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Thermodynamic aspects of Fe-Cu-S mineralization in black shales: an example from the Fore-Sudetic copper deposit (Poland)*

A relatively simplified calculation method, presented on two and three dimensional diagrams of $\log a_{\text{Cu}} - \log a_{\text{FeS}_2} - \log f_{\text{S}_2}$ for the Cu-Fe-S system ($T = 298 \text{ K}$, $p = 1 \text{ bar}$), includes the regions and fields of stability for chalcocite, digenite, bornite, chalcopyrite, covellite, and pyrite (marcasite). The utility of the aforementioned diagrams for the interpretation of sulphide mineralization in black shales is demonstrated with Fore-Sudetic copper resources as an example.

INTRODUCTION

Black shale formations are found in rocks of widely differing ages, but almost always share several common features, one of the most characteristic being their similar style of mineralization. Iron sulphides such as pyrite and marcasite occur in almost all mineralized black shales, the occurrence of copper sulphides is also common. The thermo-chemical properties of iron and copper sulphides are, therefore, ideally suited to describe and constrain the mineralization processes in black shales and black shale formations. Such an approach is also useful for more efficient prospecting and the exploitation of sulphide deposits in general. In this paper, the main sulphide mineralization in the Polish Fore-Sudetic copper deposit is discussed in terms of the thermodynamic variations of Fe, Cu and S.

Petrographic observations made on samples from the Lubin, Polkowice and Rudna region provide the paragenetic sequence common for this type of black shale mineralization and other sedimentary deposits in which black shales occur. Thermodynamic calculations have been made on mineral species for which there is adequate data, namely pyrite,

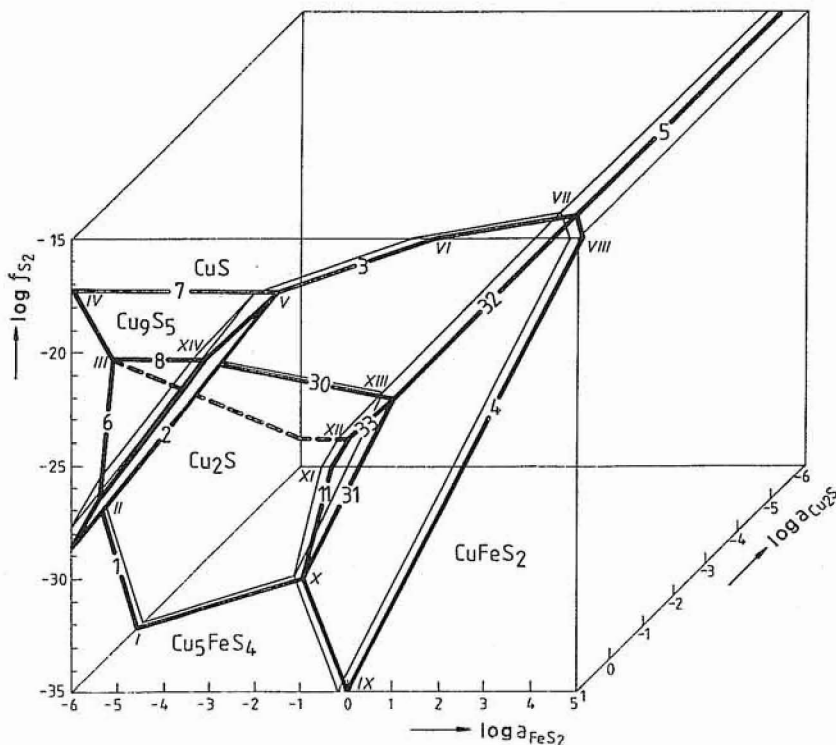


Fig. 1. The $\log a_{\text{FeS}_2} - \log a_{\text{Cu}} - \log f_{\text{S}_2}$ diagram for the Cu-Fe-S system ($T = 298 \text{ K}$, $p = 1 \text{ bar}$, $\log a_{\text{Cu}} = 0$)
 Roman numerals stand for intersection points and edges of various planes; arabic numerals of lines stand for numbers of reactions from the Table 1 ("line and reaction number"); thick and thin lines for pyrite and marcasite in reactions, respectively

Wykres $\log a_{\text{FeS}_2} - \log a_{\text{Cu}} - \log f_{\text{S}_2}$ dla układu Cu-Fe-S ($T = 298 \text{ K}$, $p = 1 \text{ bar}$, $\log a_{\text{Cu}} = 0$)

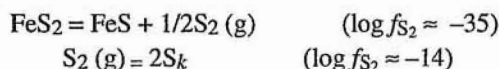
Liczby rzymskie oznaczają punkty i krawędzie przecięcia płaszczyzn; liczby arabskie linii oznaczają numery reakcji z tab. 1 („numer linii i reakcji”); linie grube i cienkie odpowiednio dla pirytu i markasytu

marcasite, chalcocite, digenite, bornite, chalcopyrite and covellite (Tab. 2). Using these data, two dimensional $\log a_{\text{FeS}_2} - \log f_{\text{S}_2}$ diagrams (for $\log a_{\text{Cu}} = 0$) and three dimensional $\log a_{\text{FeS}_2} - \log a_{\text{Cu}} - \log f_{\text{S}_2}$ diagrams for the Fe-Cu-S system at $T = 298 \text{ K}$ and $p = 1 \text{ bar}$ have been constructed.

