ON THE CHALCOPYRITE INCLUSIONS IN SPHALERITE (1)

by

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CONTENTS

I. Abstract

The first purpose of this work was to measure the relative percentages of chalcopyrite inclusions in the well-known intergrowth sphalerite-chalcopyrite, observed in hydrothermal ores. It seems to exist a relation between percentage and hydrothermal intensity, and between percentage and sphalerite variety as well. Low-temperature deposits show percentages of 1-2% of chalcopyrite inclusions in sphalerite, while higher temperature ores show 5-6%.

The chalcopyrite inclusions follow: a. sphalerite (110) cleavage planes; b. sphalerite twinning composition surface; c. sphalerite grain boundaries, as blebs or rims; d. subsequent fractures in sphalerite, as veinlets.

Etching experiments brought out the texture of the sphalerite, and had small effect upon the chalcopyrite. Aqua regia and nitric acid were the more convenient and satisfactory reagents.

X-ray investigation has been carried out mostly by the rotation picture method. The pictures have revealed the orientation of the chalcopyrite inclusions with respect to the sphalerite crystal structure. There is evidence that sphalerite [100] direction is parallel to the chalcopyrite [130] direction, in the specimens studied.

Inclusions of dendrite-like sphalerite crystals have been reported in a few specimens of chalcopyrite.

Exsolution is the more likely explanation for the chalcopyrite inclusions, inferred from evidences such as: texture of the intergrowth, crystal structure of sphalerite and chalcopyrite, two generations of chalcopyrite, sphalerite inclusions in chalcopyrite, size, orientation, and distribution of the chalcopyrite inclusions.

II. Introduction

Many intergrowth textures, which closely resemble exsolution textures often reported in metallography and produced by experimentation in metallurgy, have been found among the ore minerals (Schwartz, 17 19). A very small amount of a foreign element in a given solid solution is found to be sufficient to form a compound which exsolves, as the temperature decreases. For instance, a few tenths of 1% carbon in iron is enough to produce the exsolution of cementite, Fe_3C.

The similar intergrowth textures reported among the ore minerals have been suggested by many authors to be derived, likewise, as a result of exsolution process. It seems however, that in most cases, there is not yet sufficient evidence to prove exsolution. Nevertheless, some intergrowths, as for example, the magnetite-hematite-ilmenite intergrowths, have already been studied experimentally, and the explanation of the exsolution process has a definite experimental basis, which is the physico-chemical equilibrium of the system $FeO\text{-}Fe_2O_3\text{-}TiO_2$ (1, 14)

Unfortunately, in the great majority of cases of ore minerals, experimentation with the physico-chemical systems has lagged far behind, because numerous elements are present in many of the ore minerals, and yet only the minerals relatively simple would be possible of experimental physico-chemical investigation.

Schneiderhöhn (15) was one of the first mineralogists in the early twenties to call attention to exsolution among ore minerals. However, Singewald (22) although has not directly suggested exsolution for some titaniferous magnetites, he has described several microstructures of this mineral. Warren (27), in 1918, proposed unmixing (exsolution) as an explanation of some textures reported in titanic iron ores. Schwartz (17. 19) has also given a considerable thought to this problem, and he tabulates more than fifty examples of exsolution in ore minerals.

The so-called exsolution texture of sphalerite and chalcopyrite has been studied by several writers. Schwartz (18) has made some experiments on the sphalerite-chalcopyrite intergrowth, concluding that the inclusions were the result of replacement. M. W Buerger (2) has carried out experiments on Leadville, Colorado, specimens of sphalerite, heating up the specimens to various temperatures, and quenching them in freezing water. Buerger found out that the chalcopyrite inclusions were redissolved at a temperature ranging from 350° to 400° C. This temperature might, therefore, be regarded as the exsolution temperature.

Although it must be assumed that the exsolution process has been proved in the Leadville specimens, some specimens from other districts show apparently two kinds of chalcopyrite, which could be called provisionally: "exsolved" and "non-exsolved" chalcopyrite (figs. 1, 3, 24).

The first kind, the "exsolved" type, occurs as little inclusions throughout the sphalerite grains, whereas the second one occurs as large masses around the sphalerite, seeming to be corroding and replacing the sphalerite, and also incorporating the "exsolved" chalcopyrite. The "non-exsolved" chalcopyrite is usually the outer chalcopyrite.

Therefore, the following problem was set up: Have these two kinds of chalcopyrite the same origin, and therefore, are they simply representatives of successive events of the same process? Or, are they a result of different processes, as exsolution and replacement, or even filling? Or yet, are they a combined product of both processes, acting simultaneous or successively?

Newhouse (9) thinks that the occurrence of inclusions of chalcopyrite related to veins is better explained by replacement, and that the occurrence of inclusions along crystallographic planes or directions in the host minerals cannot be used as a criterion of exsolution. Lasky and

Teas (24) think also in terms of replacement, but Schneiderhöhn and Van der Veen (26) advocate strongly the exsolution hypothesis.

As a step toward the solution of the problem, a survey of specimens of sphalerite-chalcopyrite intergrowth was started. This work, however, is plainly but a beginning. Only further investigations, chiefly concerning the physico-chemical systems between iron, copper, zinc, and sulphur, or systems between compounds of these elements, would give a definite answer to the problem. In the meantime, it would be satisfying if geological and textural evidence of several kinds pointed to a given solution.

III. Occurrence

This typical sphalerite-chalcopyrite "intergrowth" texture appears to occur most commonly in sphalerite with which normal chalcopyrite is also present. This "intergrowth" has been found pratically in all levels of intensity of the hydrothermal range, although it seems to be rare in the magmatic segregation ores, and in the lowest levels of the hydrothermal range. According to Teas (24), who regarded the Mississippi Valley and similar ores as of meteoric origin, the sphalerite of these occurrences does not show the pattern of included chalcopyrite here being considered.

FIG. 1 — "Non-exsolved" and "exsolved" chalcopyrite. The first kind seems to be replacing both pyrite and sphalechalcopyrite inclusions. (Telluride 1017 rite. Borders of sphalerite richer in — Harvard collection). Approximate magnification: 140 X.

FIG. 2 — Galena is replacing selectively the sphalerite, but not attacking the chalcopyrite blebs. Galena is confined to sphalerite grain boundaries. (Ouray 1154 — Harvard collection). Approximate magnification: 140 X.

On the assumption that the pattern here dealt with is due to exsolution, three possibilities can be entertained for those sphalerites in which the pattern is not observed: a) no copper may have entered the sphalerite initially; b) the copper (and iron) may still be in the state of solid solution, instead of having exsolved; c) the size of the exsolved particles of chalcopyrite may be below the limit of microscopical resolution. The third possibility seems to be very likely, for it is known that usually in the high-intensity sphalerites, the chalcopyrite inclusions get smaller and smaller, seeming to exceed all the limits of obtainable magnification.

Some pyrrhotite inclusions have been found in sphalerite. Pyrrhotite inclusions in sphalerite were reported as occurring in the Matehuala district, Mexico (Shenon, 20). However, such pyrrhotite inclusions are much less common than chalcopyrite, and none has been seen in the specimens examined by the present writer. As pyrrhotite seems to occur only in the deep-seated type of the hydrothermal range, it would be less likely to appear in sphalerite, at least in the low-temperature sphalerites.

FIG. 3 — "Non-exsolved" and "exsolved" chalcopyrite. (Ouray 1158 — Harvard collection). Approximate magnification: 140 X.

Several districts, belonging to different levels of intensity, were the object of attention. The purpose was to cover several mineral districts, in order to obtain, not only more quantity of data, but also, to reach a more general conclusion about the problem. However, some of the districts, notably Cananea and Ouray, were the object of more careful attention than others because of their inclusion-rich sphalerite would be apt to show more recognizable relationships between the two minerals. Cananea specimens were used for X-ray investigation, because of their higher content of chalcopyrite inclusions.

The following districts were studied: Hollinger, Porcupine district, Ontario, Canada (hypothermal); Silver Bell, Arizona (pyrometasomatic); Bingham, Utah (pyrometasomatic); Cananea, Mexico (pyrometasomatic and mesothermal); Butte, Montana (mesothermal and leptothermal); Ouray, Rico, and Telluride, in Colorado (leptothermal); Tintic, Utah (leptothermal); Tonopah, Nevada (epithermal); Mogallon district, New Mexico (epithermal); and Coeur d'Alene, Idaho (mesothermal)

IV Chalcopyrite inclusions in sphalerite

A. Microscopical studies

The texture is quite constant in the specimens from several levels of intensity of the hydrothermal range, though there is a variability in size and percentage of chalcopyrite particles. This brings about slight differences from specimen to specimen. Usually, the chalcopyrite inclusions are not evenly distributed throughout the sphalerite grains. The inclusions along the boundaries are usually much smaller than the ones in the middle of the grains. At the center the inclusions retain more or less the same size, with a slight variation. The small particles are usually as much as ten times smaller than the larger ones (figs. 25, 26)

Generally large inclusions of chalcopyrite do not have many neighbors around them, fact that could be regarded as an evidence for exsolution (Frondel, 3).

1 Shape

In the following discussion on shape and size of the chalcopyrite inclusions, it should be emphasized that similar grains could be cut in different orientations, following different planes in the sphalerite, thus showing different shapes and sizes.

The size of the chalcopyrite inclusions seems to be extremely variable according to the intensity of a given deposit and according to the position of the chalcopyrite particles in the sphalerite grain, but the shape seems to be more or less constant. However, in the low-intensity deposits, where the percentage of chalcopyrite inclusions is very small, the size of the chalcopyrite particles is very minute (a few microns), and they look like small drops or globules. But, with a higher magnification the true shape can nearly always be determined; most of the chalcopyrite inclusions have edges and geometrical contours.

