7.4 Interpretation of the Sediment-Hosted Mineralization

Ore textures, styles of mineralization, mineral zoning and chemical characteristics of the 
Cu-Au ore bodies allow the distinction between different types of Cu mineralization within 
this particular deposit.

7.4.1 Interpretation of Ore Textures and Styles of Mineralization

Mineralization styles are listed below in order of decreasing abundance:

- Disseminated mineralization; mainly chalcocite.
- Fracture-hosted mineralization, mainly chalcocite.
- Late tectonic breccia zones; bornite-chalcopyrite-chalcocite-acidite intergrowths.
- Pseudomorphs after epsomites and pyrite; mainly chalcocite.

The first three types of mineralization suggest a strong permeability control of the mineralization. For a detailed interpretation of the history of sulphide emplacement, it is essential to know during which geological period the permeabilities existed and when they were reduced or destroyed. Nevertheless, such an interpretation is considerably restricted by the present impermeability and complete cementation of all rock types. Mudstones, siltstones and quartz arenites have lost all previous existing permeability due to the emplacement of quartz and minor amounts of calcite cement. The recrystallization of these cements hinders the distinction between possible different generations of cementing material and prevents a reconstruction of the diagenetic/metamorphic evolution of the permeability in these rocks. Thus the interpretation of pre-existing permeabilities and timing of the destruction of these, must be an indirect approach, and in the present case is mainly based on the interrelationships of ore textures. The following sections give interpretations of the different types of mineralization and is followed by a discussion of these results.

Disseminated chalcocite mineralization occurs predominantly within the coarser layers of interlaminated mudstone and siltstone units whereas the relatively dense mudstone layers are barren of any mineralization. Strongest mineralization occurs at the interface between the fine mud- and coarse siltstone fine sandstone layer, but is always hosted by interstitial spaces in the coarser-grained layers. The mineralization is restricted to the pore space with the grain size of the host rock controlling the grain size of the ore minerals. Although some chalcocite grains show cubic shapes, suggesting the replacement of finely disseminated diagenetic pyrite, most chalcocite grains display allotriomorphic shapes. Further evidence for pyrite replacement is the finely dispersed hematite which was released during this process. Only very rare examples have been found where disseminated mineralization is hosted by relatively homogeneous layers of mudstone.

The permeability of these siltstone layers has been destroyed by cementation of intergranular spaces by quartz and calcite. A distinction between early and late diagenetic cements is impossible due to the metamorphic recrystallization of both calcite and quartz cement. However, partial decementation of these layers, necessary to introduce mineralization or remobilize it, has been observed in the close vicinity of (mineralized) fractures. The effect of decementation did not extend beyond one millimetre from these fissures (Plate 7.1G, 7.1F). Consequently, the disseminated chalcocite mineralization must have been emplaced prior to this diagenetic destruction of primary (sedimentary) permeability. The barren nature of the intercalated mudstones is evidence for the permeability control on this type of mineralization and suggests a post-depositional introduction of Cu into coarser layers.

In contrast to the first type of mineralization, the fracture-hosted mineralization is controlled by permeable features of tectonic origin. The mineralization occurs mainly in fractures or forms narrow halos of disseminated mineralization accompanying these (Plate 7.14E). Generally these
mineralized halos are only developed in coarser layers, where they are developed in a similar fashion to the disseminated mineralization described above (Plate 7.1). Generally the fractures host a homogeneous filling of chalcocite but in some cases the mineralization post-dates an earlier generation of anhedral quartz crystals that rim the fractures (Plate 7.1E). The disseminated mineralization which is associated with the fractures occupies intergranular spaces where it has replaced the cement and filled open spaces. Although these disseminations are dense and mineralization is of high grade, it did not penetrate the wall rock further than one millimetre from the fracture.

In one sample from the narrow bornite-chalcopyrite zone at the outer fringes of the ore body, disseminated chalcopyrite has been replaced in the vicinity of a bornite-bearing vein. Here, the fracture is completely filled by bornite. Disseminated chalcopyrite in the close vicinity to the fracture is also replaced by this mineral. Further away from the fracture, however, the bornite grains contain cores of chalcocite (Plate 7.2B) indicating a replacement from the direction of the fracture.