THERMODYNAMIC CALCULATIONS

Thermodynamic calculations are based on the thermodynamic data of (J. R. Craig, P. B. Barton, 1973; R. M. Garrels, C. L. Christ, 1965; H. C. Helgeson *et al.*, 1978; A. W. Jasiński, 1987; R. A. Robbie *et al.*, 1978; D. J. Vaughan, J. R. Craig, 1978). For digenite

and bornite these data are only approximations. Minerals observed under the microscope form the basis for the mineral reactions between iron and copper phases used to construct the set of diagrams. The lines in the diagrams are taken from the reactions given in Table 1. $\log a_{\text{FeS}_2}$, $\log f_{\text{S}_2}$ and $\log a_{\text{Cu}_2\text{S}}$ range from -6 to -5 , -15 to 35 , and 0 to -1 , respectively. The limits of a_{FeS_2} and a_{Cu} were chosen to include the areas of thermodynamic stability of chalcocite, digenite, bornite, chalcopyrite and covellite, both in undersaturated ($\log a_{\text{FeS}_2} < 0$; $\log a_{\text{Cu}} < 0$), saturated ($\log a_{\text{FeS}_2} = 0$; $\log a_{\text{Cu}} = 0$), and oversaturated ($\log a_{\text{FeS}_2} > 0$; $\log a_{\text{Cu}} > 0$) conditions relative to a_{FeS_2} and a_{Cu} . The $\log f_{\text{S}_2}$ range of -15 to -35 is given by the reactions:



where $\text{S}_2(\text{g})$ and S_k stand for gaseous and crystalline sulphur, respectively. Values of the Gibbs' energy change of reaction (ΔG_r^0) and related $\log f_{\text{S}_2}$ values were calculated from:

$$\Delta G_r^0 = \Delta G_{\text{products}}^0 - \Delta G_{\text{substrats}}^0 = RT \ln K$$

where: $K = \Pi a_{\text{products}} / \Pi a_{\text{substrats}}$ (a stands for the activity of components in mineral phases).

In the calculations the activities of Cu-bearing components in equilibrium are equal (see appendix). Figure 1 shows the $\log a_{\text{FeS}_2} - \log a_{\text{Cu}} - \log f_{\text{S}_2}$ diagram seen from the Cu oversaturated side. In both the two (Fig. 2) and three dimensional diagrams, it can be seen that in addition to phases stable relative to FeS_2 and Cu for $\log a_{\text{FeS}_2} = 0$ and $\log a_{\text{Cu}} = 0$, metastable phases also exist. This is true for both undersaturated and oversaturated conditions in the FeS_2 and Cu parts of the diagrams.

Volumes in the three dimensional diagrams and fields in the two dimensional diagrams of thermodynamic stability of different phases can be observed. For example, for $\log a_{\text{Cu}} = 0$, bornite, chalcopyrite and covellite are in equilibrium with pyrite ($\log a_{\text{FeS}_2} = 0$). With increasing $\log a_{\text{Cu}}$ the field of digenite expands significantly at the expense of chalcocite, covellite and bornite, and lines 7 and 2 (Tab. 1) cut the line with $\log a_{\text{FeS}_2} = 0$ up to the point that $\log a_{\text{Cu}} = 1.79$ (i.e. is oversaturated with respect to Cu). Under such conditions the digenite-pyrite association appears to be metastable. With decreasing $\log a_{\text{Cu}}$ the stability field of digenite decreases significantly, disappearing when $\log a_{\text{Cu}} = -0.21$. Starting from this point, the chalcocite-covellite paragenesis is stable. The digenite field expands with increasing $\log a_{\text{Cu}}$ and $\log f_{\text{S}_2}$ and decreasing $\log a_{\text{FeS}_2}$. In this diagram bornite is disequibrated with respect to pyrite when $\log a_{\text{Cu}} < -1.89$ (lines 3, 4 and 5 cut the $\log a_{\text{FeS}_2} = 0$ line). Below this value chalcopyrite and covellite are in equilibrium with pyrite. When $\log a_{\text{Cu}} < -2.66$ the field of bornite disappears and the chalcocite-chalcopyrite-covellite paragenesis is stable. Simultaneous increases in $\log a_{\text{Cu}}$, $\log a_{\text{FeS}_2}$, and $\log f_{\text{S}_2}$ result in an

