

## SPHALERITE — CHALCOPYRITE INTERGROWTHS FROM BORSABÁNYA. (NE CARPATHIANS.)

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In ore bodies where sphalerite and chalcopyrite are present, intergrowths of the two minerals usually appear. These intergrowths have been described and the reasons for their origin examined by several authors. According to these investigations sphalerite-chalcopyrite intergrowths may be produced by following factors :

1. Unmixing [Schneiderhöhn (17)\*, Ramdohr (18), Schwartz (22), Seifert (24, 25), Niggli (12).
2. Simultaneous crystallization [Seifert (25), Schneiderhöhn (19), Schwartz (22)].
3. Replacement [Lindgren (10), Ramdohr (18), Schneiderhöhn (19), Schwartz (22)].
4. Recrystallization [Ramdohr (18), Schwartz (22)].
5. Colloid phenomena [Ramdohr (14)].

Different factors effect nearly similar textural features, pseudo-eutectic textures in Lindgren's terminology. Generating factors cannot therefore be always precisely ascertained. Contradictions and inconsistencies occur among different authors because of isolated observations. I have made minute examinations of the textures of the sphalerite-chalcopyrite intergrowths and have tried to furnish accurate data about their origin on the basis of my observations.

At the microscopical study of the ores from Toroiaga lode system (Nwards from Borsabánya) I could observe very interesting textural forms of sphalerite-chalcopyrite intergrowths. My samples derived from the Mihály-lode, which is an offshoot of the Stefánia lode. It is 40 cm thick, dips S 75° Ewards at a 70° slope and is enclosed

\* See bibliography.

by holocrystalline porphyric dacite. Prospecting was started by cuts along strike at 1400 m altitude on both sides of the Murgu valley (tributary of the Secu valley at  $\phi$  1004.).

The lode has banded structure, consisting of pyrite, sphalerite, chalcopyrite, galena, mispickel, tetrahedrite, bournonite. The gangue is chiefly calcitic.

In the clear brown sphalerite, having grains of  $\frac{1}{2}$ —2 cm, chalcopyrite inclusions are common. Textural pattern shows clearly that there are two different sphalerite-chalcopyrite systems to be dealt with. (Fig. 1.)

a) Most of sphalerite grains contain droplike nonhomogeneously scattered chalcopyrite patches of  $\frac{1}{2}$ —3 micron size. These »droplets« are characteristic ovoids, isometric or slightly stretched, always with even, convex outlines. In places they are condensed in clouds in other instances they appear only sporadically. The dispersion of minute or relatively large »droplets« does not reveal any regularity. Chalcopyrite patches crop out on about 5% of the sphalerite surface.

b) In a few cases another type of sphalerite-chalcopyrite systems was observed along zones outlined by crystallographic directions. The width of these zones varies between 5 and 100 microns, and they are several millimeters in length. Accurate study of these zones reveals a strictly determined, oriented intergrowth with the chalcopyrite lamellae standing precisely at right angles to each other. Average density of the chalcopyrite lamellae makes up 40 percent of the zone surface. The lamellae are very fine, 20—200 millimicrons in width and  $\frac{1}{2}$ —5 microns in length. Their width decreases gradually on both ends so that they have lenticular cross-cuts. The orientation of the chalcopyrite lamellae changes along the zone according to the alternating twin-plates of sphalerite second (111). Orientation in neighbouring plates differs by 45°.

The zone of lamellar sphalerite-chalcopyrite intergrowths includes even grains of chalcopyrite. Their size varies largely from 1—2 microns (size of the surrounding chalcopyrite »droplets«) up to 100 microns. As to the outlines, these grains have a sharp distinction from the »droplets«, showing characteristic corroded edges. The border of the chalcopyrite grains is recessive, bitten. In a few cases fringing margins were noticed, threads of the fringe lying parallel with the proximate chalcopyrite lamellae. (Table Fig. 2., 3.)

An attempt was made to correlate these observations with our present conceptions about the origin of sphalerite-chalcopyrite inter-

growths. Different factors may have operated in producing the first and the second kind of intergrowths.

a) The first type of intergrowth occurs very frequently in deposits where sphalerite and chalcopyrite are present. Their appearance is not influenced at all by the type, temperature at which formed or average composition of the deposit. Quantity of chalcopyrite »drops« approximates 5 per cent of sphalerite on the average (18, 11, 27).

