tatasi mine has a wide range of the solid solution with kesterite from 12.3 to 90.7 mole% Cu_2ZnSnS_4. Stannite sometimes contains indium of 0.0 to 0.3 (Siete Suyos) and 0.0 to 2.4 (Tatasi) atomic %, while kesterite has 0.0 to 0.1 (Siete Suyos) and 0.2 to 1.1 (Tatasi) atomic % In. X-ray powder data and optical reflectance for stannite were given by SUGAKI et al. (1981a).

Rhodostannite: Analytical data by EPMA for rhodostannite from the Trinacria mine are also shown in Table 2. Atomic values of each element for total atoms equal to 14 are Cu: 2.20–2.39, Fe: 1.12–1.15, Sn: 2.86–2.93 and S: 7.53–7.69. The amounts of copper and iron are more than that for the ideal composition $Cu_2FeSn_3S_8$ of rhodostannite, but other ele-

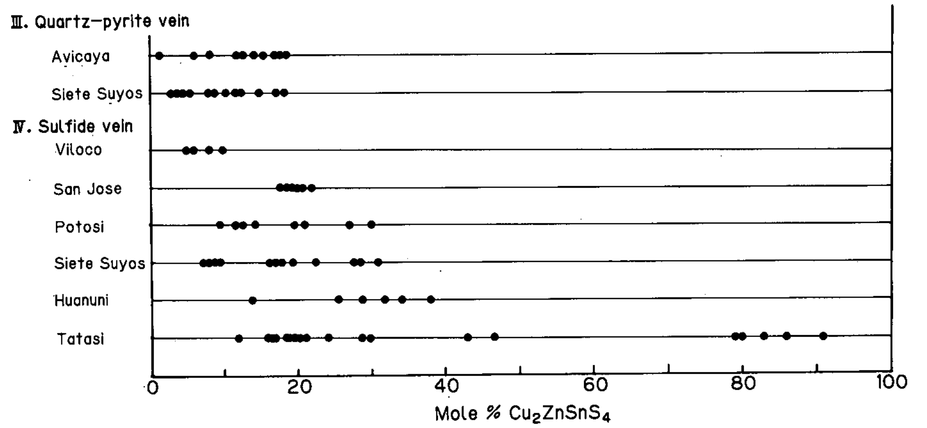

Fig. 9 Chemical compositions of stannite-kesterite system minerals from quartz-pyrite (III) sulfide (IV) veins.

Table 3 Data of X-ray powder diffraction for rhodostannite from Trinacria

	(1)			(2)	
hkl	I	d(obs)	d(calc)	I	d(obs)
101	50	5.93	5.93	60	5.965
112	10	3.64	3.65	35	5.655
211	100	3.12	3.12	100	3.117
202	10	2.99	2.95	20	2.984
220	70	2.585	2.587	80	2.585
213	5	2.362	2.369	15	2.3719
312	5	2.113	2.110	15	2.1102
321	40	1.992	1.991	55	1.9896
224	60	1.825	1.825	100	1.8272
411	15	1.745	1.749	25	1.7477
332	3	1.634	1.635	7	1.6345
413	-	-	-	35	1.5766
422	-	-	-	15	1.5586
404	-	-	-	35	1.4924
501	-	-	-	15	1.4477
424	1	1.380	1.381	8	1.3814
503	3	1.347	1.346	40	1.3460
440	5	1.294	1.293	40	1.2922
307	-	-	-	2	1.2628
208	-	-	-	3	1.2181
505	-	-	-	30	1.1935
602	-	-	-	6	1.1854
228	5	1.153	1.153	40	1.1554
541	-	-	-	10	1.1343

(1) Rhodostannite, Trinacria mine, Tetragonal, a=7.316, c=10.303 A.
(2) Synthetic rhodostannite (SUGAKI et al. 1980), Tetragonal, a=7.309, c=10.336 A.

ments exist in amounts smaller than the ideal value.

X-ray powder data for rhodostannite from Trinacria are given in Table 3 along with those of a synthetic one (SUGAKI et al., 1980). Both sets of data are in good accord with each other. The cell parameters for rhodostannite from Trinacria are tetragonal, **a**=7.316(3), and **c**=10.303(5) Å. Its **c** value is slightly smaller than that of the synthetic one.