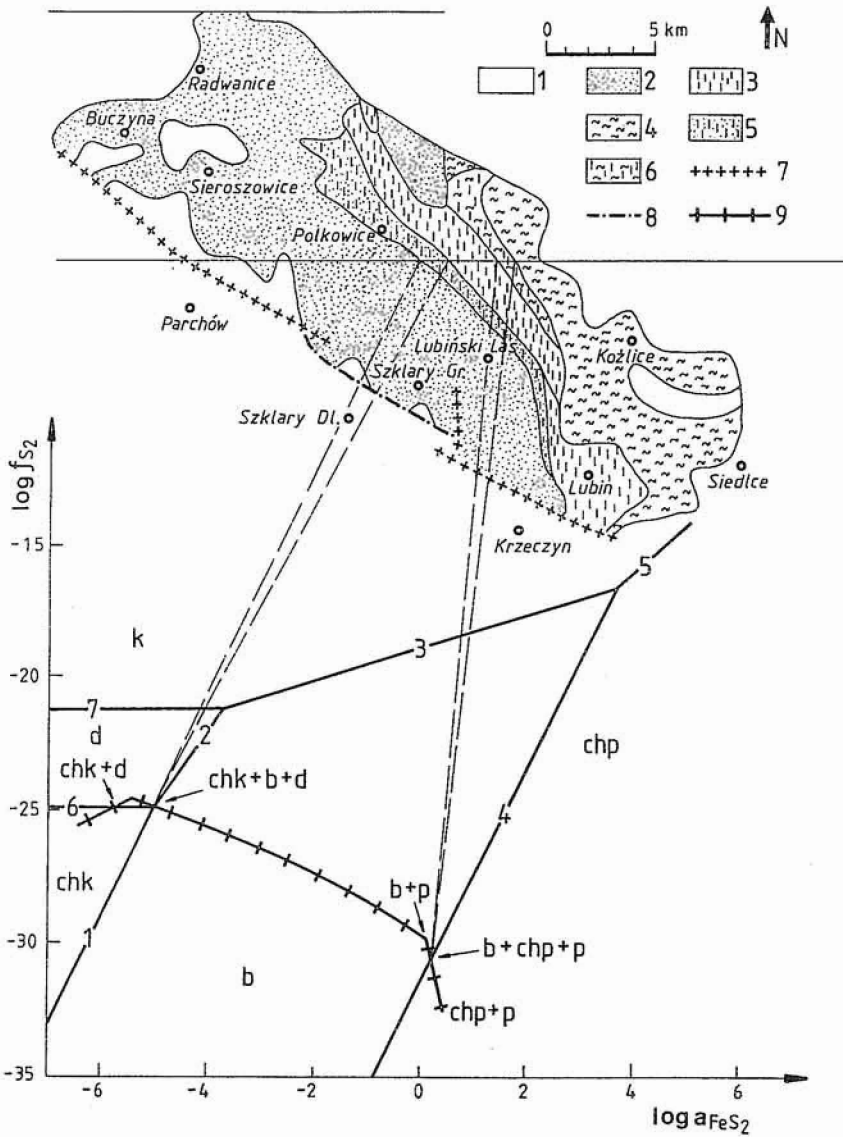


Fig. 2. The comparison of the $\log a_{\text{FeS}_2} - \log a_{\text{Cu}} - \log f_{\text{S}_2}$ diagram for the Cu-Fe-S system ($T = 298 \text{ K}$, $p = 1 \text{ bar}$, $\log a_{\text{Cu}} = 0$) with the map of mineralization with the main Cu and Cu-Fe sulphide minerals of the Fore-Sudetic copper deposit

1 — insignificant sulphide mineralization; 2 — economic chalcocite (chk) mineralization; 3 — economic bornite (b) mineralization; 4 — economic chalcopyrite (chp) mineralization; 5 — economic chalcocite-bornite mineralization; 6 — economic chalcopyrite-bornite mineralization; 7 — faults; 8 — probable Zechstein outcrops; 9 — probable patch of parameter changes during the formation of mineralization; k — covellite; p — pyrite; d — digenite; other explanations as in Fig. 1

expansion in the bornite and covellite fields. When $\log f_{S_2}$ is sufficiently high, chalcopyrite alters to covellite. The presence of relicts of other sulphides, metastable under these conditions, indicates a slow reaction rate during the alteration process. The large chalcopyrite field when $\log a_{FeS_2} = 0$ explains its frequent equilibrium with pyrite. This is enhanced at low $\log f_{S_2}$. Increases in f_{S_2} , a_{FeS_2} and a_{Cu} reduce the stability of chalcopyrite.

The intersections of various lines illustrating reactions from Table 1, and the intersection of planes in Figures 1 and 2 provide some insights into the paragenetic development of some of the parageneses found in black shales. For example, point X (Fig. 1) and line 31 illustrate the paragenesis chalcocite, bornite and chalcopyrite, stable up to $\log f_{S_2} = -27.1$, $\log a_{FeS_2} = -1.82$ and $\log a_{Cu} = -2.66$, after which covellite forms at the expense of chalcocite. Parameters describing the new paragenesis are constrained by line 32 (up to $\log a_{FeS_2} = 5.78$, $\log f_{S_2} = -12.38$ and $\log a_{Cu} = 1$ in this diagram). On the other hand decreasing $\log a_{FeS_2}$ and increasing $\log a_{Cu}$ and $\log f_{S_2}$ shift the parameters of the bornite-chalcopyrite-chalcocite-covellite paragenesis from point XIII along line 30 (where chalcopyrite disappears) towards point XIV, where digenite now appears. When $\log a_{FeS_2}$ decreases with constant $\log a_{Cu}$ and $\log f_{S_2}$, bornite disappears. Decreasing $\log a_{Cu}$, along with increasing $\log a_{FeS_2}$ and $\log f_{S_2}$ (point II) along edge 2 leads to a change from a bornite-chalcocite-digenite paragenesis to a bornite-chalcocite-digenite-covellite paragenesis at point XIV. Moving from point XI where chalcocite and chalcopyrite are stable, towards point XII, covellite joins the paragenesis. Further parameter changes along edge 33 to point XIII add bornite to the paragenesis.