The chalcopyrite inclusions follow the planes of least resistance of the sphalerite, the cleavage and twinning planes. The chalcopyrite inclusions are chiefly located along such planes or at their intersections. In the first case, they are usually platy, appearing as a string of dashes in the two-dimensional plane under the microscope (figs. 4, 5) In the second case they are more equant, showing pseudo-idiomorphic habits (figs. 4, 6, 7), which can be easily detected where the particles are large enough. They have ordinarily from 3 to 12 edges, which are controlled by the dodecahedral planes of the sphalerite (cleavage pla-

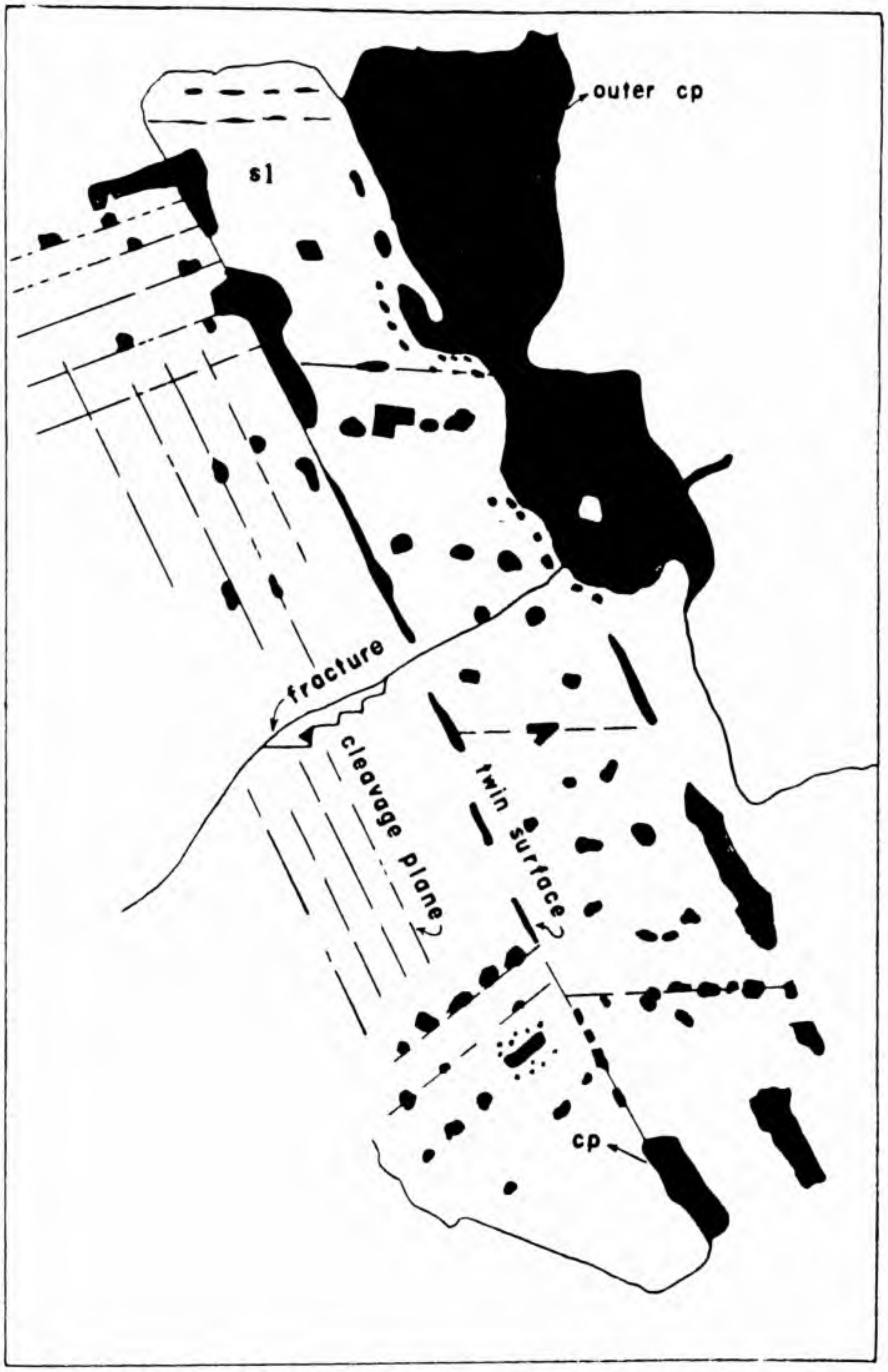


FIG. 4 — Different shapes of chalcopyrite inclusions, which are following cleavage and twinning planes of sphalerite. Outer chalcopyrite (replacing). (Cananea 1229 — Harvard collection). Approximate magnification: 140 X.

nes). Thus, this inclusion type is usually triangular, rectangular, square, hexagonal, octogonal, etc., in shape (fig. 6).

However, the chalcopyrite areas confined to the sphalerite grain boundaries do not have a geometrical shape. They are elliptical, hooklike, or stringlike in shape. Nevertheless, it is remarkable that they very seldom form a continuous vein or rim (figs. 8, 17)

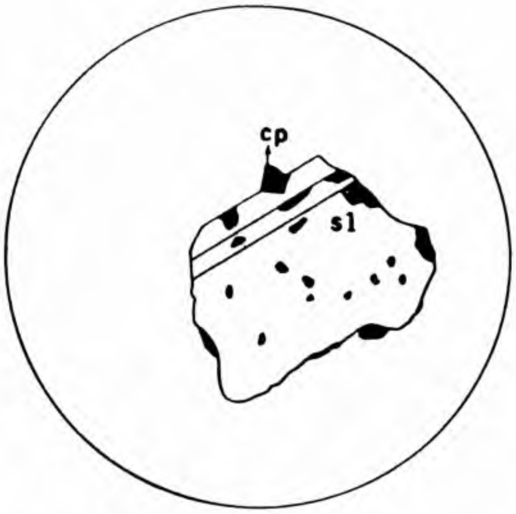


FIG. 5 — "Exsolved" chalcopyrite (cp) following twinning composition surface and grain boundaries of sphalerite (sl). Etched with conc. HNO_3. (Cananea 1229 — Harvard collection). Approximate magnification: 140 X.

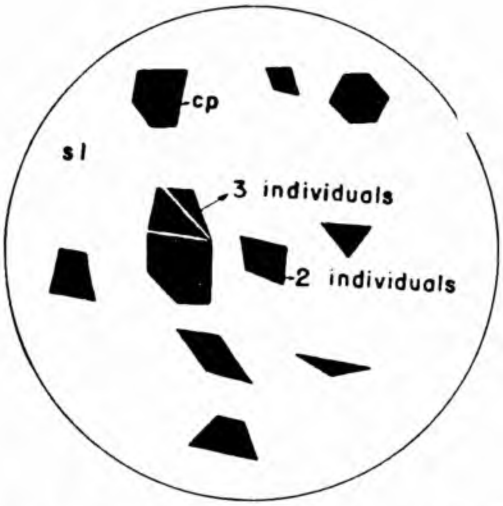


FIG. 6 — Different shapes of chalcopyrite inclusions in sphalerite. The shape is controlled by the sphalerite (110) cleavage planes. The 2- and 3-component groups in the center of the field are reveaded by polarized light. (Cananea 1229 — Harvard collection). Approximate magnification: 140 X.

When following the twinning composition plane of sphalerite the chalcopyrite inclusions are definitely strung out in dashes. At the same time, the chalcopyrite inclusions follow the cleavage plane (figs. 4, 7). V-like and X-like shapes are likewise very common (fig. 4).

2. Size

The sizes are extremely variable. The inclusions are not only more numerous, but they are also larger in the high-temperature deposits. Nevertheless, in the same deposit and in the same specimen the size varies. Near the periphery of the sphalerite grains, the size is usually smaller than near the center (figs. 9, 10, 26). Very likely the larger sizes of chalcopyrite inclusions in the high-temperature deposits are due, not only to the high content of iron and copper in the original solid solution, but also due to the increasing of rate of diffusion in solid state at high temperatures.

Usually, the larger inclusions are fewer in number, whereas the tiny ones are more numerous.

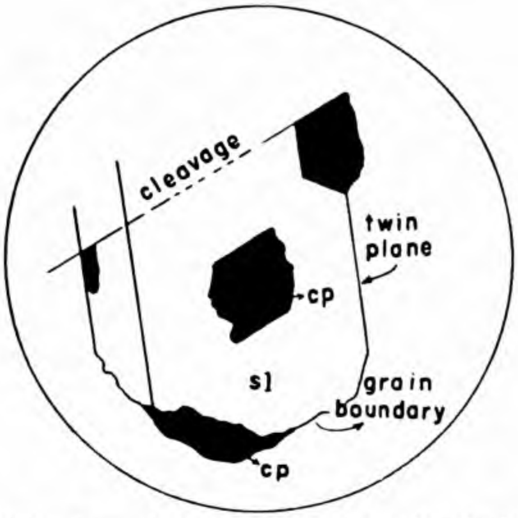


FIG. 7 — Edges of chalcopyrite inclusions parallel to cleavage plane and twinning composition plane of sphalerite. Etched with aqua regia. (Cananea 1229 — Harvard collection). Approximate magnification: 140 X.

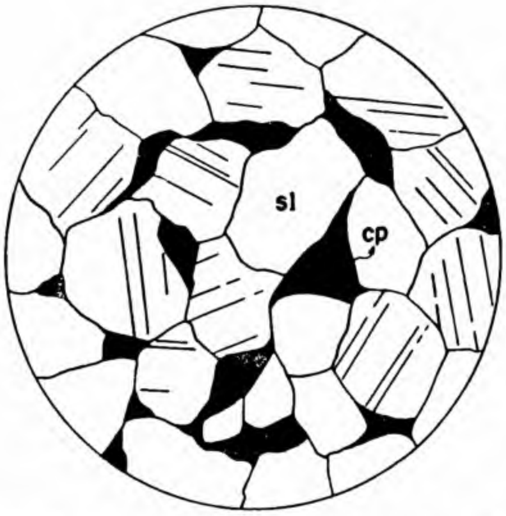


FIG. 8 — Chalcopyrite blebs confined to the sphalerite grain boundaries. Due to the fine grain of the sphalerite? Etched with aqua regia. (Coeur d'Alene 2008 — Harvard collection). Approximate magnification: 140 X.

Schneiderhöhn (15) says the chalcopyrite inclusions never exceeds 5µ X 10µ in size. However, some Cananea specimens studied have shown inclusions with 150µ in diameter, and some are still larger, distinguishable even with the naked eye.

