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TIN IN SPHALERITE FROM THE SLOCAN DISTRICT

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INTRODUCTION

This paper is a report on microscope work done on sphaler -ite from several mines in the Slocan District. Previous to the time this work was initiated, many samples of ore from all over British Columbia had been spectrographically analysed*. This work indicated that the sphalerite from many of the mines in the Slocan District contained tin in small, yet significant percentages.

Following is given a list of Slocan Mines, with the percentage of tin found in the sphalerite from each*, spectrographically.

Property	Mineral Shot	% Tin
Lucky Jim	Sphalerite	.05 to .25
Mammoth	tf	.05 to .10
Noble Five	11	.10
Bosun	17	• 10
Surprise	"	<.05
Payne	11	• 10
Deadman	11	.15
American Boy	18	.15
Van Roi	11	.05 to .10
Hewitt	11	<. 05
Boon	18	• 05

* Thompson, R.M., University of British Columbia.

Property	Mineral Shot	% Tin	
Charleston	Sphalerite	Nil	
Silversmith	11	• O5	
Ivanhoe	11	• 05	
Standard	11	• 10	

The work done for this paper was to study microscopically the sphalerite from some of these mines to discover if possible the mode of occurrence of the tin. This study, though incomplete, was partially successful, and, it ishoped, will pave the way for future investigation. This paper presents not only the results of the present investigation, but also some of the special methods developed for determining the tin minerals.

THE LUCKY JIM MINE

The Lucky Jim consists* of a number of replacement bodies in limestone. The limestone belt, which varies from a few feet to over 100 feet in thickness, is cut nearly at right angles by a series of straight, persistent, and almost parallel fractures. Replacement outward from groups of these fissures has formed a succession of chimney-shaped ore-bodies varying from 10 feet to 50 feet in diameter and extending vertically for 150 to 250 feet. The ore in some of the shoots is almost solid sphalerite. In others, it is a mixture of sphalerite with a little galena,

^{*} Cairnes, C.E., C.G.S. Memoir 173, "Slocan Mining Camp, British Columbia". 1954, p. 100.

pyrite, calcite, and, more rarely, quartz, and varying amounts of unreplaced limestone.

Polished sections were made of the sphalerite from the No's. 10, 20, and 30 ore-bodies. Following is given a description of the significant minerals as they occur in these sections.

<u>Sphalerite</u>

In the three sections, massive sphalerite forms the continuous ground mass in which are embedded euhedral to anhedral grains of other minerals.

Stannite

Stannite is found in the Lucky Jim No. 10 section. It occurs as long, narrow, irregular anhedral grains up to 7.1 mm. (110 microns) in length, and up to 15 microns in width. The grains vary considerably in size, the majority of them being one micron or less in diameter. With the high-power objective, the tiny, irregular masses can be seen shot through most of the section.

The colour of the stannite is very faint tan. It is distinctly brighter than the sphalerite in which it is embedded, the reflectivity of stannite being about 29, while that of sphalerite only 18.5*. Its hardness is D+, and thus is a little harder than tetrahedrite. It is also weakly anistropic. It was identified by the following etch reactions: HgCl₂ neg., KOH neg., FeCl₃ neg., KCN neg., HCl neg., HNO₃ positive: stains iridescent (takes over half a minute to act). The identification was confirmed microchemically: a drop of * Short, M.N., U.S.G.S., Bulletin 914 "Microscopic Determination of the Ore Minerals", 1940, p. 296.

1:1 HNO₃ was placed on a grain of the mineral in the section, allowed to react for 2 minutes, then transferred to a glass slide, and the tests recommended by Short* carried out. Copper, iron, and tin were found to be definitely present. The formula for stannite is Cu₂S. FeS.SnS₂.

The stannite grains are, in general, surrounded by sphalerite. Though one side of some of the grains are straight, the usual contact between the stannite and sphalerite is extremely irregular, the sphalerite apparently intruding the stannite, suggesting replacement of the latter by sphalerite, (see fig. 1). Further evidence to support this is the great many groups of tiny grains of stannite, surrounded by sphalerite, which appear to be corroded remnants of larger single grains (see fig. 2).

Stannite is not found in the other two sections, Lucky Jim No's. 20 and 30.