When similar calculations are made using thermodynamic data for marcasite instead of pyrite no significant changes occur in the stability fields though there is a minor expansion of the stability fields of Cu-Fe sulphides at the expense of Cu sulphides.

Porównanie wykresu $\log a_{FeS_2} - \log a_{Cu} - \log f_{S_2}$ dla układu Cu-Fe-S ($T = 298$ K, $p = 1$ bar, $\log a_{Cu} = 0$) z mapą okruszczenia głównymi minerałami siarczkowymi miedzi oraz miedzi i żelaza w przedsudeckim złożu miedzi 1 — nieznaczna mineralizacja siarczkowa; ekonomiczna mineralizacja: 2 — chalkozynowa (chk), 3 — bornitowa (b), 4 — chalkopirytowa (chp), 5 — chalkozynowo-bornitowa, 6 — chalkopirytowo-bornitowa; 7 — uskoki; 8 — prawdopodobne wychodne cechsztynu; 9 — prawdopodobna ścieżka zmian parametrów podczas tworzenia się mineralizacji; k — kowelin; p — piryty; d — digenit; pozostałe objaśnienia jak na fig. 1

Table 1

Equations of reactions, ΔG_r° and $\log f_{S_2}$ for basic copper and iron sulphide minerals

Line and reaction number	Reaction; $\Delta G_{reaction}^\circ$ (ΔG_r° [kcal]), $\log f_{S_2}$
1	2
1	$4Cu_5FeS_4 + S_2 + 10Cu_2S + 4FeS_2$ $\Delta G_r^\circ(p) = -6.71$; $\Delta G_r^\circ(m) = -5.11$ $\log f_{S_2}(p) = -4.92 + 4 \log a_{FeS_2} + 6 \log a_{Cu}$ $\log f_{S_2}(m) = -3.75 + 4 \log a_{FeS_2} + 6 \log a_{Cu}$
2	$9Cu_5FeS_4 + 3.5S_2 = 5Cu_9S_5 + 9FeS_2$ $\Delta G_r^\circ(p) = -57.73$; $\Delta G_r^\circ(m) = -54.13$ $\log f_{S_2}(p) = -12.1 - 1.14 \log a_{Cu} + 2.57 \log a_{FeS_2}$ $\log f_{S_2}(m) = -11.34 - 1.14 \log a_{Cu} + 2.57 \log a_{FeS_2}$
3	$Cu_5FeS_4 + 1.5S_2 = 5CuS + FeS_2$ $\Delta G_r^\circ(p) = -38.66$; $\Delta G_r^\circ(m) = -38.24$ $\log f_{S_2}(p) = -18.9 + 0.67 \log a_{FeS_2} + 2.67 \log a_{Cu}$ $\log f_{S_2}(m) = -18.69 + 0.67 \log a_{FeS_2} + 2.67 \log a_{Cu}$
4	$5CuFeS_2 + S_2 = Cu_5FeS_4 + 4FeS_2$ $\Delta G_r^\circ(p) = -42.96$; $\Delta G_r^\circ(m) = -41.36$ $\log f_{S_2}(p) = -31.5 + 4 \log a_{FeS_2} - 4 \log a_{Cu}$ $\log f_{S_2}(m) = -30.32 + 4 \log a_{FeS_2} - 4 \log a_{Cu}$
5	$CuFeS_2 + 0.5S_2 = CuS + FeS_2$ $\Delta G_r^\circ(p) = -16.32$; $\Delta G_r^\circ(m) = -15.92$ $\log f_{S_2}(p) = -23.93 + 2 \log a_{FeS_2}$ $\log f_{S_2}(m) = -23.34 + 2 \log a_{FeS_2}$
6	$9Cu_2S + 0.5S_2 = 2Cu_9S_5$ $\Delta G_r^\circ = -17.05$ $\log f_{S_2} = -25 - 14 \log a_{Cu}$
7	$Cu_9S_5 + 2S_2 = 9CuS$ $\Delta G_r^\circ = -58.05$ $\log f_{S_2} = -21.28 + 4 \log a_{Cu}$
8	$Cu_2S + 0.5S_2 = 2CuS$ $\Delta G_r^\circ = -14.79$ $\log f_{S_2} = -21.69 + 2 \log a_{Cu}$