The size, as well as the shape, is a good evidence for exsolution, chiefly when it is known that the size of the chalcopyrite grains is not extremely large, and they can have any dimension below the maximum limit, or in other words, the inclusions can possibly be so minute as not to be visible under the microscope.

3. Distribution and orientation

At first sight, it often appears as if the chalcopyrite inclusions do not follow any rule of distribution throughout the sphalerite grains. However, the alignment of several blebs suggests that they must be following some crystallographic plane in the sphalerite. (Figs. 11, 12, 13). Where the percentage is high this alignment becomes more evident; in the low-percentage specimens the regular distribution is less conspicuous.

Some authors have suggested that the chalcopyrite inclusions are parallel to the (100) planes of sphalerite (Gross, 7). Gruner (8) says the inclusions are parallel to (111) planes.

However, as far as the present study goes, it seems that the chalcopyrite inclusions are controlled by:

a. cleavage of sphalerite, which is along the (110) plane. The polygonal shape of these inclusions has been already discussed (figs. 4, 7 14).

FIG. 9 — "Non-exsolved" and "exsolved" chalcopyrite. Zoning of sphalerite grains revealed by the different sizes of chalcopyrite inclusions. (Porcupine 66 — Harvard collection). Approximate magnification: 140 X.

FIG. 10 — Large range of variability in the size of the chalcopyrite inclusions. (Silver Bell 1005 — Harvard collection). Approximate magnification: 140 X.

b. twinning composition surface, which mostly is a plane surface, though not necessarily. The fig. 15 shows how the twinning composition surface may not be plane. The shape of this type of inclusion has likewise been already discussed in the previous section (fig. 4).

c. grain boundaries. The chalcopyrite blebs here are usually irregular in shape, and more or less elliptical or egg-shaped (figs. 5, 13, 14). In some cases the chalcopyrite forms a rim of more or less constant width around the sphalerite grains (fig. 18). This case seems to resemble the case of pentlandite-pyrrhotite, where pentlandite surrounds pyrrhotite grains. This intergrowth is also reported as due to exsolution, and it has been already investigated experimentally (Newhouse, 10).

d. fractures in sphalerite. In these cases chalcopyrite usually is directly connected with the outer chalcopyrite, and seeming to be of the replacing type rather than due to exsolution (figs. 19, 20).

It must be emphasized that the first three types do not show any direct connection with the outer chalcopyrite, and they seem to belong to the "exsolved" type.

The chalcopyrite inclusions formed along the twinning composition surface of the sphalerite are frequently themselves twinned, and the composition plane coincides with that of the sphalerite. This can be tested in some Cananea specimens (fig. 21). In this case there seems to exist a definite orientation of chalcopyrite inclusions, for all the inclusions within a given grain of sphalerite give extinction at the same time under polarized light. Furthermore, the inclusions are oriented with respect to sphalerite. To test these indications an X-ray investigation was undertaken.

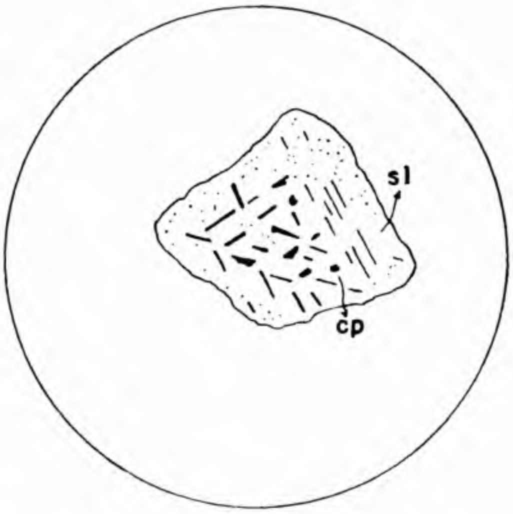


FIG. 11 — Chalcopyrite inclusions following the (110) planes of sphalerite. Section nearly perpendicular to [111] direction. (Rico 1086 — Harvard collection). Approximate magnification: 140 X.

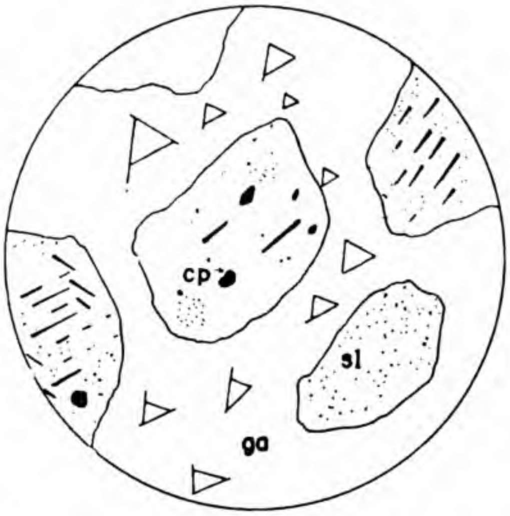


FIG. 12 — Uneven distribution of the chalcopyrite inclusions. Cleavage control. Galena replacing sphalerite. (Rico 1013 — Harvard collection). Approximate magnification: 140 X.

The observation under polarized light suggests that very likely the chalcopyrite (112) plane is parallel to the sphalerite (111) plane. This is, as matter of fact, similar to the well-known case of the overgrowth of chalcopyrite crystals on the tetrahedron faces of sphalerite.

The inclusions that are controlled by sphalerite cleavage are not always single, individual crystals of chalcopyrite. Some inclusions are aggregates of 2, 3, 4 or more crystal orientations (fig. 6). Very likely they represent a multiple twinning of chalcopyrite. It is quite possible that the chalcopyrite has been segregated as single crystals, undergoing a secondary twinning afterwards.

Frequently galena and pyrite occur with chalcopyrite in sphalerite, as inclusions or grain-boundaries aggregates (figs. 2, 18, 22). In these cases, it is remarkable that the galena blebs are only confined to the sphalerite grain boundaries, and never observed inside of sphalerite grains, following cleavage planes or twinning surfaces. This leads to

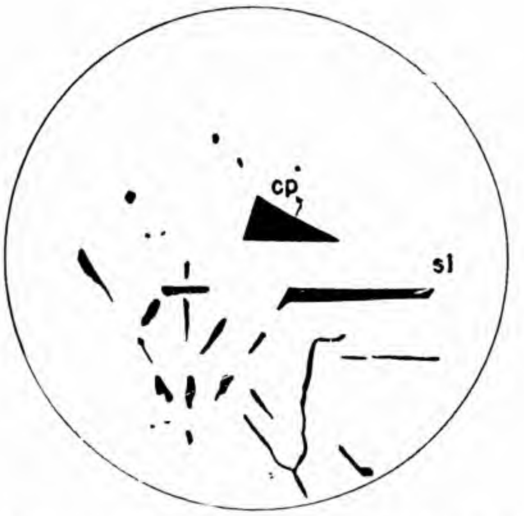


FIG. 13 — Different shapes of chalcopyrite inclusions following sphalerite cleavage planes. (Telluride 1018 — Harvard collection). Approximate magnification: 140 X.

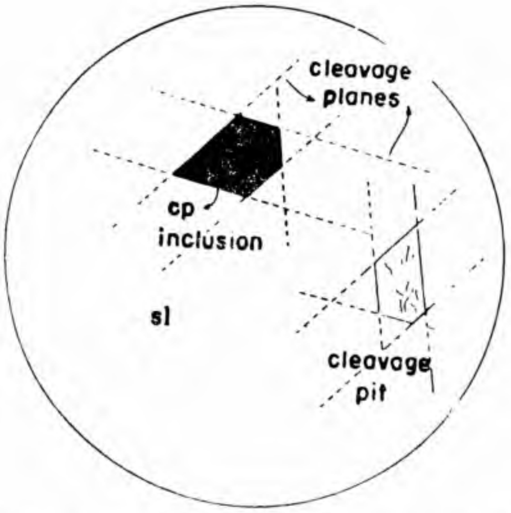


FIG. 14 — Showing the parallelism of edges of chalcopyrite inclusions and (110) cleavage planes. (Cananea 1229 — Harvard collection). Approximate magnification: 140 X.

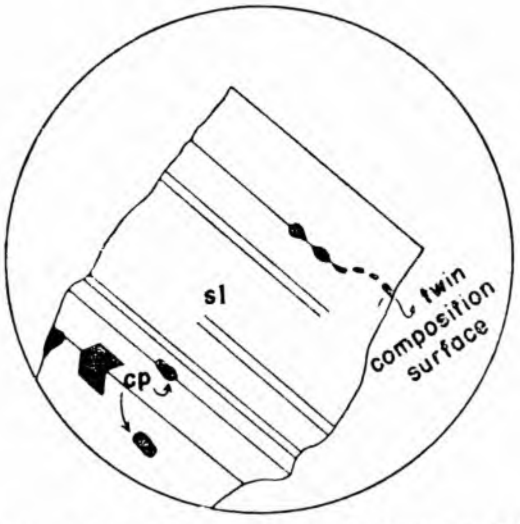


FIG. 15 — Chalcopyrite inclusions following a not plane twinning composition surface of sphalerite. Chalcopyrite twin. Etched with aqua regia. (Cananea 1229 — Harvard collection). Approximate magnification: 140 X.

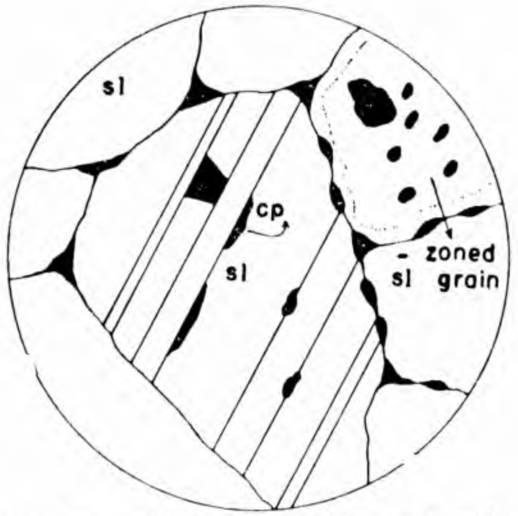


FIG. 16 — Chalcopyrite following sphalerite grain boundaries and twinning planes. Zoning of sphalerite grain revealed by etching. Etched conc. HNO_3. (Cananea 1229 — Harvard collection). Approximate magnification: 140 X.

a supposition that galena had a different origin, and very likely by replacement. Moreover, galena blebs show here and there connections with the outer galena.