Franckeite: Chemical compositions obtained by EPMA for franckeite from the San Jose, Trinacria, San Francisco and Siete Suyos mines are given in Table 4. Franckeite always contains iron from 2.9 to 5.2 atomic % in addition to the principal elements of lead, antimony, tin and sulfur. As pointed out by MACOVICKY (1974), it may be said that iron is necessary as a constituent element to form franckeite structure. Thus, the ideal composition of franckeite may be newly given as $FePb_6Sb_2Sn_2S_{14}$ instead of $Pb_5Sb_2Sn_3S_{14}$, as given by PALACHE et al. (1944). Franckeite from Siete Suyos also has small amounts of indium from 0.0 to 0.4 atomic %. The compositions of franckeite from San Jose, Siete Suyos and Trinacria are shown in the Pb-Sb-(Sn+In) diagram (Fig. 10). As seen in the figure, franckeite from these mines is more tin rich than that of the ideal composition.

Optical reflectance and micro-indentation hardness of franckeite are given by Table 5. These values are in good agreement with those reported by UYTENBOGAARDT and BURKE (1971). X-ray powder data for franckeite from San Jose are also given in Table 6.

Cylindrite: Analytical data by EPMA for cylindrite from the Trinacria mine are shown in Table 4. Cylindrite always contains small amounts of iron from 3.3 to 3.8 atomic %, the

Table 4 Chemical compositions analysed by EPMA for franckeite and cylindrite

	Weight percent							Atomic percent					
	Fe	Pb	Sb	Sn	In	S	Total	Fe	Pb	Sb	Sn	In	S
Franckeite	San Jose mine, D vein												
	2.4	54.3	10.6	12.5	0.0	20.5	100.3	3.7	23.1	7.6	8.3	0.0	56.2
	2.3	55.4	10.5	11.7	0.0	20.4	100.2	3.7	23.6	7.6	8.7	0.0	56.2
	2.5	54.4	10.9	11.9	0.0	20.6	100.3	3.9	23.0	7.9	8.8	0.0	56.3
	1.9	54.1	10.9	12.3	0.0	20.8	100.0	2.9	23.0	7.9	9.1	0.0	57.1
	2.5	55.7	11.0	12.3	0.0	20.0	101.5	4.0	23.8	8.0	9.2	0.0	55.0
	Trinacria mine												
	2.4	55.6	11.1	10.8	0.0	19.9	99.8	3.8	24.1	8.2	8.2	0.0	55.7
	2.4	55.7	11.2	11.1	0.0	19.9	100.3	3.8	24.1	8.3	8.3	0.0	55.6
	2.3	55.5	11.0	11.2	0.1	20.1	100.2	3.7	23.9	8.1	8.4	0.1	55.9
	2.4	55.9	10.4	11.1	0.6	19.9	100.3	3.9	24.1	7.7	8.4	0.4	55.5
	2.1	55.2	10.3	11.7	0.4	19.9	99.6	3.4	24.0	7.6	8.9	0.3	55.8
	San Francisco mine, Falla Poopo vein												
	2.6	54.4	11.3	10.4	0.1	19.9	98.7	4.2	23.6	8.3	7.9	0.1	55.9
	2.5	54.4	11.5	10.8	0.1	20.0	99.2	4.1	23.5	8.4	8.1	0.1	55.8
	2.4	55.7	10.4	11.4	0.1	19.9	99.9	3.9	24.1	7.7	8.6	0.1	55.7
	3.3	54.7	9.8	11.8	0.1	20.1	99.7	5.2	23.3	7.1	8.8	0.1	55.5
	2.5	55.3	11.2	10.8	0.1	20.0	100.1	4.0	23.8	8.2	8.1	0.1	55.7
	Siete Suyos mine, Salvadora vein												
	2.5	54.4	11.5	10.8	0.1	20.0	99.2	4.1	23.5	8.4	8.1	0.1	55.8
	2.4	55.5	11.3	11.0	0.1	19.9	100.1	3.9	24.0	8.3	8.3	0.1	55.5
	2.4	55.9	10.4	11.1	0.6	19.9	100.3	3.9	24.1	7.7	8.4	0.4	55.5
	2.7	54.3	11.0	11.4	0.1	19.9	99.4	4.2	23.4	8.1	8.6	0.1	55.6
	2.1	55.2	10.3	11.7	0.4	19.9	99.6	3.4	24.0	7.6	8.9	0.3	55.8
Cylindrite	Trinacria mine												
	2.8	35.8	12.2	24.7	0.0	25.1	100.6	3.8	13.1	7.6	15.9	0.0	59.6
	2.6	35.0	11.8	25.9	0.0	25.3	100.6	3.5	12.7	7.4	16.6	0.0	59.8
	2.8	34.0	12.1	26.3	0.0	25.1	100.3	3.8	12.4	7.5	16.8	0.0	59.5
	2.6	34.6	11.9	26.7	0.0	24.8	100.6	3.6	12.7	7.5	17.2	0.0	59.0
	2.4	34.6	12.0	26.9	0.0	24.6	100.5	3.3	12.7	7.6	17.4	0.0	58.9