Tab. 1 continued

1	2
9	$\text{FeS} + 0.5\text{S}_2 = \text{FeS}_2$ $\Delta G_{r(p)}^\circ = -34.68$; $\Delta G_{r(m)}^\circ = -34.09$ $\log f_{\text{S}_2}(\text{p}) = -34.68$ $\log f_{\text{S}_2}(\text{m}) = -34.09$
11	$\text{Cu}_2\text{S} + 2\text{FeS}_2 = 2\text{CuFeS}_2 + 0.5\text{S}_2$ $\Delta G_{r(p)}^\circ = 17.85$; $\Delta G_{r(m)}^\circ = 17.05$ $\log f_{\text{S}_2}(\text{p}) = -26.17 - 2 \log a_{\text{Cu}} + 4 \log a_{\text{FeS}_2}$ $\log f_{\text{S}_2}(\text{m}) = -25 - 2 \log a_{\text{Cu}} + 4 \log a_{\text{FeS}_2}$
30	$\text{Cu}_5\text{FeS}_4 + 0.5\text{S}_2 = 2\text{Cu}_2\text{S} + \text{CuS} + \text{FeS}_2$ $\Delta G_{r(p)}^\circ = -9.07$; $\Delta G_{r(m)}^\circ = -8.67$ $\log f_{\text{S}_2}(\text{p}) = -13.3 + 2 \log a_{\text{FeS}_2} + 4 \log a_{\text{Cu}}$ $\log f_{\text{S}_2}(\text{m}) = -12.71 + 2 \log a_{\text{FeS}_2} + 4 \log a_{\text{Cu}}$
31	$3\text{Cu}_5\text{FeS}_4 + 1.5\text{S}_2 + 3\text{CuFeS}_2 = 6\text{FeS}_2 + 9\text{Cu}_2\text{S}$ $\Delta G_{r(p)}^\circ = -31.81$; $\Delta G_{r(m)}^\circ = -29.41$ $\log f_{\text{S}_2}(\text{p}) = -15.55 + 4 \log a_{\text{FeS}_2} + 2 \log a_{\text{Cu}}$ $\log f_{\text{S}_2}(\text{m}) = -14.38 + 4 \log a_{\text{FeS}_2} + 2 \log a_{\text{Cu}_2\text{S}}$
32	$\text{Cu}_5\text{FeS}_4 + 4\text{CuFeS}_2 + 3.5\text{S}_2 = 5\text{FeS}_2 + 9\text{CuS}$ $\Delta G_{r(p)}^\circ = -103.96$; $\Delta G_{r(m)}^\circ = -101.96$ $\log f_{\text{S}_2}(\text{p}) = -21.78 + 1.43 \log a_{\text{FeS}_2} + 1.14 \log a_{\text{Cu}}$ $\log f_{\text{S}_2}(\text{m}) = -21.36 + 1.43 \log a_{\text{FeS}_2} + 1.14 \log a_{\text{Cu}}$
33	$\text{CuFeS}_2 + \text{Cu}_2\text{S} + \text{S}_2 = 3\text{CuS} + \text{FeS}_2$ $\Delta G_{r(p)}^\circ = -31.12$; $\Delta G_{r(m)}^\circ = -30.72$ $\log f_{\text{S}_2}(\text{p}) = -22.81 + \log a_{\text{Cu}} + \log a_{\text{FeS}_2}$ $\log f_{\text{S}_2}(\text{m}) = -22.52 + \log a_{\text{Cu}} + \log a_{\text{FeS}_2}$

p — data for pyrite; m — data for marcasite

FORMATION OF THE MAIN Cu- AND Cu-Fe-BEARING SULPHIDES IN TERMS OF THERMODYNAMIC PARAMETERS

For $\log a_{\text{FeS}_2} = 0$ and $\log a_{\text{Cu}} = 0$ to -1 the stable paragenesis is bornite, chalcopyrite and pyrite. As $\log a_{\text{FeS}_2}$ decreases, chalcopyrite is the first to disappear (below the line and plane 3, absence of covellite) followed by bornite which is in equilibrium with digenite along line 2, but which becomes unstable after line 2 is crossed. As conditions shift along

plane 2 and reach plane 6, chalcocite also apparently becomes stable. Remnants of pyrite should disappear under these conditions through reaction and dissolution. A decrease of $\log f_{S_2}$ favours such a process, making pyrite and marcasite more common. Paragenetic sequences which can be expected are from pyrite rich, chalcopyrite-pyrite, or bornite-pyrite through bornite-pyrite-digenite towards chalcocite, with or without traces of pyrite.

Other possibilities include changes in parameters starting from the $\log a_{FeS_2} = 0$ plane (or under oversaturated conditions, from $\log a_{FeS_2} > 0$) but with low values of $\log a_{Cu}$. In that case the system might evolve towards the $\log a_{Cu} = 0$ plane through the following steps:

- chalcopyrite → bornite → chalcocite (for low $\log f_{S_2}$),
- chalcopyrite → bornite → chalcocite (slightly higher a_{Cu} and f_{S_2}),
- chalcopyrite → bornite → covellite (with higher f_{S_2}),
- chalcopyrite → bornite → digenite → chalcocite (when a_{Cu} increases and f_{S_2} and a_{FeS_2} decrease),
- chalcopyrite → bornite → digenite → chalcocite → covellite (when slightly undersaturated relative to Cu and with relatively high f_{S_2} and decreasing a_{FeS_2}).

Cu AND Cu-Fe SULPHIDE MINERALS IN THE FORE-SUDETIC COPPER DEPOSITS IN TERMS OF THERMODYNAMICS PARAMETERS

The below mentioned description of minerals from the Fore-Sudetic copper deposit are based on M. Banaś *et al.* (1982), C. Harańczyk, J. Jarosz (1973), A. W. Jasiński (1978), W. Mayer, A. Piestrzyński (1985).

Pyrite — one of the main sulphides in this deposit, is mostly on the limits of the Cu-bearing, and in Pb-Zn-bearing zones. This suggests a removal of pyrite from the Cu zone during formation of Cu phases, especially chalcocite, when undersaturated conditions relative to pyrite predominated ($\log a_{FeS_2} < 0$). Pyrite occurs in several forms in the deposit.