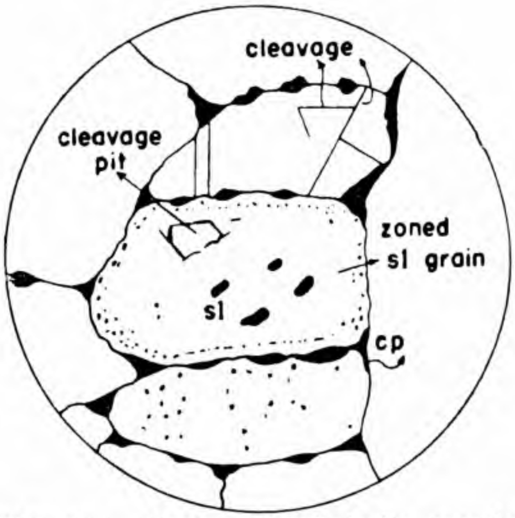


FIG. 17 — Zoning of sphalerite revealed by etching. Sphalerite grains cut at different levels. Etched with HNO_3 conc. (Cananea 1229 — Harvard collection). Approximate magnification: 140 X.

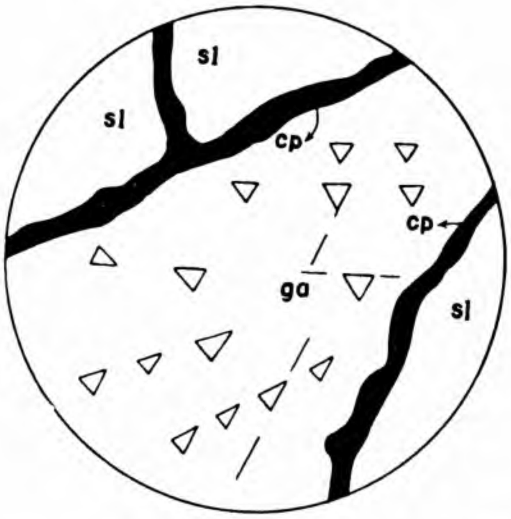


FIG. 18 — Rims of chalcopyrite surrounding sphalerite. Exsolved? chalcopyrite. (Tintic). Approximate magnification: 140 X.

4. Percentage of the chalcopyrite inclusions in the sphalerite host: procedure of measuring

The percentage of chalcopyrite inclusions in the sphalerite host was calculated by measuring the respective area of each mineral in the field of the microscope. The measurements were undertaken with a grating eyepiece. Some reference charts of the various possible percentages have been drawn first, and the other subsequent measurements have been made by comparison with them. The accuracy could not be expected to be very precise, although some measurements were carried out several times, showing a margin of error not greater than 10%, plus or minus of the quantity estimated. In the low-percentage specimens, as for example with 1-2% of chalcopyrite inclusions, the accuracy is still less precise.

The measurements were also carried out by means of the integrating stage. The Wentworth-Hunt recording micrometer has been used. However, this device was reliable only for specimens with a high content of inclusions. In the low-content specimens the error was very great, and the grating eyepiece system seemed to give a more satisfactory result.

Some of the ideas about the measuring methods were taken from Thomson (25).

The percentage figures herein tabulated are given in volume percentages, which are the direct inferences from the area percentages. However, as the specific gravities of the two minerals, sphalerite (sp. gr. = 4.083) and chalcopyrite (sp. gr. = 4.283) are closely similar, the volume percentages do not differ materially from the weight percentages. Moreover, as the figures obtained will be compared among themselves, the comparison between volume percentages would lead to the same conclusions as the weight percentages.

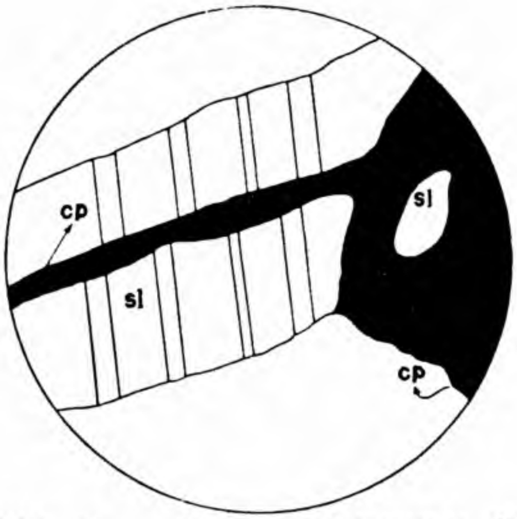


FIG. 19 — Vein of chalcopyrite following fracture in sphalerite, and connected with outer chalcopyrite. Outer chalcopyrite replacing sphalerite. Offset of the two sphalerite grains along the chalcopyrite veinlet. (Ouray 1151 — Harvard collection). Approximate magnification: 140 X.

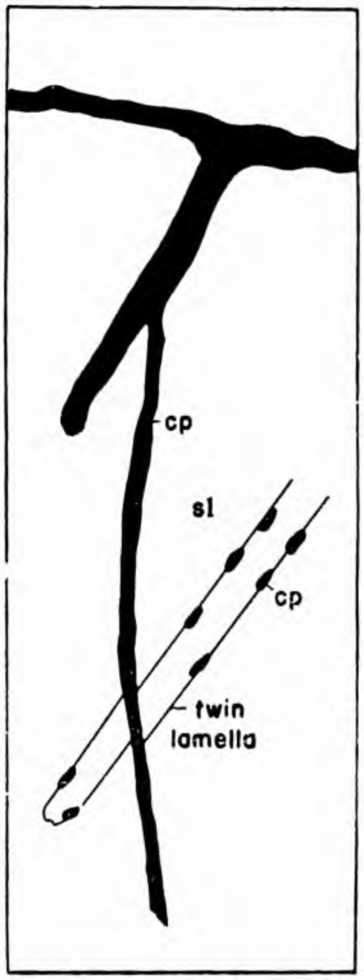
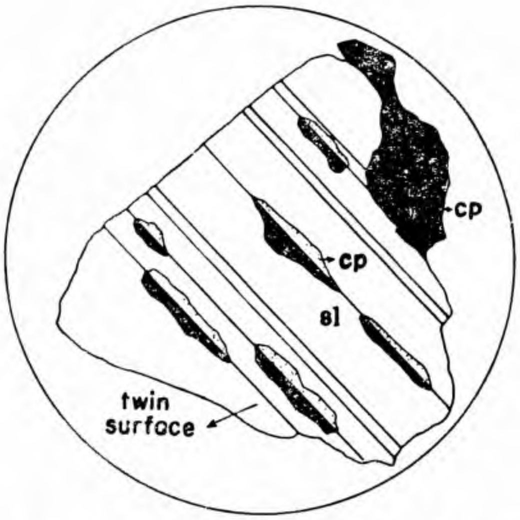


FIG. 20 — "Non-exsolved" (replacing?) chalcopyrite along sphalerite fracture. Offset of the sphalerite lamella along the fracture, shown by the twinning plane. (Telluride 1018 — Harvard collection). Approximate magnification: 140 X.

5. Relation of the chalcopyrite percentage to the varieties of sphalerite

Sphalerite occurs in nature in several varieties which are conditioned mostly by the presence of a higher or lower percentage of iron. There are representatives over a wide range, from the iron-rich sphalerite, variety marmatite, with about 26% Fe, to a pure, colorless and transparent variety, christophite, that contains no iron at all. The intermediate iron-bearing sphalerites are red, green, or yellow, according to the percentage of iron.



FIGo 21 — Twinning composition plane of chalcopyrite parallel to twinning composition plane of sphalerite. Polarized light. — Etched conc. HNO_3 — (Cananea 1085. — Harvard collection). Approximate magnification: 140 X.

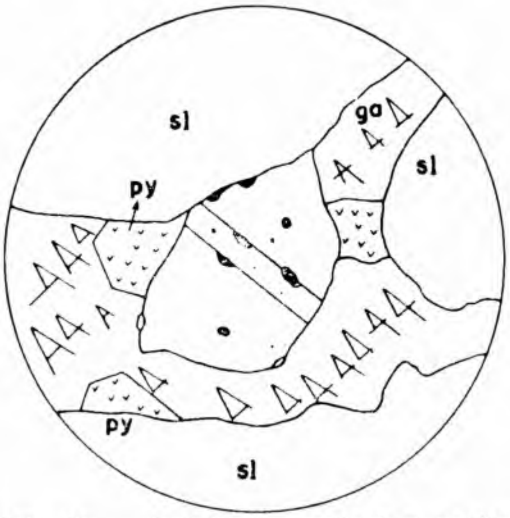


FIG. 22 — Sphalerite replacing pyrite, and galena replacing both. (Rico 1006 — Harvard collection). Approximate magnification: 140 X.

A survey was made in order to determine the relationship between variety of sphalerite and content of chalcopyrite inclusions.

The color of sphalerite was determined on the polished surface by the oblique illumination method. The obtained data are tabulated on the accompanying table.

It can be seen that, excluding some individual cases, in general, the lighter varieties of sphalerite contain a smaller amount of chalcopyrite inclusions. However, it must be pointed out that the personal element enters in determining the color of sphalerite, chiefly in distinguishing from "black" (deeply-colored) to red, yellow from light green, or even yellow from light red varieties. Some green varieties from Ouray show no inclusions of chalcopyrite at all. The inclusions of chalcopyrite seem to be closely related to the iron-content of sphalerite. But this may not be the only factor, for some "black" varieties of sphalerite with absence of chalcopyrite inclusions have been described. The annexed table shows that sometimes the red varieties are very poor in chalcopyrite inclusions. However, it is remarkably striking that the light-colored varieties show always a low content of chalcopyrite.

It is obvious that the formation of chalcopyrite would depend also upon the copper content of sphalerite.