Chalcopyrite

Chalcopyrite seems to occur in two ways. (a) As long, straight, very narrow stringers, running in several directions, forming a vague pattern. These are possibly due to exsolution of chalcopyrite from sphalerite along cleavage planes. It is to be further noted that these chalcopyrite stringers in a number of places, cut across grains of stannite without deviation. This is further evidence that the sphalerite, to which these chalcopyrite stringers are believed to be related to in time, is later than the stannite.

* Short, M.N., op-cit., p. 288.

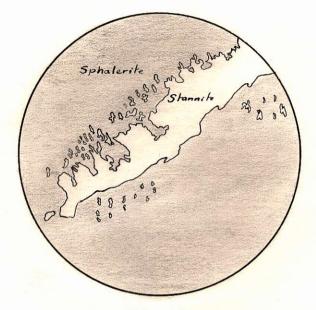
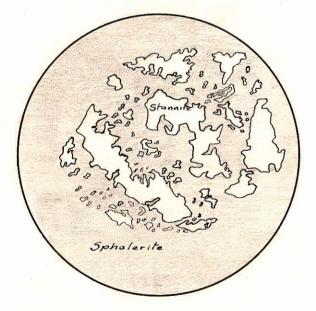


Fig. 1

Camera-lucida sketch of Lucky Jim No. 10 ore, under high-power, showing sphalerite replacing stannite (?). This is part of large grain of stannite.





Camera-lucida sketch of Lucky Jim No. 10 ore, under high-power, showing a corroded remnant of a large grain (?) of stannite which has been partially replaced (?) by sphalerite. (b) As randomly distributed blebs, the majority of which are about one micron in diameter, though some are considerably larger--up to 25 microns. This chalcopyrite seems to be definitely related to the stannite. The manner of occurrence of these two minerals is quite similar. In a number of places, they are in contact, and the boundary is smooth and curving. This chalcopyrite also seems to have been partly replaced by the sphalerite, though not to as great an extent as the stannite, probably because it is more resistant to replacement (See fig. 3).

There is a grain of chalcopyrite 25 microns in diameter in which one corner is a grain of stannite 15 microns. The contact between the two is irregular but smooth. This group of two is completely surrounded by sphalerite. The chalcopyrite-sphalerite contact is irregular, the sphalerite apparently intruding upon the chalcopyrite. The stannite-sphalerite contact is however, smooth. Within the chalcopyrite grain are tiny inclusions of both sphalerite and stannite having straight to curved contacts. (See fig. 3).

Minerals of Minor Importance

There are several minerals present in the Lucky Jim sections with which we are not primarily concerned. These are pyrite, calcite, arsenopyrite, and quartz. These all occur in small amounts. Most of the calcite occurs as small, euhedral, diamond-shaped grains. Much of the quartz is euhedral, being long, well-formed crystals. The quartz will be described later in more detail in connection with acid digestion of the Lucky



Fig. 3

Camera-lucida sketch of Lucky Jim No. 10 ore, under high-power, showing a grain made up of chalcopyrite and stannite, partially replaced (?) by sphalerite. Note the tiny inclusions of both stannite and sphalerite in the chalcopyrite. Jim ore. All the arsenopyrite and much of the pyrite occurs as euhedral grains.

Cassiterite

This mineral was positively identified in Lucky Jim ore, from No's 10, 20 and 30 ore bodies. It was not, however. recognized in polished section. Twenty-gram samples of the ore were partially crushed to about small pea-size, care being taken not to pulverize it. These were placed in large beakers and well covered with concentrated sulphuric acid, placed over low heat, and allowed to simmer for one or two days. The free sulphur is scooped off while still molten. The contents of the beaker were then dumped into large florence flasks, carefully diluted with water to the full capacity of the flask, and shaken. This dissolved the zinc sulphate and other soluble salts present. This liquor is decanted off. More water was added and the process repeated until all soluble material had been dissolved If any sphalerite or pyrite pellets remain in the resaway. idue, more concentrated acid must be added, and the digestion The final residue when washed clean and dried, and continued. examined under the microscope, using the ultropack, or even using the binoculars, was found to be mostly well-formed, long crystals of quartz. Besides this, however, there were some smaller, almost perfectly-formed tetragonal crystals having an amber to slightly violet colour. This violet tint decreased towards the center of the crystals. Some of the crystals were geniculated twins. One of the largest crystals found measured 170 microns in length. Some of these crystals were spectro-