The most interesting textures are:

- a — framboidal: suggesting an oversaturation with respect to pyrite, causing the rapid nucleation and growth of spherical pyrite grains;
- b — idiomorphic: suggesting a saturation with respect to FeS_2 favouring crystallization;
- c — hypidiomorphic inclusions in bornite and digenite: suggesting the growth of younger Cu minerals on older pyrite grains;
- d — lamellae, fan shaped and myrmekitic structures in bornite: suggesting common growth of both minerals under FeS_2 saturated conditions when the line of evolution cuts the edge formed by $\log a_{FeS_2} = 0$ and plane 4 (see Fig. 1). These structures suggest that $\log f_{S_2}$ values were constrained between planes 3 and 4 (i.e. a lack of chalcopyrite and covellite). For $\log a_{Cu} = 0$, $\log f_{S_2}$ values are -31.5 to -19 for pyrite and -30.7 to -18.8 for marcasite. The presence of pyrite and lack of Cu minerals in anhydrite bearing sandstone

Table 2

Thermodynamic data used in calculations

Mineral	ΔG_f° 298 K; 1 bar	Mineral	ΔG_f° 298 K; 1 bar
CuFeS ₂ chalcopyrite	-44.30	Cu ₅ Fe ₄ bornite	-92.35
Cu ₂ S chalcocite	-20.40	CuS covellite	-12.87
Cu ₉ S ₅ digenite	-95.60	FeS ₂ pyrite	-38.30
FeS ₂ marcasite	-37.90	FeS pyrrhotite	-24.10
S ₂ sulphur gas.	18.91	-	-

G_f° — the change of Gibb's energy of mineral formation

suggest that when minerals formed in the rock the system was saturated with respect to pyrite ($\log a_{\text{FeS}_2} = 0$) and undersaturated with respect to Cu ($\log a_{\text{Cu}} < 0$).

Marcasite in places forms up to 10% of the total FeS₂ of the deposit. In some cases it is clearly later than pyrite, forming rosettes around cores of pyrite and galena. Marcasite as a metastable form alters with time to pyrite (negative ΔG). The presence of marcasite, or marcasite with pyrite in some deposits, indicates the sluggishness of the reaction at low temperatures.

Chalcocite is the commonest Cu sulphide in the Fore-Sudetic copper deposit, especially in the clayey shales rich in organic material, suggesting saturation or possibly oversaturation with respect to Cu ($\log a_{\text{Cu}} \geq 0$) accompanied by significant undersaturation with FeS₂ ($\log a_{\text{Cu}}$ reaches 0 when $\log a_{\text{FeS}_2} = -5$ and $\log f_{\text{S}_2} = -25$). The coexistence of chalcocite with digenite indicates a change of parameters along plane 6 towards point XIV. The presence of covellite suggests that the parameters evolved towards plane 8, probably after the syngenetic stage.

Bornite occurs as single grains and in association with other sulphides, indicating changes in the parameters of ore formation along plane 2 (bornite plus digenite), below plane 3 (single bornite grains), in a section of the $\log a_{\text{FeS}_2} = 0$ plane in the field of bornite (bornite plus pyrite), and a section of plane 4 (bornite with chalcopyrite plus pyrite).

Chalcopyrite occurs in significant concentrations in the bottom and top parts of the Cu horizon, perhaps as a result of mineral differentiation. CuFeS₂ usually occurs as disseminations and veinlets and in association with other sulphides, in particular bornite and pyrite. This is represented by a section of the $\log a_{\text{FeS}_2} = 0$ plane in the field of chalcopyrite, close to plane 4. The occurrence of chalcopyrite with digenite is a secondary

process, digenite replacing chalcopyrite and other sulphides. The fact that the fields of chalcopyrite and digenite are separated by bornite in the presented figures suggests they cannot be of the same age, and are developed from different solutions. Chalcopyrite coexisting with covellite is evidence of oversaturation with FeS_2 and with $\log a_{\text{Cu}}$ values ranging from -1 to 0 . Covellite replacement of chalcopyrite is developed after the syngenetic stage during later diagenesis and infiltration alteration.

Covellite is present in all varieties of the ore, in different quantities. Occasionally, massive covellite is seen, but usually it occurs as single grains or associated with other sulphides. Covellite replaces bornite, digenite, more rarely chalcocite, and other Cu-bearing sulphides. This is in response to a change in thermodynamic parameters along plane 3 (bornite alters to covellite), then along plane 7 (digenite alters to covellite) and more rarely, along plane 8 (chalcocite alters to covellite) close to point XIV in the field of low $\log a_{\text{FeS}_2}$ and weakly undersaturated with Cu ($\log a_{\text{Cu}} = -0.21$). Covellite is a late stage mineral related to post depositional diagenesis.