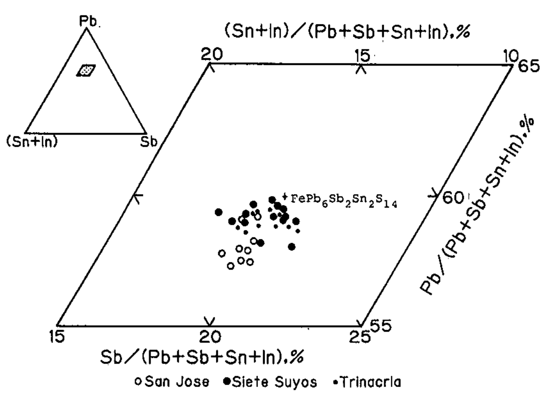

Fig. 10 Compositions of franckeite from the San Jose, Siete Suyos and Trinacria mines in the Pb-Sb-(Sn+In) diagram.

same as that of franckeite. From the analytical values, the ideal formula for composition is given as $FePb_3Sb_2Sn_4S_{15}$ instead of $Pb_3Sb_2Sn_4S_{14}$ given by PALACHE et al. (1944). The compositions of cylindrite from Trinacria are shown in Fig. 11 along with other data for cylindrite from Poopo reported by PALACHE et al. (1944) and MACOVICKY (1974). These data are very close to each other.

Table 5 Reflectance and microhardness for franckeite and cylindrite

	Franckeite		Cylindrite	
	San Jose	1	Trinacria	1
Reflectance (%)				
480nm	32.5-38.2	31.6-35.1	31.2-33.5	30.4-32.9
546	31.7-37.4	26.6-34.3	28.7-32.8	28.2-30.9
589	30.4-36.3	29.9-33.8	28.5-32.1	28.1-30.9
660	29.3-35.1	29.1-33.8	28.2-31.8	27.9-30.6
Microindentation hardness (kg/cm^2)				
	38 - 88	32 - 85	51 - 85	31 - 131

San Jose (D vein) : This study
Trinacria: This study
1 : UYTENBOGAARDT and BURKE (1971)

Table 6 X-ray powder data for franckeite from the San Jose mine

(1)				(2)	
I	d(obs)	hkl	d(calc)	I	d
5	5.85	010	5.83	-	-
10	5.78	006	5.77	25	5.73
5	5.44	-	-	-	-
3	5.15	-	-	-	-
20	4.32	008	4.33	50	4.30
5	4.14	810	4.15	-	-
5	4.13	-	-	-	-
5	3.997	-	-	-	-
5	3.804	-	-	-	-
5	3.680	-	-	-	-
70	3.466	0,0,10	3.462	100	3.44
5	3.172	-	-	-	-
30	3.125	15,0,1	3.132	50	3.11
5	3.030	15,0,3	3.035	-	-
100	2.938	16,0,1	2.938	100	2.91
15	2.914	020	2.914	-	-
80	2.888	{0,0,12 1,0,12	2.885} 2.880	100	2.86
80	2.857	{2,0,12 16,0,3	2.860} 2.857	100	2.82
5	2.771	024	2.763	-	-
10	2.710	16,0,5	2.713	-	-
10	2.648	15,0,7	2.654	-	-
10	2.528	16,0,7	2.533	-	-
10	2.430	15,0,9	2.435	-	-
40	2.348	16,0,9	2.340	50	2.36
20	2.300	-	-	-	-
15	2.260	-	-	-	-
15	2.228	-	-	-	-
50	2.161	1,0,16	2.159	50	2.22
15	2.155	2,0,16	2.152	-	-
15	2.133	-	-	-	-
65	2.071	16,2,0	2.073	75	2.05