These intergrowths most probably originate as the result of unmixing. Reliability of this supposition is enhanced by crystal lattice relations. Both sphalerite and chalcopyrite lattices are of identical constitution. The nearly complete identity of ionic radii (Zn : 1.33 A. U., Fe : 1.26 A. U., Cu : 1.30 A. U.) brings about mutual substitution of metallic components. But the sphalerite-chalcopyrite isomorphism is not a simple »regular« phenomenon. Irregularity arises by the fact that chalcopyrite is a solid solution itself. Chalcopyrite is a product of Cu-Fe-S systems stable only in a limited composition and temperature range, as revealed by the prominent investigations of Borchert (1). According to the different solubility of FeS and CuS in sphalerite unequal amounts of them become dissolved (3). Another irregularity of sphalerite-chalcopyrite mixed crystals is manifested by an abnormal augmentation of dimensions due to anomalous intercalation of dissolved material in the lattice (divergence from Retger's rule).

Solubility of chalcopyrite is greater in wurtzite, than in sphalerite. Solution of chalcopyrite in sphalerite and its thermal variation depends on different factors each of which augment solubility with raising temperature.

Experimental determination of the critical temperature of sphalerite-chalcopyrite separation seems to be reached most easily by heating the system up to homogenization. Buerger found that suspended solutions became homogeneous at 350—400° and by slow cooling inclusions reappear. Experimentally established temperatures of homogenization does not correspond to critical temperatures of the unmixing due to the retardatory proceeding of homogeneity in the solid state as emphasized by Seifert (24). According to hydrothermal conditions the dissolving sphalerite crystal is supposed to be solidified at higher temperatures corresponding to greater solubility of chalcopyrite. Unmixing might have proceeded very slowly below the critical temperature of unmixing after the formation of an epithermal lode. Heating experiments between

200—600° were registered by Schwartz as showing no indication of sphalerite-chalcopyrite unmixing (23).

Chalcopyrite „droplets“ in sphalerite may only be formed by unmixing. Unmixing is evidenced by the following facts: 1. „Droplets“ consisting of chalcopyrite and pyrrhotite as described by Ramdohr (18, p. 109, fig. 45.) Superfluous amounts of dissolved sulphides were separated by the sphalerite crystal. 2. Correlation between „drop“-size and distribution (more advanced diffusion) and slowness of cooling or thermal metamorphism respectively. (Legraye 9., Clar 4.) 3. Nearly equal quantities of chalcopyrite in systems of different occurrences. The amount of chalcopyrite „droplets“ may represent the quantity of which sphalerite crystals were oversaturated at the unmixing temperature. Greater oversaturation may be produced if primarily wurtzite was deposited. This phenomenon, which seems to occur only under conditions of very high temperatures is described by Ramdohr on ore-inclusions of basalt (15).

b) The lamellar chalcopyrite-sphalerite system shows oriented intergrowth. Structural reasons of the intergrowth were analysed by Gruner (7) and Gross (6). According to their investigations planes of intergrowth are (111). In this directions planes of sulphur and of metallic atoms alternate in both lattices. Sulphur planes coincide nearly completely. This is in full correlation with the microscopic observations and crystallophysical experiments of Hikoro ku - Shôji (8). Transformation of sphalerite to wurtzite at 880° was followed by this author. Sphalerite (111) corresponds to wurtzite (0001), this lattice plane may be bound therefore the least closely.

1. Diffusion is reasonably less impeded along (111) planes, lamellae lying in this plane may therefore likewise be produced by unmixing too. Several lamellar systems are deduced by Ramdohr (18), Niggli (12), Schwartz (22) from unmixing. The samples, I examined, it did not appear as though originated in this way. The relative quantity of sphalerite and chalcopyrite in the lamellar system indicates another manner.\*

\* I received unfortunately the last paper of K. Sztrókay (Über die Erzminerale des Kreuzberges [Kereszthegy] bei Nagybánya [Kom. Szatmár]. Math. u. Naturw. Anzeiger der Ung. Akad. d. Wiss. 62. 322. 1943.) dealing with similar sphalerite-chalcopyrite systems only after closing the manuscript. Lamellar sphalerite-chalcopyrite intergrowths are therefore not exceptional in the ore deposits of the Carpathian Basin, may be, they are characteristic for them. About the origin I consent with Sztrókay's conclusions, but the supposition, that (110) should serve as plane of intergrowth does not correlate with the constitution of the crystal lattice.