District	Color of sphalerite	Volume percentage of chalcopyrite inclusions
Porcupine	red	7%
Silver Bell	red	8%
Cananea	red	6%
Ouray	yellow	2%
Ouray	red	Less 1%
Ouray	red-yellov	Less 1%
Ouray	yellow	0.5%
Ouray	red	Less 0.5%
Ouray	yellow	Less 0.5%
Ouray	red-yellow	0.5%
Rico	yellow	Less 0.5%
Rico	yellow	Less 1%
Rico	yellow	Less 0.5%
Telluride	red-yellow	1%
Telluride	red	about 0.05%
Telluride	red-yellow	about 0.02%
Telluride	yellow	0.5%

6. Relation of the chalcopyrite percentage to the intensity of the hydrothermal class

The percentage of chalcopyrite inclusions in sphalerite seems to be variable in the same deposit, perhaps according to depth and occurrence. This fact could be tested at Ouray, where some specimens have a very high percentage for an occurrence of leptothermal intensity, while other specimens from the same deposit have an amount of chalcopyrite inclusions as low as almost zero.

It has been noticed is some Ouray specimens that where there is some outer chalcopyrite, suggested as "replacing" or "non-exsolved" chalcopyrite, the amount of inclusions in sphalerite is higher. Thus, some Ouray specimens of sphalerite in contact with outer chalcopyrite show 4 to 6% of chalcopyrite inclusions, whereas in specimens without such outer chalcopyrite, the percentage is low as 0.5% to 1%. This fact would show that replacement might be responsible for some additional chalcopyrite inclusions, thus increasing the percentage, and then, both processes, exsolution and replacement, seem to have been involved.

The percentage varies also in the same sphalerite grain. At the borders the percentage is generally lower. However, in one case at Ouray, a sphalerite grain surrounded by "non-exsolved" chalcopyrite showed higher percentage at the borders (fig. 1).

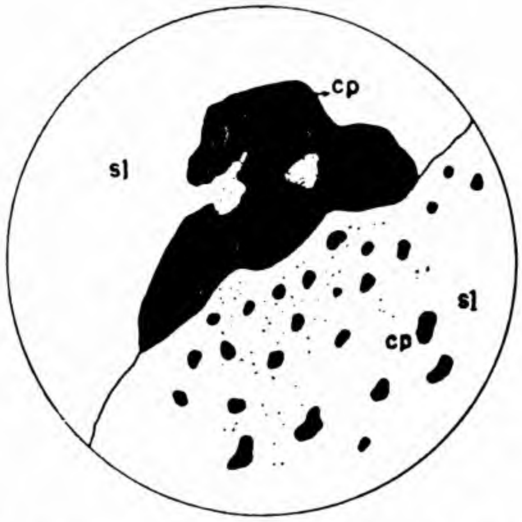


FIG. 23 — Various sizes of chalcopyrite inclusions. Outer chalcopyrite replacing the sphalerite. (Ouray 1203 — Harvard collection). Approximate magnification: 140 X.

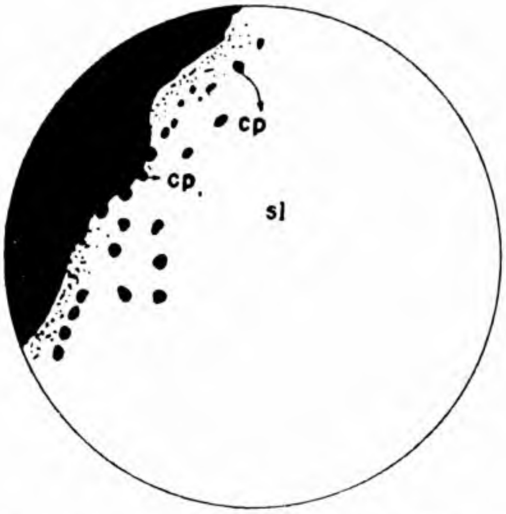


FIG. 24 — "Replacing" and "exsolved" chalcopyrite. Outer chalcopyrite replacing zoned sphalerite grain and embodying chalcopyrite "exsolved" grains. (Cananea 1085 — Harvard collection). Approximate magnification: 140 X.

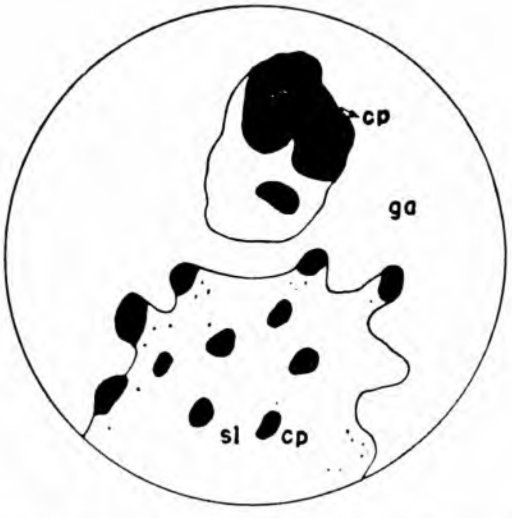


FIG. 25 — Various sizes of chalcopyrite inclusions. Two kinds? (Silver Bell 1005 — Harvard collection). Approximate magnification: 140 X.

FIG. 26 — "Replacing" and "exsolved" chalcopyrite. Zoning of sphalerite grains revealed by variation of the chalcopyrite inclusions sizes. (Cananea 1085 — Harvard collection). Approximate magnification: 140 X.

Percentages of chalcopyrite inclusions in sphalerite

District	Intensity of hydrohermal zone	Volume percentages of chalcopyrite inclusions		
		Maximum	Minimum	Average
Porcupine	hypothermal			7%
Silver Bell	pyrometasomatic			8%
Cananea	pyrometasomatic & mesothermal	13%	1%	6%
Cananea	"			4.5%
Coeur d'Alene	mesothermal			9%
Butte	mesothermal & leptothermal			1%
Ouray	leptothermal	4.5%	0.5%	2%
Ouray	"			1%
Ouray	"			1%
Ouray	"	2%	0	0.5%
Ouray	"	9%	1%	2%
Rico	"			0.5%
Rico	"	1%		0.5%
Rico	"	1%		0.5%
Rico	"	7%		1%
Tintic	"	6%		1%
Telluride	"			3%
Telluride	"			0.02%
Telluride	"	1%	0.25%	0.5%
Telluride	"	8.5%		1%
Mogallon	epithermal	2-3%		1-0.5%

The distribution is not, therefore, uniform and even throughout the section, and this can be explained either by an original variability in iron and copper content of the sphalerite crystals, or by the fact that the polished section cuts the sphalerite crystals at different levels and at different orientations, giving an impression of an uneven distribution.

From the examination of the accompanying table, it can be seen that the amount of chalcopyrite inclusions decreases as the hydrothermal intensity decreases. This variability according to the intensity could be very good evidence for exsolution, for replacement would follow no rule concerning amount of chalcopyrite present. It is also very striking that the percentage never reaches figures over approximately 13%, there being therefore a maximum limit, which would not be expected in the case of replacement or some other process not involving exsolution.

It is known that at higher temperatures the rate of diffusion in the solid state is higher, and the solid solubility increases with the temperature. Thus, high-temperature sphalerites could dissolve a larger amount of copper and iron, which would be precipitated as chalcopyrite as the temperature falls off.

Statistically, it has been found that the more common percentage of chalcopyrite in leptothermal deposits is around 1-2%, whereas in the hypothermal and pyrometasomatic deposits this percentage reaches values as much as 5-6%.

B. Etching experiments

On the suspicion that there exist two different varieties of chalcopyrite, the "exsolved" and the "non-exsolved" types, etching experiments have been undertaken, with the supposition that some minor chemical differences might cause the two types to etch differentially by the same etch reagent. Unfortunately, no success was reached in obtaining this differential reaction with the applied reagents. However, good results were obtained with etching in revealing the relationships between the sphalerite and chalcopyrite, otherwise not noticed on the ordinary polished surface.

The etching procedure has been used for a long time in metallography for bringing out textures of metals. The etching reveals not only the textures and relationships between the minerals, but also the orientation and twinning of the isometric compounds, which would be impossible under polarized light, unless some abnormal birefringence occurs. For the sphalerite, therefore, this technique was very satisfactory.

Gebhardt (4) has carried out etching experiments on sphalerite, attacking polished surfaces with a hot 10% HCl solution, during 10 to

30 minutes. No etch pits were developed with this technique, but the areas attacked became velvety.

Schneiderhöhn (16) recommends $KMnO_4+H_2SO_4$, acting during 10 to 30 minutes, in order to bring out the texture of sphalerite. The etching was revealed to be faster on $(1\bar{1}1)$ than on (111)

In the technique used in this investigation, a suite of usual reagents, recommended by Short (21) for the identification of opaque minerals (aqua regia, HNO_3, HCl, KCN, KOH, and $HgCl_2$) has been applied. However, good results were attained only with the first two. The others behaved negatively, even with a prolonged exposure of 48 hours. No longer period than 48 hours has been tried with any reagent.

The variety of sphalerite seems to have little influence on duration of the reaction. The iron-rich varieties, however, seem to act more slowly.

The aqua regia was seen to be a better and faster etch reagent for bringing out the texture. A few seconds (10" to 30") are enough for a good result. The procedure of etching is very simple, consisting merely of immersing the specimen in a plate containing aqua regia. The specimen must be left there for the time recommended, and then rinsed with plain water.

Sometimes, the etching is excessive, or the presence of other easily-attacked minerals, such as galena, forms a coat over the whole polished section, usually making difficult the microscopic examination. This difficulty, however, may be overcome by rubbing the polished surface with a soft tissue paper several times, and then examining under the microscope. This technique can be repeated several times, until the polished surface is shown to be completely clear.

The HNO_3 produces the same effect on the sphalerite as the aqua regia. However, the attack is slower, and requires a few minutes (5 to 10 minutes). The procedure for HNO_3 follows closely the aqua regia procedure.

Sometimes, when there is a need for etching only a certain portion of the polished section, it is advisable to use a small piece of blotting paper soaked in the reagent, and placed over the surface. In this case the reaction is much slower.

Etching, either with aqua regia or with nitric acid, proved to be a good tool for revealing textural relationships between sphalerite and chalcopyrite.

The etching made it possible to distinguish between the several types of chalcopyrite inclusions already described. Also, the etching revealed the zoning of the sphalerite grains. In general, the rims along the boundaries are more refractory to the reagents than the central portion (figs. 16, 17).