Another type of mineralization, also associated with zones of tectonic permeability, occurs in late tectonic breccia zones. Here, fractures and spaces between breccia clasts host intimately intergrown aggregates of bornite, chalcopyrite and hematite in subordinate amounts of chalcocite, digenite, covellite, hematite and rare occurrences of Bi-sulphides. A great variety of replacement phenomena, e.g. bornite by chalcopyrite and vice versa, indicate numerous phases of metal introduction and remobilization within these permeable zones of preferential fluid migration. An overall introduction of Fe is indicated by the commonly found replacement of covellite by bornite and chalcopyrite, as well as by the abundance of fibrous and finely dispersed hematite in these domains. Although these breccias display the widest variety of ore minerals and textures, they occur only locally as narrow zones and have probably formed during a very late stage of development of the Klein Aub fault zone.

Chalcocite pseudomorphs after gypsum and pyrite provide contrasting evidence with regard to the timing of metal emplacement.

(a) The wrap-around textures of the surrounding interlaminated siltstone and mudstone of gypsum crystals or their replacement products imply an origin prior to the diagenetic compaction of the sediment. These crystals generally seem to have nucleated in coarser layers of interlaminated siltstone and mudstone and the subsequent replacement processes were probably also permeability controlled. Even the relatively well preserved pseudomorphs of chalcocite after gypsum show distinct signs of deformation. All aggregates are associated with quartz-chlorite (calcite) pressure shadows and some chalcocite has been remobilized into these. Deformation resulted in the commonly observed lensoid shape of the sulphide aggregates which obscures originally angular crystal shapes. The textures described above suggest that the replacement of gypsum by chalcocite must have occurred prior to tectonic deformation, probably even before destruction of the sedimentary permeability by diagenetic cements and possibly even before sediment compaction. Thus an early diagenetic to diagenetic origin is suggested.

(b) A rather different time of metal emplacement is implied by the chalcocite cubes which represent former pyrite crystals. The pyrite formed under reducing conditions subsequent to burial within the soft sediment. Anaerobic bacteria converted sulphate-sulphur into sulphide-sulphur as suggested by an isotopic signature with $\delta^{34}S$ values in the range of -22 to -35 permill (Shannon and Hugo, 1975; Preston, 1981, 1986). Deformation left the hard pyrite cubes unaffected but produced prominent pressure shadows adjacent to them and distorted the chalcocite cubes pseudomorphic after gypsum. These relatively soft chalcocite pseudomorphs commonly display perfect, undistorted cube shapes with sharp 90° angles.
placement of large pyrite cubes by chalcocite had happened prior to deformation, the pseudomorphs would have been distorted by such a tectonic event. Thus the replacement process of the pyrite cubes by chalcocite must post-date the last (Ds) deformation and is illustrated in Fig. 7.11.

![Diagram](image)

**Fig. 7.11:** Three-stage sketch diagram illustrating the replacement of diagenetic pyrite cubes after deformation. (A) Diagenetic pyrite cubes in undeformed quartz arns. (B) Compression of the quartz arenite and development of pressure shadows that are filled with quartz and chlorite. (C) Introduction of Cu-bearing fluids and pseudomorphic replacement of pyrite. Fe, released by the reaction, forms dissemination halos of hematite, around the pseudomorphs which show a 21% mass loss compared with the original pyrite.

Most features described above give evidence for the introduction of mineralization along permeable conduits, of both pre- and post-diagenetic origin. Fracture-related mineralization is associated with the introduction of mineralization into permeable layers of the surrounding host rock. Remobilization of disseminated chalcocite has been observed only in one sample. Here, chalcocite was remobilized into a fracture from a zone less than one millimetre wide. The amount of chalcocite now hosted by the fracture accounts approximately for the amount mobilized from the adjacent wall rock. Thus the mineralization remained within the same rock and cannot account for the introduction of disseminated chalcocite elsewhere in the ore bodies. Textural evidence does not indicate the large-scale remobilization of significant amounts of pre-existing mineralization from any areas within the underground workings. Virtually all ore textures, but especially the fracture-hosted mineralization, indicate subsequent additional introduction of Cu mineralization.

