THE UNMIXING OF CHALCOPYRITE FROM SPHALERITE

N. W. Buerger, *Massachusetts Institute of Technology.*

Previous Work

Schneiderhöhn and Ramdohr[1] suggest that certain intergrowths of sphalerite and chalcopyrite may be due to an unmixing of chalcopyrite from sphalerite. To the best of the writer's knowledge, Schwartz[2] is the only one who has carried on any experiments which might show chalcopyrite dissolving in sphalerite. Nine specimens from Leadville, Colorado, were heated at temperatures ranging from 200° to 650°C. for time intervals of from 22 hours to 240 hours. The results of all runs were negative.

Gross[3] states that chalcopyrite is oriented parallel to the sphalerite (100) planes and Gruner[4] says that it is just as commonly oriented parallel to the (111) sphalerite planes.

Professor W. H. Newhouse, in an examination of some specimens of sphalerite from Bingham Canyon, Utah, noted blebs of chalcopyrite arranged in planes within the sphalerite. These small masses of chalcopyrite were observed near or on the borders of clear growth bands in the sphalerite. A specimen was heated for one week and then quenched in water. Dark haloes seemed to have developed about the chalcopyrite blebs. This strongly suggested that the chalcopyrite had dissolved in the sphalerite. These observations led to the present investigation of the phenomenon.

Method of Attack

The writer has been fortunate in obtaining euhedral sphalerite from Bingham Canyon, Utah. The larger crystals in thin section show growth zones ranging from clear and transparent to opaque. The chalcopyrite blebs seem to be confined to the clear zones adjacent to the opaque zones, and probably merge into the opaque zones.

---

[1] Schneiderhöhn, H., and Ramdohr, P., Lehrbuch der Erzmikroskopie, Bd. II, *Berlin,* **1931**,, pp. 106–110.

[2] Schwartz, G. M., Experiments with sphalerite-chalcopyrite intergrowths: *Bull. Geol. Soc. Amer.*, vol. **42**, 1931, pp. 187–8.

[3] Gross, R., and Gross, N., Die Atomanordnung des Kupferkieses und die Struktur der Berührungsflächen gesetzmässig verwachsender Kristalle: *Neues Jahrb.*, Beil. Bd. **48**, 1923, pp. 128–134.

[4] Gruner, J. W., Structural reasons for oriented intergrowths in some minerals: *Amer. Min.*, vol. **14**, 1929, pp. 230–231.

In order to study these minerals in three dimensions, and also to combine the advantages of polished section study with thin section study, an entirely new method of procedure has been adopted. This is the use of polished thick sections. A polished thick section consists of a "thin" section of about 0.5 to 1 mm. in thickness, polished on both surfaces. In making a section of this kind the following method is used: One surface of the specimen is ground and polished. This surface is firmly fastened to a glass slide by means of Canada balsam. A cut is then made with a diamond saw so as to leave about 2 mm. of the specimen attached to the slide. This is ground down to the desired thickness (usually about 0.8 mm.) and polished. The slide is next heated on a hot plate and section slipped off. The excess Canada balsam is dissolved in methyl alcohol, and the section is ready for use.

In the examination of the section both reflected and transmitted light were used. This was made possible without shifting the speciment by employing a metallographic microscope with a sub-stage attachment for transmitted light. The section was placed on a glass slide and examined. The regions in which the blebs occurred were noted on a small sketch map of the section in order that the same regions could be studied both before and after heating.

An electric furnace was set up which had a range of from 200°C. to 1000°C. Each specimen was enclosed in a pyrex glass tube of a size into which the particular specimen best fitted. A small pyrex tube was then joined onto the end of this and the container evacuated and sealed.

All specimens were rapidly cooled in a blast of air, since it was found that water quenching shattered the specimen to such an extent that it could not be used.

EXPERIMENTAL DATA ON RE-MIXING

Temperature and time are factors in any mixing or unmixing process. In order that the results of all runs made during this investigation would be consistent, the time factor was kept constant at seven days (168 hours). Runs were made at temperatures ranging from 200°C. to 500°C.

In some cases it was found possible to use the same specimen for a sequence of runs. This was most desirable since exactly the same areas were examined at the end of each run. The same specimen was used in runs 1, 2, 3 and 4. In all other runs new specimens were used each time.

Eight runs were made and these will be described separately:

Run 1.

Temperature: 200°C.

Time: 168 hours.

Results: No observable change has taken place either in the chalcopyrite blebs or in the surrounding sphalerite.

Run 2.

Temperature: 250°C.

Time: 140 hours.

Results: No change in the chalcopyrite blebs or in the surrounding sphalerite.

Run 3.

Temperature: 305°C.

Time: 169 hours.

Results: When the tube was opened, a peculiar odor was noticed which could not be identified since it was unfamiliar to those who detected it. It was certainly not hydrogen sulphide.

No observable change in either the chalcopyrite blebs or in the surrounding sphalerite.

Run 4.

Temperature: 350°C.

Time: 169 hours.

Results: The peculiar odor was again noticed, together with some hydrogen sulphide.

Although no marked change was noted, it was thought that there was a perceptible darkening of the sphalerite around each bleb of chalcopyrite. This darkening was so slight, as to be nearly unnoticeable. However, the writer felt that this indicated a proximity to the possible mixing temperature.