FORMATION OF THE Cu AND Cu-Fe SULPHIDE MINERALIZATION IN THE FORE-SUDETIC COPPER DEPOSIT IN THERMODYNAMIC TERMS

Two stages can be distinguished in the mineralization process. The first stage, saturated or oversaturated with respect to FeS_2 and strongly undersaturated with respect to Cu, led to pyrite formation. The second stage, overlapping the first, was enriched with Cu and depleted in Fe. This stage, comprising several steps, started with the formation of chalcocite (chalcocite field: $\log a_{\text{Cu}}$ ranges from 0 to 0.2 , $\log f_{\text{S}_2}$ ranges between points II and III (-28 to -22) and $\log a_{\text{FeS}_2}$ from -6 to -4). Cu saturation occurs at $\log a_{\text{FeS}_2} = -5$ and $\log f_{\text{S}_2} = -25$. Under these conditions primary pyrite is unstable and may be dissolved or removed from the system through reaction. f_{S_2} increases as sulphur dissolved from pyrite is added to the system. 0.5 of a sulphur atom corresponds to 1 metal atom in chalcocite. This explains why the organic rich clayey shales with chalcocite mineralization contain only minor traces of pyrite. Even small decreases in $\log a_{\text{Cu}}$, in the range 0.2 to 0.21 , small increases in $\log a_{\text{FeS}_2}$, and increases in $\log f_{\text{S}_2}$, to cut the plane between the fields of chalcocite and digenite, lead to digenite formation. In addition, chalcocite, metastable under these conditions, will alter to digenite or allow Cu_9S_5 to precipitate from solution. The small volume of digenite stability (Fig. 1) decreasing towards point II could explain the relatively small amount of digenite. Compared to chalcocite the digenite volume expands towards an environment oversaturated with Cu. In this case pyrite is unstable as well, and its rate of disappearance can be explained in terms of the kinetics of the reactions. If the replacement of chalcocite by digenite or precipitation of digenite occurs under conditions of point XIV then only a very minor increase of f_{S_2} will result in covellite replacing digenite or chalcocite, or if the change in f_{S_2} reaches plane 8, both of these phases. Covellite can also replace bornite. A further increase of a_{FeS_2} drives reactions towards the bornite field. A decrease in

f_{S_2} results from decreasing sulphur content in solution and the increasing stability of pyrite. To form bornite one metal atom needs 0.67 sulphur atoms. If the parameters during reaction run along the plane between bornite and covellite these minerals can be expected. A further increase in a_{FeS_2} to reach the $\log a_{FeS_2} = 0$ plane means that pyrite becomes stable, allowing coexistence with bornite and a faster decrease in f_{S_2} . If such an intersection overlaps on the plane between bornite and chalcopyrite a bornite-chalcopyrite-pyrite paragenesis can be expected. If parameter changes reach line 32 at the point of intersection with the $\log a_{FeS_2} = 0$ plane then a bornite-chalcopyrite-covellite-pyrite paragenesis would be stable. The section of the plane between chalcopyrite and covellite towards lower a_{FeS_2} and higher f_{S_2} shows that covellite replacement of chalcopyrite can be expected. The relatively large fields of bornite for higher a_{Cu} and large range of f_{S_2} located between the chalcocite-digenite and chalcopyrite fields means bornite can occur in a wide range of associations depending on the kinetics of reactions responding to changing parameters.

In evolutionary terms we can say that the stage of pyrite formation ($\log a_{FeS_2} = 0$) was followed by the stage of formation of Cu and Cu-Fe minerals. The deposition of large volumes of chalcocite and digenite in the main part of the deposit ($\log a_{FeS_2} < -4$; $\log a_{Cu} > 0$; and $\log f_{S_2}$ ranging from -22 to -28) and the main phase of chalcopyrite deposition in the SE and E parts of the deposit are attributed to this phase. This chalcopyrite-pyrite mineralization has the parameters $\log a_{FeS_2} \approx 0$, $\log a_{Cu}$ ranging from 0 to -1 and $\log f_{S_2} < 28$. The main bornite mineralization of this stage is found in a transitional zone between chalcocite and chalcopyrite-pyrite areas and was probably formed under condition of $\log a_{FeS_2}$, between -4 and 0, $\log a_{Cu}$ between -0.21 and 0 and $\log f_{S_2}$ between -31 and -18 (for $\log a_{FeS_2} = 0$). When $\log a_{FeS_2} = 0$ a bornite-pyrite paragenesis occurs. In the Fore-Sudetic copper deposit two clear NW-SE overlapping bands of mineralization are present.

1. The chalcocite-digenite zone with bornite. This is longer along the SW limit of the bornite zone. This paragenesis is illustrated by the plane between the fields of chalcocite and bornite (Fig. 2) with the line representing the change in parameters, and also by the conditions along the line between the chalcocite and bornite fields.

2. The bornite-chalcopyrite zone, which is shorter, running along the NE limit of the bornite zone. This is represented by the section produced when the line of parameter changes cuts the plane between the bornite and chalcopyrite fields. The frequent occurrence of pyrite also suggests the section with the $\log a_{FeS_2} = 0$ plane.

During the infiltration and diagenesis stage of the evolution of the deposit, previously formed minerals were affected by solutions derived from the dewatered sediments. The solution chemistry dependent on a number of factors, including the stability of the syngenetic minerals and interaction between the fluid and surrounding rocks. Metastable phases such as pyrite in the chalcocite zone will, through reaction, alter the solution chemistry, and salinity will increase as the solutions pass through salt formations in the region. In this way