The interpretation needs to explain the problem that the silstone-mudstone layers apparently lost their permeability during diagenesis, sealing the disseminated mineralization, while the quartz arenite remained at least partially permeable until after deformation. The different timing of cementation of these rock types probably reflects grain size control on pressure solution. Since pressure solution affects finer-grained sediments more easily than coarser ones, a more abundant supply of quartz cement in the mudstones and siltstones would be expected. Such a difference in supply of cementing material by pressure solution could account for the complete diagenetic cementation and sealing of the finer clastic rocks during diagenesis. The coarser-grained quartz arenites were probably also affected, but to a lesser extent by pressure solution and an incipient cementation but retained a reduced permeability until a much later post-deformational stage.
Sulphide mineral zonation in stratiform sediment-hosted Cu deposits has been used in many cases to determine the migration path of the mineralizing fluids (Brown, 1971, 1978; Haynes, 1986a; Rawn, 1974; Haynes and Bloom, 1987b). It is assumed that Cu-bearing fluids successively replace pre-existing pyrite or precipitate Cu and Cu-Fe sulphides and a zonation from Cu-rich sulphides (chalcopyrite) to Cu-poorer phases (bornite-chalcopyrite) and finally to pyrite results from this process. This zonation commonly includes other base metals and a Pb (galena) and Zn zone ( sphalerite) can be found in many deposits between the chalcopyrite and pyrite zone. The Cu-rich end of this sequence points in the direction from where the Cu-bearing fluids approached and the pyrite end indicates where the migration was directed to.

With regard to the palaeoenvironmental interpretation, all mineralization is hosted within an approximately 400 m wide zone, contained entirely by intertidal sediments adjacent to the ancient shoreline. The zonation generally follows the sedimentary layering up dip and is developed from Cu-rich (chalcopyrite) zones, more basinward in the south, to Cu-poor or Cu-free (chalcopyrite and pyrite) zones to the north towards the inferred paleoshoreline. Such an interpretation is in disagreement with earlier interpretations which suggested an introduction of the Cu and zonation of Cu minerals in the opposite direction introduced by rivers entering near-shore parts of the basin (Holz, 1967; Killick, 1980; Ruston, 1981, 1986). No evidence has been found for such a zonation from north to south, or in the present (deformed) setting from higher mine levels to deeper ones.

**Fig. 7.12:** Modelled evolution of Cu-Fe sulphide zonation in a sediment-hosted deposit. Whereas all other physicochemical parameters remained the same, the solution that produced the pattern of (B) was run ten times faster than that of (A). The pattern of (B) is similar to the ore mineral zonation found at Klein Aub Mine. (Adapted from Merino et al., 1986).
In the present structural setting of the Klein Aub ore bodies, the sulphide mineralization (chalocite - bornite - chalcopyrite - pyrite) is directed upward and outward from the root zone of the Klein Aub Fault. The Cu-poor phases occur furthest away from the fault in the highest parts of the ore bands and this direction of decreasing Cu content is also accompanied by an overall decrease in Cu-grades in the same direction.

The characteristic predominance of chalcocite, divided from the pyrite-bearing unmineralized host rocks by the narrow fringe of bornite/chalcopyrite, is similar to distribution patterns derived from kinetic modelling of zonation patterns by Merino et al. (1986). Figure 7.12 shows the numerically modeled evolution of a zoned sequence of Cu-, Cu-Fc-, and Fe-sulphides in a stratiform-sedimentary hosted deposit. Whereas metal concentrations and other physico-chemical parameters of the metal-bearing solution remained the same in example A and B, the solution in case B migrated ten times faster than in A and produced a sulphide zonation pattern similar to that observed at Klein Aub. This might imply that the mineralizing events at Klein Aub occurred during rather short periods of geological time to produce such characteristic zonation.

A systematic change with depth is displayed by the varying Cu:Ag ratio of the ores from different mine levels. The Cu:Ag ratio changes from relatively Ag-rich Cu ores closer to the present surface (e.g. Cu:Ag = 1.25 on 360 m level) to Ag-poorer ores further down in the deposit (e.g., Cu:Ag = 1.12 on 630 m level). Therefore, the ores on higher levels of the mine have a Cu:Ag ratio with Ag twice as high as those from deeper levels and this phenomenon can be explained in two ways:

- One possible explanation is the preferential precipitation of Cu from ascending fluid in the deeper parts of the ore bodies which is also suggested by the previously explained zoning of sulphide minerals. Such an explanation might be supported by the rather constant absolute Ag contents of the ores from all levels, which hardly exceed 80 to 100 ppm.

- Another possible explanation for the changing Cu:Ag ratio might be the supergene enrichment of Ag in the upper part of the ore bodies, closer to surface. Such a process would be supported by the presence of native Ag occurring along deeply penetrating fault structures where meteoric waters had easy access to the hypogene mineralization.