2. Hypothesis of synchronous deposition is even less evidenced. Supposing that even for chalcopyrite the surrounding solution should be oversaturated, a growing sphalerite crystal may get a chalcopyrite-envelope. But the chalcopyrite lamellae do not seem to be cross-cuts of chalcopyrite envelopes, they do not correlate with sphalerite crystal edges at all.

3. Resorbed edges of the chalcopyrite grains occurring in the zone of the lamellar system indicate the importance of secondary phenomena in producing chalcopyrite lamellae. Fringy edges of chalcopyrite grains could signify replacement-texture. But chalcopyrite lamellae are not restricted to the neighbourhood of chalcopyrite grains.

4. It seems much more reasonable to suppose that the lamellar chalcopyrite-sphalerite systems occurred as the result of recrystallization, change of structure (Umlagerung) in the ore material. Changes of shape and size were produced to reach a more stable state. Resorption of chalcopyrite grain shows that the material of the chalcopyrite lamellae was supplied by the formers. Chalcopyrite grains in the surroundings but outside of the lamellar zone have equally resorbed edges. Such a rebuilding again involves necessity of diffusion. Temperature might have raised subsequent to the formation of the lode and this does not necessarily imply rejuvenation according to *Schneiderhöhn* (20). The lamellar system can be considered as an anomalous mixed crystal of sphalerite, the forming of oriented chalcopyrite lamellae from smaller chalcopyrite grains is therefore a form of accumulative crystallization (Sammelkristallisation). But the constancy of composition is not a necessary attribute of this process. What causes the uniform proportion of about 40 per cent chalcopyrite — and 60 per cent sphalerite throughout the zone of the lamellar system? Where it was necessary, chalcopyrite was furnished even by the surrounding grains (fig. 1.) in other instances resorption of the grains within the zone stopped before exceeding the dominating proportion. The system as a whole is very eutectic-like though the formation of hydrothermal ores may not be expected from fusions.

*Ramdohr* describes a similar network-like intergrowth of chalcopyrite-bornite, due to recrystallization (15). Heating experiments of *Borchert* carried out with chalcopyrite-chalcopyrrhotite show that two phases, which are unstable relative to one another at a certain temperature, begin to mingle, flow into one another with

measurable speed (Einwanderung) producing pseudo-eutectic textures (1). Similar phenomena might have influenced the formation of the lamellar sphalerite-chalcopyrite system.

5. Colloid phenomena may effect concentrations of chalcopyrite on concentric surfaces in sphalerite-gels. As a result of crystallization concentric lamellar zones of chalcopyrite appear, as shown by R a m d o h r from Rammelsberg. The material examined by the author showed no similar texture.

### SUMMARY.

Formation of droplike inclusions of chalcopyrite in sphalerite is due to unmixing. The amount of chalcopyrite inclusions is limited by the quantity of which the sphalerite crystal became oversaturated at the unmixing temperature. This oversaturation occurred at about 5 per cent chalcopyrite content of the sphalerite in most instances.

Zones of lamellar intergrowths were observed in the sphalerite. The intergrowth is oriented second (111) planes where the sphalerite-chalcopyrite proportion is about 60:40. Chalcopyrite grains inside and near the zone of lamellar intergrowth have resorption edges. Formation of the lamellar sphalerite-chalcopyrite system is probably due to recrystallization.

Sphalerite-chalcopyrite intergrowths do not have any value in „geologic thermometry“. The factors, which give rise to them are very complex and occur over a great range of temperature.

### IRODALOM. — BIBLIOGRAPHY.

1. B o r c h e r t, H.: Über Entmischungen im System Cu—Fe—S und ihre Bedeutung als »geologische Thermometer«. *Chemie der Erde* 9. 145—172. 1934/35.
2. B u e r g e r, N. W.: The Unmixing of Chalcopyrite from Sphalerite. *Am. Mineralogist*. 19. 525—530. 1934.
3. C h u d o b a, K. F.—M a c k o w s k y, M.: Über die Isomorphie von Eisen und Zink in der Zinkblende. *Centralblatt f. Min. Geol. u. Pal.* 1939. Abt. A. 12—21.
4. C l a r, E.: Zwei Erzentmischungen von Schneeberg in Tirol. *Centralblatt f. Min. Geol. u. Pal.* 1931. Abt. A. 147—153.
5. C o t t a, B.: Die Erzlagerstätten der südlichen Bukowina. *Jahrbuch d. kk. geol. Reichsanst.* 6. 103—135. 1855.
6. G r o s s, R.—G r o s s, N.: Die Atomanordnung des Kupferkieses und die Struktur der Berührungsflächen gesetzmässig verwachsener Kristalle. *Neues Jb. f. Min. Geol. u. Pal.* 48. 113—135. 1923.