(1) Franckeite, D Vein, San Jose mine.
(2) Franckeite, Bolivia (COULON et al.,1961)

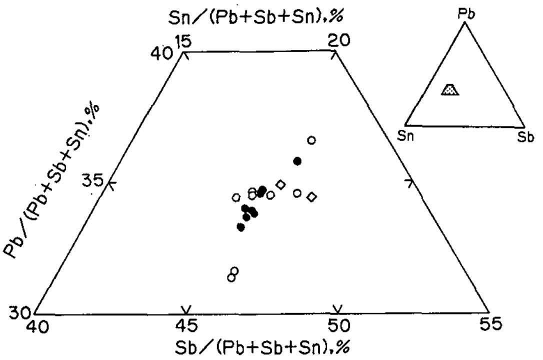

Fig. 11 Chemical composition of cylindrite from Trinacria mine in the Pb–Sb–Sn diagram together with data by MACKOVICKY (1974) and PALACHE et al. (1964).

Table 7 X-ray powder data for cylindrite from the Trinacria mine

(1)		(2)		
I	d	I	d	hkl
30	5.85	45	5.8	200
10	4.28	-	-	
10	3.963	-	-	
50	3.904	90	3.90	300,111
40	3.828	100	3.85	111
20	3.755	45	3.73	111
20	3.498	55	3.47	211
15	3.350	10	3.39	211
15	3.227	20	3.33	
30	3.172	45b	3.16	
5	3.150	-	-	
5	3.132	-	-	
70	3.075	65	3.06	002
40	3.014	-	-	
100	2.927	20	2.927	400
30	2.881	100	2.885	020
65	2.842	65	2.849	120,102
75	2.793	45	2.786	102,311
20	2.726	-	-	
5	2.708	-	-	
5	2.646	-	-	
5	2.591	-	-	
5	2.558	-	-	
5	2.526	10	2.485	
10	2.405	20b	2.387	320,302
10	2.371	10	2.324	500
5	2.334	-	-	
5	2.282	-	-	
5	2.251	-	-	
7	2.191	10	2,194	
5	2.165	-	-	
5	2.072	-	-	
45	2.047	65	2.044	022
50	2.037	65	2.026	122

(1): Cylindrite, Trinacria mine.
(2): Cylindrite, Poopo (MACOVICKY, 1974).

Reflectance and micro-hardness of cylindrite compared with those of franckeite are given in Table 5. Cylindrite is slightly darker than franckeite for all of the wavelengths measured.

X-ray powder data for cylindrite from Trinacria are given in Table 7 in comparison with those from Poopo reported by MACOVICKY (1974). The main reflections are very similar to each other.

Hocartite: Analytical data by EPMA for hocartite from the Siete Suyos mine are given in Table 8. Hocartite contains zinc and copper as minor elements in addition to silver, iron, tin, and sulfur as principal elements. Its zinc

Table 8 Analytical data by EPMA for hocartite from the Salvadora vein, Siete Suyos mine

Weight percent							Atomic percent					
Cu	Ag	Fe	Zn	Sn	S	Total	Cu	Ag	Fe	Zn	Sn	S
0.2	41.3	8.6	2.2	22.5	24.3	99.1	0.2	25.2	10.2	2.2	12.5	49.8
0.1	41.3	8.9	2.3	22.6	24.4	99.6	0.1	25.0	10.4	2.3	12.4	49.8
0.2	41.1	8.9	2.4	22.7	24.6	99.9	0.2	24.8	10.4	2.4	12.4	50.0
0.1	41.3	8.8	2.5	22.6	24.4	99.6	0.1	25.0	10.3	2.5	12.4	49.7
0.2	41.1	8.8	2.6	22.7	24.4	99.7	0.2	24.8	10.3	2.6	12.5	49.7