the physico-chemical characteristics of the solution, pH, Eh, activities etc., will change drastically with respect to the original composition. This would explain the diagenetic alteration of primary textures and sedimentary structures in the syngenetic mineralization through recrystallization, dehydration, compaction, remobilization and so on. Typical diagenetic minerals are covellite replacing Cu and Cu-Fe sulphides, and marcasite. Diagenesis had led to a vertical differentiation of sulphide minerals, with a central core of pyrite free chalcocite in the organic rich clayey shales surrounded above and below, firstly by layers mineralized with digenite, then a bornite-pyrite association, then a chalcopyrite-pyrite association, and the zonation is completed with an outer zone of pyrite both above and below the Cu zone. During chalcocite formation under conditions of $\log a_{\text{Cu}} \approx 0$, $\log a_{\text{FeS}_2} < 0$ and $\log f_{\text{S}_2}$, metastable pyrite dissolved was and redeposited outside the organic matter rich clayey shale. Increases in $\log a_{\text{FeS}_2}$ and $\log f_{\text{S}_2}$, coupled to a slight decrease in $\log a_{\text{Cu}}$, resulted in digenite formation either as a new mineral or as a replacement of chalcocite. Metastable pyrite is again removed, but not so effectively. A further increase in $\log a_{\text{FeS}_2}$ resulted in bornite and pyrite formation due to the $\log a_{\text{FeS}_2} = 0$ plane cutting the bornite volume with $\log a_{\text{Cu}}$ close to zero. Finally, the increase in a_{FeS_2} results in the formation of a stable chalcopyrite-pyrite assemblage.

The model of the mineralization is complicated by possible epigenetic processes. Figure 2 shows the map of the region and its relation to the $\log a_{\text{FeS}_2} - \log a_{\text{Cu}} - \log f_{\text{S}_2}$ diagram, and it can be seen that $\log a_{\text{FeS}_2} = -6$ plane corresponds to the SW limit of the deposit, while the chalcopyrite field corresponds to NE boundary, suggesting epigenetic control.

CONCLUSIONS

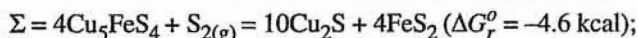
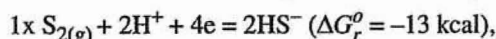
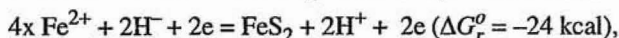
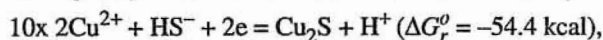
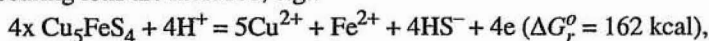
Two and three dimensional $\log a_{\text{FeS}_2} - \log a_{\text{Cu}} - \log f_{\text{S}_2}$ diagrams for the Cu-Fe-S system at $T = 298$ K and $p = 1$ bar can be useful in interpreting the formation of Cu and Cu-Fe mineralizations in sedimentary deposits. The Fore-Sudetic copper deposit is an example of this. These diagrams should be helpful in interpreting Cu mineralizations in black shales, where mineralization with pyrite and/or marcasite and Cu or Cu-Fe sulphides is common.

The main problem in constructing these diagrams is the lack of thermodynamic data for different mineral species. However, even approximate data allow qualitative evolution of the change in parameters during alteration in mineralizing systems. Diagrams constructed for minerals with the same chemical formulae will not differ significantly when the ΔG^0 of polymorphic transition is not too high (e.g. pyrite to marcasite).

APPENDIX

The presented, semi-thermodynamic approach is a sort of simplification, in which:
 — $\log a_{\text{Cu}}$, $\log a_{\text{FeS}_2}$ and $\log f_{\text{S}_2}$ stand for activities of all Cu-, Fe-, and S-bearing ions of a solution in contact with Cu-, Fe- and S-bearing mineral phases;

— presented reactions are combinations of several partial ones, in which Cu-, Fe- and S-bearing ions are included, e.g.:



— each of the Cu-bearing phases is in contact with a solution of the same activity of Cu ions (for diluted solutions identity of activity and concentration is assumed). So, if from 4 grains of bornite 10 grains of chalcocite are formed, both dissolution of the former and precipitation of the latter from the same solution, with activity of Cu ions common for both mineral phases. Dissolution of 4 grains of bornite forms four volumes of the solution, with Cu-concentration of "c", which might be presented as 10 smaller volumes of the same solution (with the same Cu-concentration "c"), which, in turn, are sources of ten grains of chalcocite. As a result, when volumes, representing products and substrats of the reaction, are taken into account, there are only six "active" volumes, with Cu-concentration "c", represented in equations as "6 log a_{Cu} ". Such a simplification is justified as in equations, concentrations and activities are related, not masses.

The main goal of this paper is to present a diagram, understandable for the ordinary reader, which may be helpful in interpreting genesis of naturally observed assemblages of mineral phases. The above simplification avoids complicated calculations, in which Cu-, Fe- and S-bearing ions are included.

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**TERMODYNAMICZNE ASPEKTY MINERALIZACJI Fe-Cu-S W CZARNYCH ŁUPKACH
NA PRZYKŁADZIE ZŁOŻA RUD MIEDZI MONOKLINY PRZEDSUDECKIEJ**

Streszczenie

Stosując uproszczoną metodę obliczeniową, przedstawiono dwu- i trójwymiarowe wykresy $\log a_{Cu} - \log a_{FeS_2} - \log f_{S_2}$ dla układu Cu-Fe-S ($T = 298$ K, $p = 1$ bar), obejmujące obszary i pola stabilności chalkozynu, digenitu, bornitu, chalkopirytu, kowelinu i pirytu (markasytu). Na przykładzie przedsudeckiego złoża miedzi wykazano przydatność wyżej wspomnianych wykresów dla interpretacji mineralizacji siarczkowej w czarnych łupkach.