The chalcopyrite etches more slowly than the sphalerite; on the other hand, it is easier to observe the chalcopyrite textures under the polarized light.

C. X-ray investigation

1 Experimental procedure

X-ray investigation of exsolution and intergrowths of different solid phases has been applied in metallurgy (Geisler, 5).

In the present experimental procedure, sphalerite containing chalcopyrite inclusions was first broken down, and cleavage pieces of sphalerite were selected. Many of such fragments were twinned and unsuitable for X-ray purposes. The fragment should not be over 0.5 mm in size, in order to produce a minimum amount of absorption and to shorten the exposure.

The percentage of chalcopyrite inclusions in this material had been estimated on the polished section, and it proved to be around 6%. Thus, only long exposures could produce chalcopyrite spots on the X-ray film. Several exposures have been tried, but exposures of 6 hours or little longer gave the best results.

The purpose of the X-ray picture was to determine whether there was any orientation of the chalcopyrite inclusions in the sphalerite structure. This orientation had looked probable in the polished section under polarized light. Here, the chalcopyrite inclusions, chiefly around the twinning composition planes of the sphalerite, appeared with their composition planes parallel to the corresponding plane in sphalerite. The fact that many authors had described the sphalerite-chalcopyrite intergrowth as due to exsolution also suggested this orientation.

Laue photographs of the small sphalerite fragments were taken first, in order to determine whether they were simple or whether twinned or aggregates. Because no dependable orientation of the sphalerite crystals could be managed satisfactorily in the available Laue camera, the Laue photographs were not considered for very accurate work.

An exact orientation of the crystals was obtained on the two-circle goniometer, and the X-ray rotation pictures were taken with the Weissenberg camera. The time of exposure was around 6 to 7 hours. Copper radiation and nickel filter were used.

The rotation pictures have been taken around the [100] axis of sphalerite. Cleavage pieces with [100] edges were selected for that purpose.

X-ray rotation pictures have been taken also around [111] and [211] axis of sphalerite, but because the identity periods along these directions are very large, the pictures have not come satisfactorily.

The sphalerite used in these experiments came from Cananea, Mexico, for it presented a relatively high percentage of chalcopyrite blebs. The sphalerite was the iron-rich red-black variety.

Clear green, low-iron content sphalerite lacking chalcopyrite inclusions, from Ouray, Colorado, was selected for X-ray pictures, in order to make comparison with the chalcopyrite-rich sphalerite. The absence of chalcopyrite inclusions of this green sphalerite was determined in the polished section previously.

Weissenberg moving picture method for the zero-layer of the rotation-pictures has been tried for both kinds of sphalerite, but without any success.

2. Discussion of the results

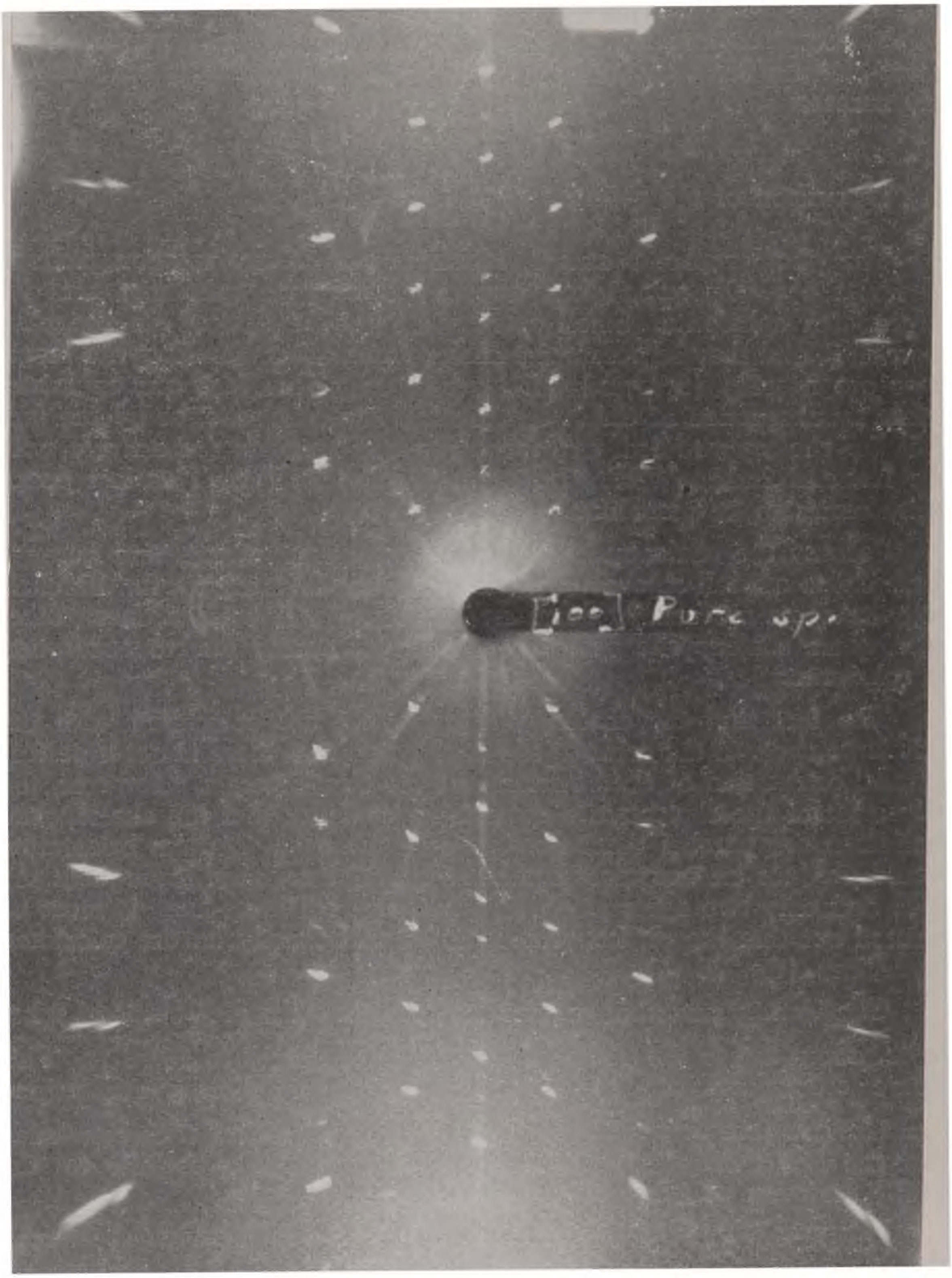
The photographs, 1 and 2, represent two X-ray rotation pictures around the [100] axis, taken respectively of pure sphalerite and inclusion-rich sphalerite. Small extra spots can be noticed on the photograph 2, and they represent the chalcopyrite. Some chalcopyrite layer-lines are missing (3rd and 6th layer-lines) This fact can explained either by absorption of the X-ray through the sphalerite, or by the fact that the chalcopyrite 3rd. and 6th layer-lines coincide respectively with the 1st. and 2nd. sphalerite layer-lines. (Fig. 26 A). This last possibility seems to be more likely.

Because the chalcopyrite inclusions are small in size, and because there exists a small amount of chalcopyrite in the intergrowth, the chalcopyrite spots are usually much smaller that the sphalerite ones. Likewise, some chalcopyrite spots are missing, probably due to absorption in sphalerite.

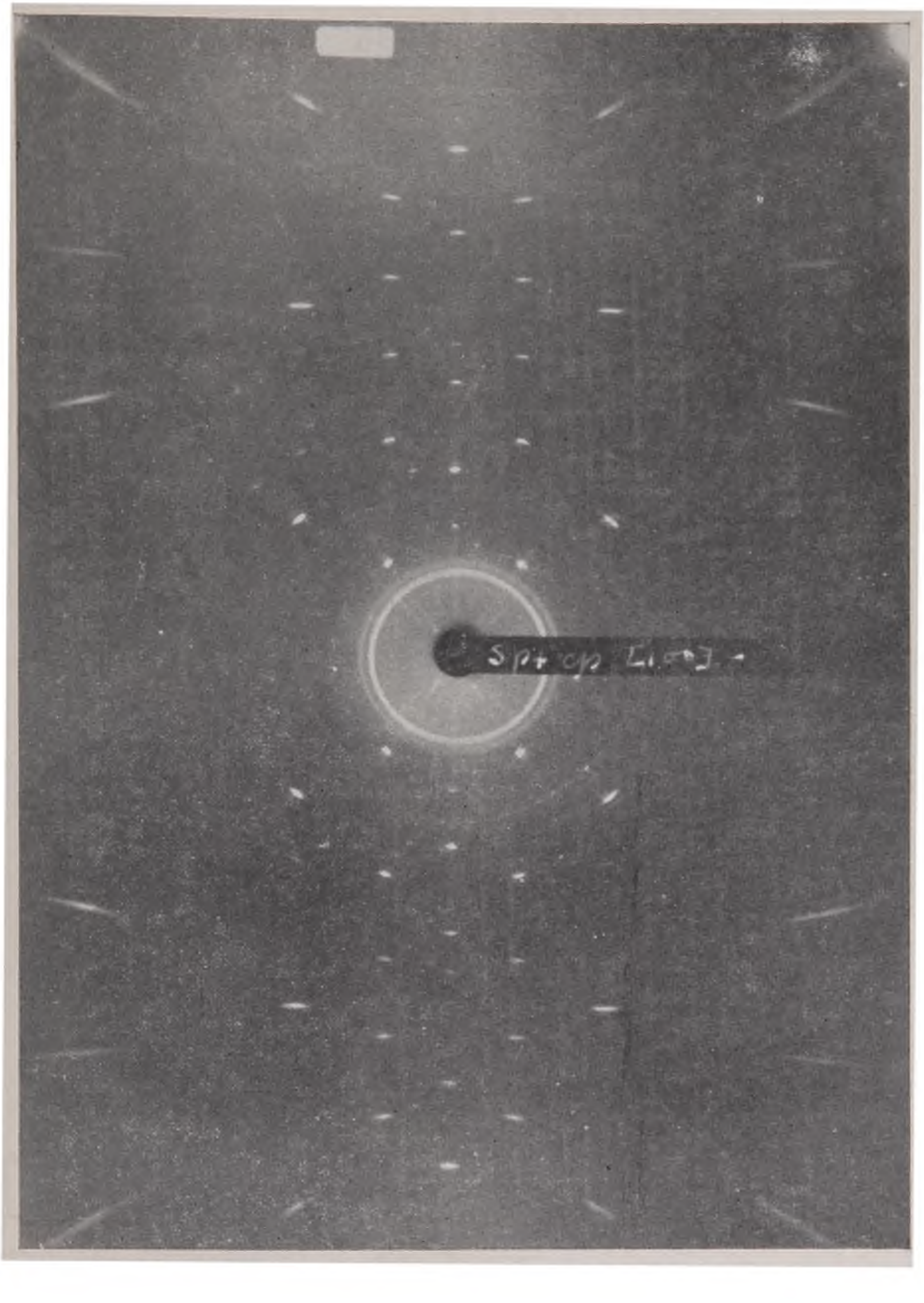
The fact that the chalcopyrite spots are not coinciding with the sphalerite spots in the same layer-lines, shows that there is not a perfect parallel orientation of the structures of the two minerals. However, the alignment of the chalcopyrite spots is an evidence that the chalcopyrite inclusions are parallel themselves in orientation. A random orientation would produce an irregular pattern of spots, distributed throughout the film, and only two spots would coincide on each layer-line. It must be pointed out that the chalcopyrite spots all fall exactly on the calculated layer-lines (fig. 26 A)