Table 9 X-ray powder data of hocartite from the Siete Suyos mine

	(1)			(2)	
hkl	I	d(obs)	d(calc)	I	d(obs)
002	-	-	-	4	5.484
101	-	-	-	10	5.106
110	-	-	-	5	4.080
112	100	3.26	3.27	100	3.274
103	-	-	-	5	3.090
200	30	2.88	2.89	30	2.886
004	20	2.73	2.72	14	2.742
202	-	-	-	4	2.554
211	-	-	-	7	2.513
114	10	2.26	2.27	3	2.276
213	-	-	-	3	2.109
220	50	2.04	2.04	35	2.041
204	60	1.98	1.98	55	1.9879
222	10	1.913	1.911	2	1.9131
301	-	-	-	2	1.8950
310	-	-	-	1	1.8255
312	50	1.730	1.731	40	1.7321
314	-	-	-	1	1.5196
323	-	-	-	1	1.4669
400	30	1.442	1.443	11	1.4431
008	-	-	-	5	1.3720
332	10	1.319	1.320	12	1.3206
413	10	1.306	1.307	1	1.3072
316	20	1.288	1.288	20	1.2920
404	-	-	-	5	1.2772
208	-	-	-	4	1.2388
415	-	-	-	1	1.1802
424	-	-	-	19	1.1679
228	10	1.133	1.133	11	1.1383
503	10	1.101	1.100	1	1.1008

(1) Hocartite, Salvadora vein, Siete Suyos mine, Tetragonal, a=5.773, c=10.898 A.
(2) Synthetic hocartite, Tetragonal, a=5.772, c=10.973 A.

Table 10 Chemical composition of teallite from the San Carlos Ramo 4 vein, Colquiri mine

Weight percent					Atomic percent			
Zn	Pb	Sn	S	Total	Zn	Pb	Sn	S
1.0	45.5	36.8	17.5	100.8	1.4	20.1	28.4	50.0
0.4	42.8	38.5	17.3	99.0	0.6	19.2	30.1	50.1
0.3	40.7	40.5	17.3	98.8	0.4	18.2	31.5	49.9
0.3	36.5	45.4	17.8	100.0	0.4	15.7	34.1	49.8
0.5	32.5	48.8	18.0	99.9	0.7	13.8	36.1	49.3
3.0	30.8	47.5	18.9	100.2	3.9	12.6	33.7	49.8
1.5	28.9	51.0	19.0	100.2	1.9	11.8	36.2	50.0
6.0	29.6	44.7	19.4	99.7	7.5	11.7	31.0	49.7
5.1	29.0	45.9	19.2	99.2	6.5	11.6	32.1	49.8
9.2	29.2	40.7	20.3	99.4	11.2	11.2	27.5	50.3

Table 11 X-ray powder data for teallite from the Colquiri mine

	(1)			(2)	
hkl	I	d(obs)	d(calc)	I	d(obs)
110	5	4.02	4.01	6	3.993
120	20	3.423	3.421	10	3.416
021	15	3.314	3.325	16	3.327
101	25	2.968	2.963	6	2.952
040	100	2.840	2.839	100	2.856
131	12	2.326	2.333	10	2.334
210	6	2.098	2.106	2	2.096
141	6	2.049	2.050	10	2.052
150	5	2.010	2.007	6	2.014
230	1	1.860	1.865	6	1.861
151	-	-	-	6	1.808
122	1	1.768	1.759	2	1.755
160	2	1.733	1.731	6	1.739
061	7	1.718	1.718	6	1.725

(1) Teallite, San Carlos vein, Colquiri mine, Orthorhombic a=4.29(1), b=11.36(2), c=4.10(1) A.
(2) Synthetic teallite (MOSBURG et al. 1961)

content is in a narrow range from 2.2 to 2.6 atomic %, while its copper content is less than 0.2 atomic %. The values of (Ag+Cu) and (Fe+Zn) in atomic % are 25.0 to 25.4 and 12.4 to 12.9, respectively, and are in good accordance with the ideal composition of hocartite, (Ag+Cu): 25.0 atomic % and (Fe+Zn): 12.5 atomic %.

X-ray powder data for the same hocartite used in EPMA is given in Table 9, in comparison with those of a synthetic one.