graphically analysed, and were found to be tin. Further. some of the crystals were pulverized and there optical properties determined microscopically, which confirmed that they were cassiterite. In order to get a quantitative estimate of the percentage of cassiterite present in a sample, the residue from the sulphuric acid digestion, after being dried, is placed in bromoform in a tube, which is then centrifuged. The clean crystals of cassiterite collect on the bottom of the tube, together with, unfortunately, some quartz-cassiterite grains. Above this is a layer of quartz crystals which were found, on microscopic examination, to have tiny, brown, somewhat globular inclusions. When these quartz crystals with the inclusions were spectrographically analysed, tin lines were given, thus showing that the inclusions are most likely cassiterite, since they are also apparently heavy. Most of the inclusions were less than 10 microns in diameter. Pure quartz collected in the top part of the tube. With great care and good judgement, the pure cassiterite could be separated from the quartz, dried and weighed. The results obtained had to be slightly increased to allow for the cassiterite included in the quartz.

The results were found to vary considerably, even with ore from the same body. Cassiterite was, however, found in all three ore bodies.

The size of the majority of the cassiterite crystals is in the neighborhood of 16 microns. It is to be remembered, however, that a small percentage at least of the cassiterite occurs as tiny inclusions, less than ten microns in diameter, in the quartz.

Following is given the assay result on the Lucky Jim ore, using the digestion method, together with spectrographic analysis for tin (including stannite, of course, if present) done by the Department of Mines in Victoria.

Ore Body	% Sn from Cassiterite	% Sn, Spectrograph
No. 10	.05 to .10	0.30
No. 20	<.05 to .18	0.15
No. 30 ·	.05 to .20	0.12

Special Method for the Determination of Cassiterite in Polished Sections

Two polished sections were made up, both with known In ore, the grains of cassiterite were large: cassiterite. in the other, the grains of cassiterite were very small, and mixed with other minerals, such as sphalerite and pyrite. A drop of 1:1 HCl is placed on the cassiterite grain, and into t this is placed a tiny fragment of metallic zinc. Nothing happens to the cassiterite surface unless heat is applied, but then, only after several minutes. A hot platinum wire was at first used as a means of supplying heat to the reaction. The result is that the surface of the cassiterite becomes reduced to metallic tin, which quickly oxidizes dark. The acid is drawn off with a pipette, and the surface washed and dried. When scratched, the brilliant silver colour of tin is revealed. It was later discovered, however, that the reaction will go on

in the cold if the tip of an iron needle (be sure that the iron is exposed) is introduced into the drop. Not only is the reduction of the cassiterite surface very rapid, but also the results much more dependable, since it never seems to fail. To confirm for the presence of tin, the drop of HCl which was drawn off with a pipette is transferred to a glass slide and microchemically tested for tin, using a fragment of rubidium chloride. For surer results, a tiny drop of water should be added to the acid drop.

This test with zinc was found to be effective even with very small grains of cassiterite, and the other minerals apparently had no effect on the reaction.

The chief difficulty arises in recognizing cassiterite in polished sections. In appearance, it is very much like quartz, though it is a little rougher and more pitted generally: quartz has a very smooth, cloudy appearance, and is, further more, a little duller than cassiterite. Under oblique arc light, the quartz is quite milky in appearance, while cassiterite is more clear and has a higher luster. It can also be quite easily mistaken for sphalerite, but its hardness of G serves to distinguish it.

OTHER SLOCAN MINES

Ore from the Payne, Bosun and Deadman, one section from each, were examined. No stannite or cassiterite, however, were found. More sections from these mines should be made,

nevertheless, because the spectrographs showed tin present. As in the Lucky Jim, it is probably erratic.

CONCLUSION

Stannite occurs in the Lucky Jim No. 10 ore body, seeming -ly associated with chalcopyrite, and apparently earlier (?) than the sphalerite. Cassiterite is present in small yet significant amounts in No's. 10, 20, and 30 ore bodies, but is erratic.

The advantages of being able to identify cassiterite in polished sections are several. Though it is best determined in thin sections, the writer found that when it is embedded in a soft mineral such as sphalerite, the hard crystals are torn out during the making of the section. Further, polished sections are usually much more available being much easier to prepare. Besides this, its paragenesis is possibly more easily determined in polished section than in thin section.

As can easily be seen, there is room for much more extensive investigation, and it is hoped that this will be carried out with as little delay as possible. The work of Mr. R.M. Thompson has shown that tin occurs in a great many mines in B.C., and it is necessary to know in what minerals it occurs. Only microscope work will do this.

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