The identity period of the chalcopyrite along the [100] axis of sphalerite, according to the photograph 2, is nearly equal to 16,58 Å. This figure corresponds to the [130] direction of chalcopyrite, where t = 16,57 Å (see accompanying table). Therefore, it must be concluded that the [130] direction of chalcopyrite inclusions is parallel to the [100] direction of sphalerite.

However, that this appears to be true for the Cananea specimens, should not be taken as indicating a general rule for all the occurrences of the sphalerite-chalcopyrite intergrowths. Although similar results were obtained in a number of photographs of Cananea sphalerite, there is a possibility that these relations would not be necessarily hold true for every Cananea specimen. Formed by exsolution or replacement, the only condition that the chalcopyrite inclusions require is that some axis



Photograph 1 — X-ray rotation picture along [100] direction of sphalerite (without chalcopyrite inclusions). Ouray, Colo.



Photograph 2 — X-ray rotation picture along the [100] direction of sphalerite, of the intergrowth sphalerite-chalcopyrite (with about 6% chalcopyrite). Cananea, Mexico.

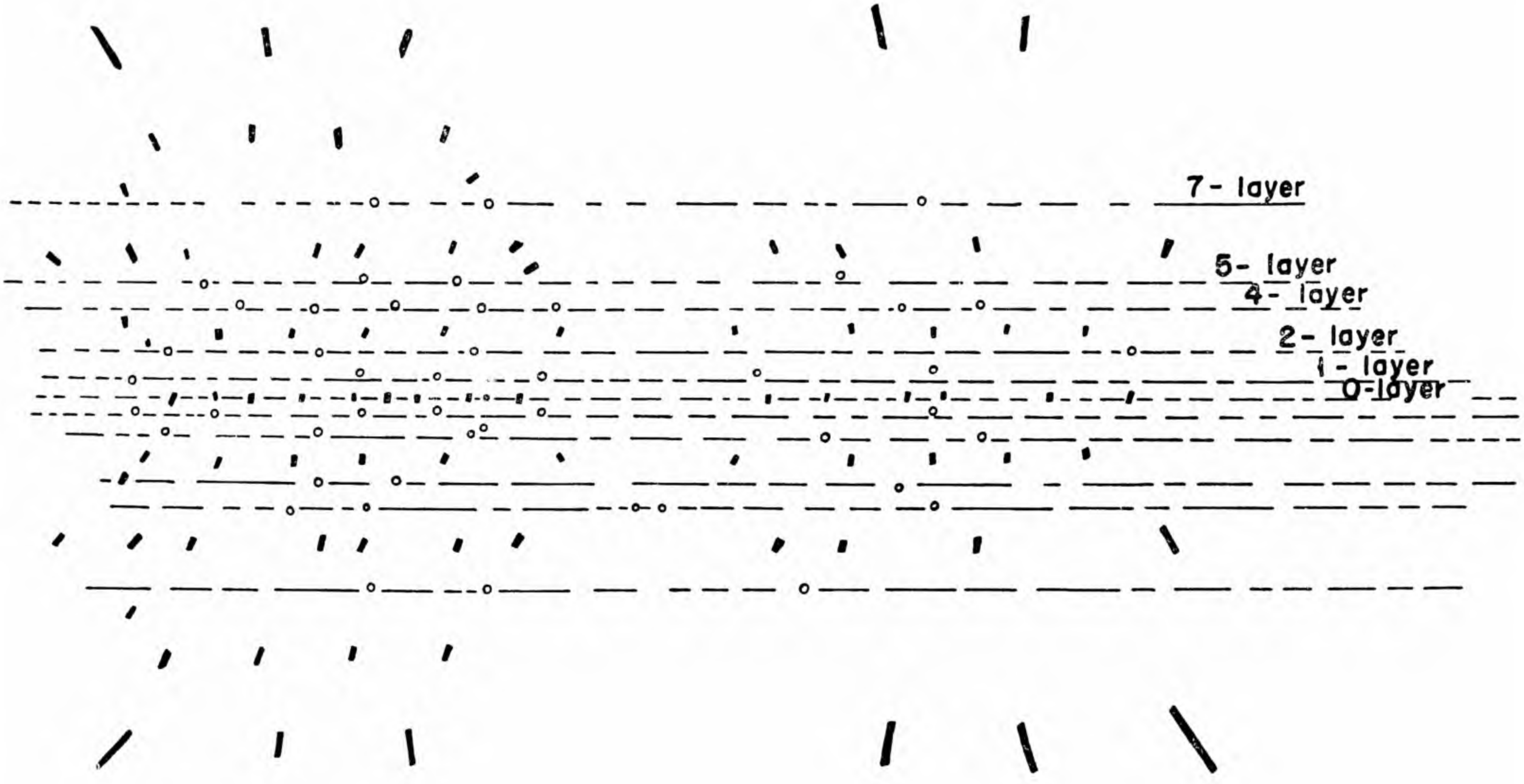


FIG. 26 A — Drawing of the X-ray rotation picture of the intergrowth sphalerite-chalcopyrite. Alignment of the chalcopyrite spots. Missing of the 3rd and 6th chalcopyrite layers.

Spacings of chalcopyrite layer-lines from the X-ray photograph 2, along the [100] axis of sphalerite.

Layer lines	Spacings (in mm)	Identity periods (t) (in Å)
0	0.00	—
1	2.55	17.35
2	5.55	16.10
3	missing	—
4	11.70	16.20
5	14.90	16.70
6	missing	—

Average identity period	— 16,58 Å
Identity period along [130] (calculated)	— 16,67 Å

be parallel to some other axis of sphalerite. This could be any direction that satisfies the equilibrium of the crystal structure of both minerals.

V Sphalerite inclusions in chalcopyrite

While the presence of chalcopyrite inclusions in sphalerite is extremely common, and found very frequently when sphalerite and chalcopyrite occur together in the same ore, inclusions of sphalerite in chalcopyrite are extremely rare, and have been reported from only a few mineral deposits. Schneiderhöhn (15,16) mentions this intergrowth. In this study only one specimen from Cananea has shown such inclusions.

The sphalerite inclusions occur as dendritic crystals throughout the chalcopyrite (figs. 27 28, 29). They vary in size, being usually smaller than the described chalcopyrite inclusions insphalerite. They have a definite orientation, which seems to be sphalerite (100) parallel to chalcopyrite (100) or (001).

Frequently, the dendrites develop into square or rectangular crystals, the corners corresponding to the branches of the dendrites. Often these square crystals contains tiny blebs of chalcopyrite.

Zonal distribution of the sphalerite in the chalcopyrite has been likesise noticed. At the periphery of the chalcopyrite grains the dendrites are much smaller in size and fewer in number.

The occurrence of these sphalerite inclusions in chalcopyrite together with the inclusions of chalcopyrite in sphalerite suggest that there must represent a reciprocal solubility of sphalerite and chalcopyrite. The small percentages of inclusions in each example leads to the idea that it is a case of partial solid solution. Furthermore, the fact of exsolution,

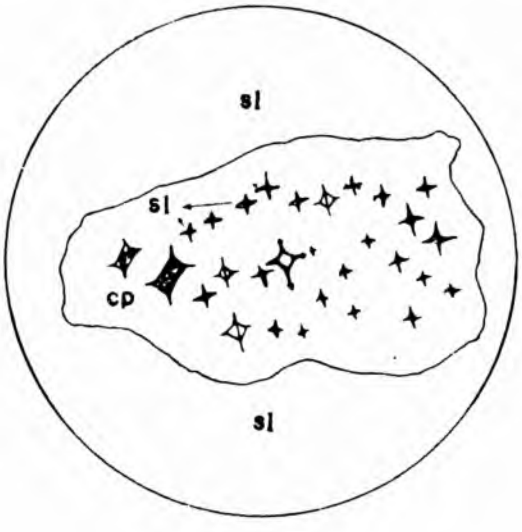
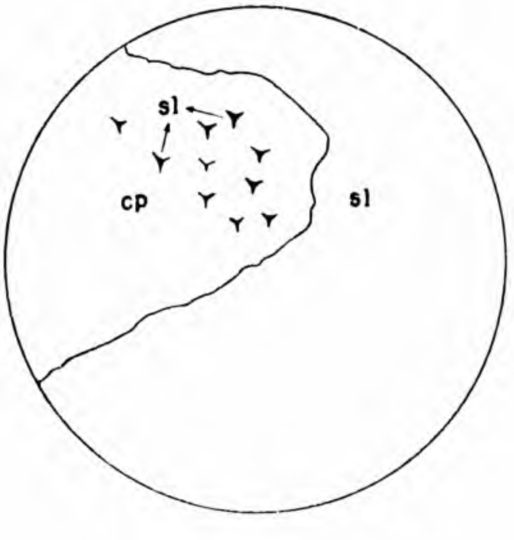


FIG. 27 — Sphalerite dendritic inclusions in chalcopyrite. Orientation of the dendrites. Section normal to [100] direction of sphalerite. (Cananea 1229 — Harvard collection). Approximate magnification: 140 X.