Teallite: Analytical data obtained by EPMA for teallite from the Colquiri mine are given in Table 10. As seen in the table, atomic ratios of

Table 12 Analytical data for canfieldite from the Asunta mine

Weight percent					Atomic percent			
Ag	Ge	Sn	S	Total	Ag	Ge	Sn	S
76.4	0.5	6.3	17.0	100.2	53.3	0.3	6.5	39.9
76.2	0.7	6.1	17.0	100.0	53.2	0.4	6.3	40.0
76.3	0.7	6.3	17.1	100.4	53.0	0.4	6.5	40.0
76.1	0.9	5.7	17.0	99.7	53.4	0.6	5.9	40.1
76.0	0.8	5.9	17.0	99.7	53.3	0.5	6.1	40.1

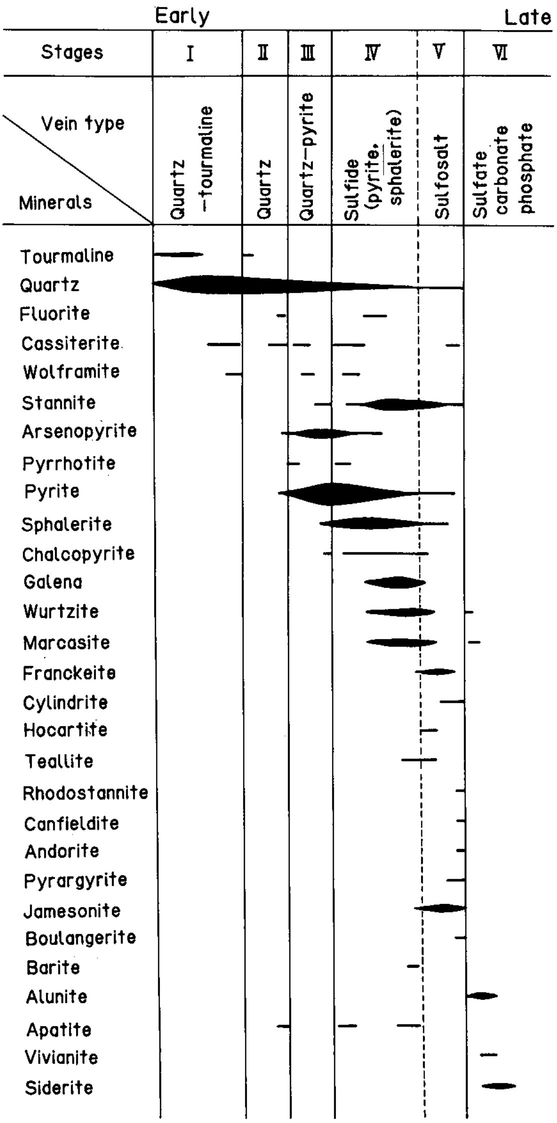

Fig. 12 Stages of mineralization on principal minerals from the Bolivian type tin deposits.

Pb/(Pb+Sn) for teallite from Colquiri show values from 24.6 to 41.4 which are more tin rich than the ideal composition of teallite $PbSnS_2$. Teallite from Colquiri also contains zinc from 0.4 to 11.2 atomic %.

X-ray powder data for teallite from Colquiri are shown in Table 11, compared with those of a synthetic one reported by MOSBURG et al. (1961). Both the data are in good agreement with each other.

Canfieldite: EPMA data for canfieldite from the Asunta mine are shown in Table 12. It contains small amounts of germanium from 0.3 to 0.6 atomic %. The values of Ge/(Ge+Sn) corresponding to argyrodite mole is in the range of 4.4 to 9.2 in atomic ratio.

Mineralization Stages of Tin Minerals

Tin-bearing polymetallic ore deposits in Bolivia were produced by six stages of mineralization, as mentioned already. Crystallization sequences of the principal minerals are shown in Fig. 12 in relation to the mineralization stages I to VI. Of these stages, the latest stage, VI, has no relation to tin mineralization.

According to TURNEAURE (1935), CAMPBELL (1947), and CHACE (1948) who studied tin deposits of the Llallagua, Colquiri and San Jose mines, respectively, cassiterite was crystallized at the early stages and stannite was crystallized at the middle to late stages of mineralization. KELLY and TURNEAURE (1970), who investigated many Bolivian tin deposits, also obtained the same results as those reported above on the tin mineralizaton stages. However, as shown in Fig. 12, cassiterite was crystallized at each stage of the mineralization except stage VI. On the other hand, crystallization of stannite (and kesterite) was mainly performed at stage IV of sulfide mineralization, but considerable amounts of stannite were also produced at stages III and IV. Franckeite, hocartite, teallite, cylindrite, rhodostannite and canfieldite were mostly crystallized at stage V along with lead-antimony sulfosalt (jamesonite, boulangerite) and silver-bearing sulfosalt minerals (pyrargyrite, andorite). Among these minerals, teallite, franckeite and hocartite were crystallized slightly earlier in the stage than cylindrite, rhodostannite and canfieldite.