Run 5.

Temperature: 400°C.

Time: 168 hours.

Results: The tube was blackened on the inside and a strong odor of H_2S was noted on opening.

The specimen had apparently blown up while the run was being made, for it was in countless fragments. This was probably due to the presence of liquid inclusions. Fortunately, however, one of the fragments was found to be large enough to examine. This measured about 10 mm. by 5 mm. There were only three small areas of clear sphalerite present. One of these contained a plane of chalcopyrite blebs running through it, but they had remained apparently unchanged.

In the examination of the surface by reflected light, evidences that a mixing of chalcopyrite and sphalerite had taken place were clearly seen. There were a number of relatively large masses of chalcopyrite present as islands in the sphalerite. Surrounding each one of these, and extending perhaps over a millimeter into the sphalerite, tiny blebs of chalcopyrite had developed. These were so small as to be just barely discernable using a number 3 objective. A high power oil immersion objective was therefore used in the detailed examination of the areas. Figure 1 is a photomicrograph of such an area. The blebs showed a definite relation to the large chalcopyrite masses. The size and number of the blebs decreased in distance from the main masses, finally disappearing altogether at about 1 to 1.5 mm. from the chalcopyrite mass.

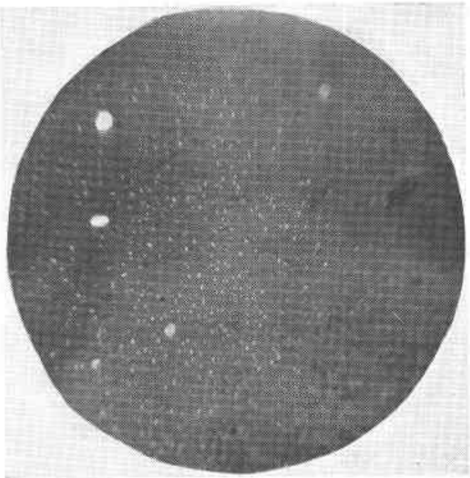

FIG. 1. Photomicrograph of an area adjacent to a large mass of chalcopyrite. Oil immersion, ×368. The large blebs are those which occur in planes throughout the sphalerite. The small blebs are those produced by mixing and unmixing as described in the text. The main chalcopyrite mass lies outside the field.

This development of minute chalcopyrite blebs in the sphalerite adjacent to large masses of chalcopyrite can only be accounted for by a mixing and unmixing process having taken place. The chalcopyrite dissolved in the adjoining sphalerite to form a solid solution of the two minerals. The cooling by air was not quite rapid enough to retain the homogeneous character of the solid solution, but allowed at least part of the chalcopyrite to exsolve, or separate out, from the sphalerite, resulting in the small blebs observed. Since the chalcopyrite in solution was more concentrated near the large mass of that mineral, more blebs have been segregated close to the mass, diminishing in number and finally disappearing further out in the sphalerite.

The fact that no mixing was apparent in the plane of blebs seen within the clear sphalerite may be accounted for by a factor not yet considered, that is the composition of the enclosing sphalerite. The only large blebs (of the type which occur in planes within the sphalerite) which may be seen by transmitted light are those in the clear portions of the sphalerite. There is no doubt that this sphalerite is of different composition than the opaque portions. The large chalcopyrite masses around which the mixing-unmixing took place are in regions of opaque sphalerite. The larger blebs of chalcopyrite, seen on the surface of the opaque sphalerite, which are undoubtedly similar to those observed in the clear portions (and are probably similarly arranged in planes within the sphalerite) also show the minute blebs of chalcopyrite concentrated about them. These facts seem to indicate that the opaque sphalerite tends to form a solid solution with chalcopyrite more readily than does the clear type. It may well be that mixing-unmixing has occurred to some extent in the clear portion, but is so slight that it cannot be observed.

It is of interest that about an island of galena in the sphalerite a similar (but less pronounced and less widespread) effect as described above for chalcopyrite, was noted. Minute blebs, probably of galena, had developed about the larger galena mass. This suggests the possibility of a solid solution of galena in sphalerite taking place. Except as a point of interest, this is not considered in the present paper.

Run 6.

Temperature: 440°C.

Time: 163 hours.

Results: The tube was blackened on the inside. Upon opening tube, there was an odor of hydrogen sulphide clearly discernible together with the unfamiliar odor noted in previous runs.

The specimen had become entirely opaque. This is taken to indicate that the mixing temperature had been exceeded with the result that some of the chalcopyrite had diffused through the sphalerite, causing discoloration. In an examination of the surface by reflected light distinct haloes were noted surrounding each chalcopyrite bleb. It is difficult to attribute this to anything other than to a difference in composition of the sphalerite due to diffusion of unmixed chalcopyrite into the sphalerite.

Run 7.
Temperature: 470°C.
Time: 168 hours.
Results: Same as for run 6.

Run 8.
Temperature: 500°C.
Time: 164 hours.
Results: Same as for run 6.

CONCLUSIONS

The results of this investigation definitely prove the existence of a solid solution of chalcopyrite in sphalerite, and the unmixing of chalcopyrite from such a solution. The unmixing temperature for this example lies within the range 350° to 400°C.