FIG. 28 — Same sphalerite dendrites, through a section perpendicular to [111] direction of sphalerite. (Cananea 1229 — Harvard collection). Approximate magnification: 140 X.



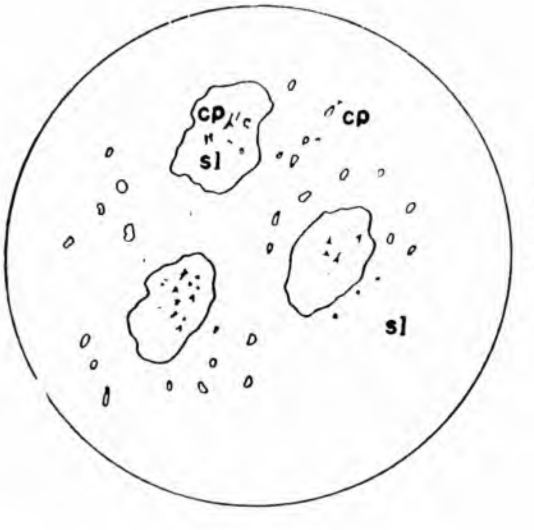


FIG. 29 — Relation between sphalerite dendrites and chalcopyrite inclusions in sphalerite. (Cananea 1229 — Harvard collection). Approximate magnification: 50 X.

itself, suggests that the equilibrium between the two phases is not perfect at all temperatures, which is the reason for the breakdown at lower temperatures.

VI. Summary and conclusions

In the introduction to this paper mention was made of the controversy which exists over the problem whether the chalcopyrite inclusions in sphalerite are due to exsolution or to replacement. The data from this paper suggest the possibility of both processes, for the formation of such inclusions in some cases. However, the inclusions and some grain boundary areas seem very likely to be derived by exsolution, while the outer chalcopyrite is rather derived by replacement.

In the great majority of studied cases, exsolution seems to be the dominant process for the formation of chalcopyrite inclusions. Below are listed the evidences for exsolution:

a. Very similar textures to some already observed in metallurgy and known to be due to exsolution. A very common example of this is the exsolution of cementite from iron to form pearlite.

b. Similarity of crystal structure of both minerals. Sphalerite is isometric with $a_0 = 5.41$ Å (Niggli, 11). Chalcopyrite is tetragonal, but can be considered isometric in terms of substitution, for the unit cell constants are very close to the sphalerite constants. The chalcopyrite constants are $a_0 = 5.24$ Å and $\frac{c_0}{2} = 5.15$ Å (Pauling and Brockway, 13).

c. Very slight difference in the atomic diameters of the metallic elements involved, copper, iron, and zinc. These elements substitute for each other and this is proved by the several varieties of sphalerite. Also, spectrographical analysis (Graton and Harcourt, 6) (Stoiber, 22) of sphalerite proves that this mineral can have copper and iron atoms in solid solution. Chemical analysis report as much as 26% iron in some sphalerites.

d. Small percentage of chalcopyrite inclusions in sphalerite. The figures are not over 13% even the high-temperature deposits.

e. Variability of the percentage of chalcopyrite inclusions according to the intensity of the deposits, and according to the variety of sphalerite.

f. Variability of the size of the chalcopyrite inclusions according to intensity and location in the sphalerite grain.

g. Arrangement of the chalcopyrite inclusions according to zones in the sphalerite crystals.

h. Variability of the percentage of chalcopyrite inclusions within the sphalerite crystals: usually higher at the center.

i. Non-connection of the chalcopyrite inclusions with the outer parts of sphalerite crystals, which favors the view that they were derived from somewhere inside.

j. Two generations of chalcopyrite: exsolved? and non-exsolved? The latter type seems to be later.

k. Ordered arrangement of the chalcopyrite inclusions in the sphalerite structure, determined both by X-ray and polarized light.

l. Dendritic inclusions of sphalerite in chalcopyrite suggested by Schneiderhöhn as having been derived from exsolution.

m. Absence of chalcopyrite in some varieties of sphalerite, chiefly the light-colored ones.

Those facts all reinforce the exsolution hypothesis. Assuming, therefore, that exsolution is the right explanation for the chalcopyrite inclusions in sphalerite, there is no sequence for both minerals, sphalerite and chalcopyrite, and they should be considered simultaneous in deposition. But, when the "replacing" or "non-exsolved" chalcopyrite is present as veinlets and adjacent outer fields, that seems to be later than the "exsolved" chalcopyrite. Therefore, the sequence would be: 1. sphalerite — "exsolved" chalcopyrite; 2. "replacing" or "non-exsolved" chalcopyrite.

According to the physical chemical principles, exsolution would be complete only at absolute zero. So, it seems logical to think that the inclusions should contain a small amount of the sphalerite-building elements, not only zinc, but other minor elements that usually are present in sphalerite in the form of solid solution (Stoiber, 22). However, only careful spectrographical analysis of many samples of the chalcopyrite inclusions could solve the problem, and give a good contribution to the problem. There is, however, a material obstacle to this undertaking, which is the extremely small size of the inclusions, that would invalidate any effort to obtain pure specimens as true representatives of the inclusions. On the other hand, many successive micro-drillings would be required, in order to obtain sufficient amount to make a complete spectrographical analysis, reporting all the minor elements, for these elements would be the main key of the problem.

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RESUMO

Uma das finalidades do presente trabalho foi medir as porcentagens de inclusões de calcopirita em cristais de esfalerita, que formam concrescimento de ocorrência relativamente frequente nas jazidas hidrotermais. Parece existir uma relação entre porcentagens de inclusões e intensidade hidrotermal dos depósitos, como também entre porcentagens de inclusões e variedades de esfalerita. Depósitos de baixa temperatura mostram porcentagens de 1-2%, enquanto aqueles de alta temperatura apresentam 5-6%.

As inclusões de calcopirita geralmente ocorrem: a) nos planos de clivagem (110) da esfalerita; b) nas superfícies de contáto dos gemi-

nados de esfalerita; c) nos contornos dos cristais de esfalerita; e d) nas fraturas subsequentes da esfalerita.

Experiências de corrosão das secções polidas com ácidos (etching) revelaram a textura dos agregados de esfalerita. As mesmas experiências tiveram pequeno efeito sôbre a calcopirita. Água régia e ácido nítrico se mostraram como os melhores e mais satisfatórios reagentes.

As investigações por meio de raios X foram levadas a efeito principalmente pelo método de rotação. As roentgeno-fotografias revelaram a orientação das inclusões de calcopirita em relação à estrutura reticular interna da esfalerita. Nas amostras estudadas a direção [100] da esfalerita parece ser paralela à direção [130] da calcopirita.

Foram observadas inclusões de cristais dendríticos de esfalerita em alguns espécimes de calcopirita.

O fenômeno da exsolução parece ser a explicação mais provável para as inclusões de calcopirita. As diversas evidências que serão indicadas abaixo comprovam êste fato.

Na introdução dêste trabalho foi mencionada a controvérsia que existe entre Autores e estudiosos do assunto, sôbre o problema das inclusões de calcopirita em esfalerita, isto é, se elas constituem o resultado de um processo de exsolução ou de substituição. Os dados obtidos para a elaboração do trabalho, sugerem a possibilidade da existência dos dois processos. Entretanto, a maioria das inclusões e grânulos de calcopirita situados no contôrno de cristais de esfalerita parecem ser produtos de exsolução, enquanto a calcopirita "exterior" provàvelmente se originou por substituição.

Na grande maioria dos casos estudados a exsolução constitui o processo dominante. São enumeradas a seguir várias provas que falam em favor do fenômeno da exsolução:

a. Texturas muito semelhantes observadas em ligas metálicas e conhecidas como produtos de exsolução. Exemplo comum é a exsolução de cementita de ferro metaálico, afim de formar pearlita.

b. Semelhança de estrutura cristalina dos dois minerais: a esfalerita é monométrica com $a_0 = 5{,}41$ Å e a calcopirita é tetragonal. Entretanto, esta pode ser considerada monométrica, em têrmos de substituição, pois as constantes de sua cela unitária são muito semelhantes às da esfalerita. As constantes reticulares da calcopirita são segundo Pauling e Brockway $a_0 = 5{,}24$ Å e $c_0/2 = 5{,}15$ Å.

c. Pequena diferença entre os diâmetros atômicos dos elementos metálicos considerados: cobre, ferro e zinco. Êstes elementos se substituem recìprocamente, o que é evidenciado pela ocorrência de diversas variedades de esfalerita. Também, análises espectrográficas de esfalerita, provam que êste mineral pode conter átomos de ferro e cobre em forma de solução sólida. Análises químicas revelam até 26% de Fe em algumas variedades de esfalerita.

d. Pequena porcentagem de inclusões na esfalerita. As porcentagens nunca excedem 13%, mesmo nos depósitos de alta temperatura.

e. Variabilidade das porcentagens de inclusões de calcopirita de acôrdo com a intensidade dos depósitos hidrotermais e de acôrdo com a variedade de esfalerita.

f. Variabilidade do tamanho das partículas de calcopirita incluidas, de acôrdo com a intensidade do depósito e de acôrdo com a localização das inclusões no cristal de esfalerita.

g. Zoneamento das inclusões nos cristais de esfalerita.

h. Variabilidade das porcentagens dentro de cada cristal de esfalerita, pois frequentemente é maior no centro do cristal.

i. Não conexão das inclusões de calcopirita com as partes exteriores do cristal, o que favorece a hipótese de que elas provàvelmente se originaram no interior do próprio cristal de esfalerita.

j. Duas gerações de calcopirita.

k. Arranjo ordenado das inclusões de calcopirita dentro da estrutura reticular da esfalerita, determinada com auxílio de raios X.

l. Inclusões dendríticas de esfalerita em calcopirita.

m. Ausência de calcopirita em algumas variedades de esfalerita, principalmente nas variedades claras.