The homogenization temperature and salinity (NaCl equivalent concentration) of the fluid inclusions in quartz crystallized at each stage from I to V were measured. These data are summarized in Table 13. As seen in the table, there is a tendency for both the homogenization temperature and the salinity of fluid inclusion to decrease with the progress of the mineralizations from the early (I) to the late (V) stages. Also, both the homogenization temperature and salinity of the fluid inclusions have conspicuously high values, especially at stages I and II. The data on the homogenization temperatures, iron content in sphalerite with pyrite and stable field of arsenopyrite, ranges of formation temperatures and sulfur fugacities at the quartz-pyrite (III), sulfide (IV) and sulfosalt (V) stages are shown in Fig. 13. The temperature and sulfur fugacity conditions at each stage overlap, but on the whole decrease from stage III to V. Iron content in sphalerite at the quartz-pyrite, sulfide and sulfosalt stages are 10 to 20, 5 to 20 and 0.5 to 5 mol%FeS, respectively.

Table 13 Homogenization temperature and salinity data for fluid inclusion in quartz at each stage of mineralizations

Mineralization stage	Homogenization temperature(°C)	Salinity Eq. wt% NaCl
I	260 - 510	18.5 - 55.4
II	250 - 405	23.4 - 26.0
III	250 - 400	4.4 - 19.7
IV	230 - 350	1.5 - 10.6
V	190 - 300	0.4 - 5.4

Summary

Cassiterite, stannite, kesterite, franckeite, hocartite, teallite, cylindrite, rhodostannite, canfieldite, herzenbergite, incaite and potosiite are tin-bearing minerals found in the Bolivian polymetallic ore deposits formed by Miocene acidic igneous activities. Ottemannite and berndtite also occur as secondary minerals in Cerro Rico de Potosi. The mineralizations produced in the Bolivian polymetallic deposits are generally divided into six progressive stages: quartz-tourmaline (I), quartz (II),

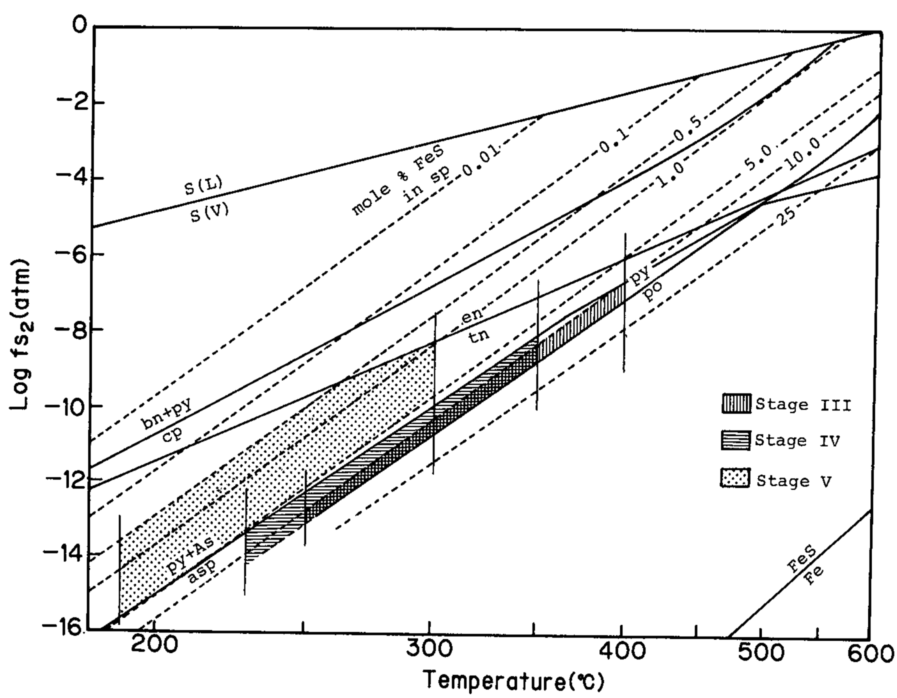

Fig. 13 Range of temperature and sulfur fugacity inferred on the basis of quartz-pyrite (III), sulfide (IV) and sulfosalt (V) stage mineralization in Bolivian tin deposits.
asp: arsenopyrite, bn: bornite, cp: chalcopyrite, en: enargite, po: pyrrhotite, py: pyrite, tn: tennantite.

quartz-pyrite (III), sulfide (IV), sulfosalt (V) and sulfate-phosphate (VI) (Fig. 12).