Probably one of the best examples for supergene enrichment of silver is the Chanarcillo District, Chile. Here fracture-hosted hypogene Cu-Pb-Zn-Co-Ag-Au mineralization has been affected by supergene enrichment of Ag down to a maximum depth of 200 m. Generally, this supergene enrichment process has produced ores with an Ag content 25 to 50 percent higher than that of the hypogene ores. Additionally, native silver is also found in fractures and fault zones of this Chilean mining district. The shapes and sizes of the primary ore bodies were not significantly changed by the supergene processes and due to a pseudomorphic relationship between supergene and hypogene sulphides, no obvious difference between both types of sulphide mineralization has been observed (Whitehead, 1979; Park et al., 1970). At Chanarcillo, one of the characteristics of the supergene sulphide minerals is their higher content of Ag compared with the hypogene minerals.

Both, the previously described ore mineral zonation and the change in the Cu:Ag ratio suggest an introduction of hypogene mineralization from the root zone of the fault ascending along the strata. This migration path is developed in rocks which were originally deposited in an approximately 400 m wide, zone parallel to the basin margin, where the fluid flow was directed to the palaeoshoreline. The hypogene mineralization has possibly undergone supergene enrichment of Ag by meteoric fluids which affected the ore bodies probably down to a depth of approximately 400 m. Hypogene mineralization (native Ag) at even deeper mine levels is restricted to fault zones. Thus at Klein Aub, mineralization has probably been introduced or
enriched by both ascending and descending fluids during different stages of the geological history.

7.4.3 Timing of Metal Emplacement - A Discussion

The previously described textures, styles of mineralization, zonation of ore minerals and metal ratios give evidence for Cu and Ag introduction and precipitation during various times during the geological history. An attempt to describe the timing of metallogenic events and any subsequent ore genesis model therefore must attempt to accommodate the evidence for these different phases of sulphide emplacement. Unfortunately every subsequent phase had the tendency to mask earlier events and as a result, the youngest features will obviously be the ones that can be explained most convincingly. Starting off on relatively safe ground the timing of mineralizing events is described in a slightly unusual fashion by beginning with the youngest, best documented event. From here the other older events will be outlined successively by discussing earlier episodes in the history of the ore deposit.

- The last mineralizing event is probably represented by the supergene upgrading of the Ag content in the Cu ores and the precipitation of native Ag and Cu on faults acting as conduits to meteoric waters.
- The next earlier mineralizing event is represented by the replacement by chalcocite pseudomorphs after diagenetic pyrite. This process clearly post-date the latest deformation, since cubic shapes are preserved undistorted and pressure shadows do not contain any chalcocite. During this phase the footwall quartz arenite had still retained sufficient permeability and was not completely cemented.
- Late tectonic breccia zones gave access to percolating fluids over extended periods of time and caused the development of economically insignificant bornite-chalcopyrite-hemimorphite mineralization.
- Various stages of post- and post-deformational sulphide emplacement are indicated by the fracture-hosted mineralization, which, locally, post-dates an earlier generation of quartz that initially filled the fractures. This mineralization also penetrated into the adjacent wall rocks where coarser layers provided better access for the fluids. However this process was only of local influence and rimmed the fractures with disseminated mineralization on a millimetre scale. It can not be established to which extent this stage of mineralization might have been associated with the two stages previously described.
- Gypsum or anhydrite crystals of more or less syndepositional origin were replaced prior to deformation which then distorted them into lensoid aggregates with chalcopyrite-filled pressure shadows.
- Disseminated chalcopyrite mineralization, hosted by the more permeable (coarser) layers of the interlaminated dolomite/mudstone was probably emplaced during early diagenesis, while original, sedimentary permeability still allowed access to the mineralizing fluids. Locally this mineralization also affected the permeable quartz arenite, although, the overall lack of sulphur prevented the development of any extensive mineralization of this type. The disseminated mineralization subsequently became necrotic by diagenetic cementation of the finer clastic rocks. Cementation of the finer clastic rocks was more complete compared with the quartz arenite due to a more abundant supply of silica from preferential pressure solution of the smaller grains.
- Virtually no mineralization has been found in the mudstone layers of the interlaminated dolomite/mudstone which would have been prime sites for metal precipita-
...tion during sedimentation due to the reducing conditions and an abundant sulphur supply from anaerobic bacteria.