7. Gruner, J. W.: Structural Reasons for Oriented Intergrowths in Some Minerals. *Am. Mineralogist* 14. 227—237. 1929.
8. Hikoroku Shōji: X-ray Investigation of the Change in Orientation of the Crystal Lattice with Change in Modification. *Z. Krist.* 87. 74. 1933.
9. Legraye, M.: L'association galène-chalcopirite-blende dans la cryolite du Groenland. *Bulletin de la Soc. Géol. de Belgique.* 61. B 109—113. 1938.
10. Lindgren, W.: Pseudo-eutectic textures. *Econ. Geol.* 25. 1—13. 1930.
11. Meng, H. M.—Chang, K.: Geology of the Hsianghualing Tin Deposits, Lingwu, Hunan. *Mem. of the Nat. Research Inst. of Geol.* 15. 15—72. 1935.
12. Niggli, P.: *Lehrbuch der Mineralogie und Kristallochemie.* 3. Aufl. I. Teil. Berlin. 1941.
13. Pantó G.: A Borsabánya melletti Toroiaga szulfidos ércfelérei. *Beszámoló a M. Áll. Földt. Int. Szaküléseiről.* 8. 1—2. füzet. 1946.
14. Ramdohr, P.: Über den Mineralbestand und die Strukturen der Erze des Rammelsbergs. *Neues. Jb. Min. Geol. u. Pal.* 57. Beil.-Bd. Abt. A. 1013—1068. 1928.
15. Ramdohr, P.: Zinkblende als Einschluss in Basalt. *Neues Jb. für Min. Geol. u. Pal.* 64. Beil.-Bd. Abt. A. 681—690. 1931.
16. Ramdohr, P.: Neue Beobachtungen über die Verwendbarkeit opaker Erze als »geologische Thermometer«. *Ztschr. f. Prakt. Geol.* 39. 65—73, 89—90. 1931.
17. Schneiderhöhn, H.: Entmischungserscheinungen innerhalb von Erzmischkristallen und ihre Bedeutung für die Lagerstättenkunde und Aufbereitung. *Metall und Erz.* 19. 501—508, 517—526. 1922.
18. Schneiderhöhn, H.—Ramdohr, P.: *Lehrbuch der Erz-mikroskopie.* Bd. 2. Berlin. 1931.
19. Schneiderhöhn, H.: Bemerkung zum Referat von 10. *Neues Jb. f. Min. Geol. u. Pal.* 1931. Ref. I. 274.
20. Schneiderhöhn, H.: Time — Temperature Curves in Relation to Mineral Associations in Cooling Intrusions. *Econ. Geol.* 29. 471—480. 1934.
21. Schneiderhöhn, H.: *Lehrbuch der Erzlagerstättenkunde.* Berlin. 1942.
22. Schwartz, G. M.: Textures Due to Unmixing of Solid Solutions. *Econ. Geol.* 26. 739—763. 1931.
23. Schwartz, G. M.: Experiments with Sphalerite-Chalcopyrite Intergrowths. *Bull. Geol. Soc. Am.* 42. 187—188. 1933.
24. Seifert, H.: *Geologische Thermometer.* *Fortschr. d. Min. Krist. u. Petr.* 14. 167—291. 1930.
25. Seifert, H.: Die anomalen Mischkristalle. *Fortschr. d. Min. Krist. u. Petr.* 19. 103—182, 1935; 20. 324—455. 1936; 22. 185—488. 1937.
26. Shennon, Ph. J.: Chalcopyrite and Pyrrhotite Inclusions in Sphalerite. *Am. Mineralogist.* 17. 514—518. 1932.
27. Sztróky K.: A Gyöngyösoroszi-i ércelőfordulás mikroszkópiai vizsgálata. *M. Tud. Ak. Mat. és Term.-tud. Ért.* 68. 904—916. 1939.