Cassiterite, the most important tin mineral, principally occurs in the quartz-tourmaline, quartz and quartz-pyrite veins although it subordinately appears in the sulfide and sulfosalt veins. Cassiterite in the quartz-tourmaline, quartz, and quartz-pyrite veins generally contains more iron than that in the sulfide and sulfosalt veins. Stannite-kesterite system mineral is the second most important tin mineral, and it mainly occurs in sulfide veins, although stannite is also found in quartz-pyrite and sulfosalt veins. Kesterite tends to occur in sulfide veins. Tin-bearing sulfide and sulfosalt minerals such as franckeite, hocartite, teallite, cylindrite, rhodostannite and canfieldite appear in small amounts in comparison with cassiterite and stannite, and are mostly found in sulfosalt veins. But teallite sometimes appears in sulfide veins consisting of sphalerite and pyrite. No tin minerals appear in sulfate-phosphate veins formed at the latest stage of mineralization. No stannoidite or mawsonit has been observed in the ores from Bolivian tin deposits up to the present, although these tin minerals are as common as stannite elsewhere.

The homogenization temperature and the salinity of fluid inclusion in quartz formed at each stage of the mineralizations were measured to estimate formation conditions of tin minrals. These measured values range widely from 510° to 190° in homogenization temperature and 55.4 to 0.4 wt% in salinity, as suggested by the telescopic features of Bolivian tin deposits. Also, based on the data on the fluid inclusion, mineral assemblage, and sphalerite iron content, temperature and sulfur fugacity of tin mineralizations at stages III, IV and V were estimated as follows: stage III: 250° to 400° and 10^{-13} to 10^{-7} atom; stage IV: 230° to 350° and 10^{-15} to 10^{-9} atom; and stage V: 190° to 300° and 10^{-16} to 10^{-9} atom.

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ボリビア型多金属鉱床産錫鉱物とその鉱化作用

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要旨：ボリビア東アンデス山地にみられるいわゆるボリビア型多金属鉱床より錫石，黄錫鉱，亜鉛黄錫鉱，フランケ鉱，黄錫銀鉱，ティール鉱，円柱錫鉱，赤錫鉱，カンフィールド鉱，インカ鉱，ポトシ鉱などの多種類の錫鉱物が産出する．この型の鉱床は新第三紀中新世の火成活動に関係して生成されたものと考えられ，その鉱化作用はⅠ石英–電気石期，Ⅱ石英期，Ⅲ石英–黄鉄鉱期，Ⅳ硫化鉱物期，Ⅴ硫塩鉱物期，Ⅵ硫酸塩–燐酸塩鉱物期の6つの晶出期よりなる．錫石は主としてⅠ，Ⅱ，及びⅢ期に産し，黄錫鉱及び亜鉛黄錫鉱はⅣ及びⅤ期にみられる．一方，フランケ鉱，黄錫銀鉱，ティール鉱，円柱錫鉱，赤錫鉱及びカンフィールド鉱は一般にⅤ期に少量産出する．上記Ⅰ～Ⅴの鉱化期に生成した石英中の液体包有物の均質化温度及びNaCl相当濃度はそれぞれⅠ：260°～510℃，18.5～55.4%，Ⅱ：250°～405℃，23.4～26.0%，Ⅲ：250°～400℃，4.4～19.7%，Ⅳ：230°～350℃，1.5～10.6%，Ⅴ：190°～300℃，0.4～5.4%であり，また上記の温度，Ⅲ～Ⅴ鉱化期に晶出した閃亜鉛鉱の組成及び鉱物組合せより求めた各鉱化作用の硫黄フュガシティー値はⅢ：10^{-13}～10^{-7} atm.，Ⅳ：10^{-15}～10^{-9} atm.，Ⅴ：10^{-16}～10^{-9} atm. である．