A syngentic origin (Holz, 1967; Ruxton, 1981) for any substantial part of the economic mineralization at Klein Aub mine is discarded. Suggestions by previous authors, involving the remobilization of syn-sedimentary or early diagenetic mineralization to form the present mineralization (Holz, 1967; Ruxton, 1981; Killick 1986) are not supported by the ore textures. The styles of mineralization imply in virtually all cases the introduction of additional mineralization. Fluids in the vicinity of fractures were derived from these fractures and transported into permeable portions of the adjacent wall rock. No significant remobilization of previously existing mineralization has been found in the Klein Aub ore bodies.

The possibility that the disseminated mineralization has been introduced during an epigenetic phase via faults and fractures (Phillips and Groves, pers. com. 1986) is also discarded. Disseminated mineralization adjacent to the fractures can be clearly distinguished from the earlier disseminations. Mineralization introduced from the fractures is of higher grade, larger grain size and locally different mineralogical composition; e.g. bornite replacing disseminated chalcopyrite in the vicinity of bornite-filled fractures.

The determination of various mineralizing events during the geological evolution of the deposit suggest a multi-phase metal emplacement process. This multi-phase process included an initial, early diagenetic phase which produced disseminated mineralization with ore grades generally in the range of 1%-2% Cu and 12-25 ppm Ag. During and after deformation more mineralization was introduced via the fault zone and the still permeable footwall arenite into fractures and the adjacent wall rock. This event upgraded the ore grades to values between 2% and 4% Cu, and 25-50 ppm Ag and subsequent supergene processes might have caused the Ag enrichment in the upper parts of the ore bodies.

**AGE GEOLOGICAL EPISODE**

| 1000-950 Ma | Sedimentation | Possibly minor metal precipitation due to a change in redox conditions |
| 600-550 Ma | Early Diagenesis | Basin dewatering, introduction of metalliferous fluids into permeable S-rich beds; precipitation of disseminated mineralization |
| 550-500 Ma | Late Diagenesis | Pressure solution and cementation of finer clastic sediments; sealing of disseminated mineralization |
| 500-600 Ma | D2 and D3 | Syndeformational introduction of metals from basalt and red beds into fractures and adjacent wall rocks |
| 5 Ma - present | Post deformation | Further metal introduction and replacement of pyrite cubes |
| 5 Ma - present | Sub-Recent | Supergene Ag enrichment of upper parts of ore body |

**TABLE 5**
7.1.1 Fluid Transport

The fluids that have mineralized the host rocks at Klein Aub in several geological episodes require different fluid transport mechanisms, suitable to the changing lithological parameters and structural settings. The three different phases which have been identified and described in the previous sections require processes that can function during early diagenetic, syn- and post-deformational, and post-depositional (Quaternary and Tertiary?) phases of metal emplacement. The possible transport mechanisms will be described from the oldest to the youngest events.

![Block diagram illustrating the seismic pumping model of Sibson et al. (1978) as a possible syn-deformational transport mechanism for epigenetic mineralizing fluids in a right-lateral strike-slip fault system.](image.png)
Basin Dewatering. To explain the fluid transport processes that actively formed the disseminated mineralization, it is necessary to consider the vertical and lateral position of the Klein Aub ore bodies within the basin. The ore deposit is situated in a marginal position within the basin and above a distinct local basement high and it is reasonable to assume that this area was, during sediment compaction and basin dewatering, the area where the flow of upward and outward migrating basinal waters focused. Here these fluids would migrate within the subsurface, from the basin towards the shoreline, percolating through aquifers provided by the more permeable sandy and silty layers of the intertidal sediments. Such basin dewatering models have been described from many ancient and modern basins (Badham, 1981; Sawkins, 1984).

Syn-deformational Fluid Transport

The active Klein Aub fault zone has possibly provided an efficient fluid transport mechanism during Dε deformation for the fracture-hosted phase of mineralization. Fault zones, such as the one at Klein Aub, commonly act as conduits to migrating fluids, especially during reactivation of fault movement. Field evidence suggests that the Klein Aub fault zone was active over an extended period of time and was possibly reactivated several times during geological history (compare Chapter 6). Sibson et al. (1975) described "seismic pumping," a driving mechanism commonly associated with high angle fault structures such as strike-slip faults.

In its simplest form, the seismic pumping model (Fig. 7.13) assumes that prior to seismic shear failure along an existing fault, the terrain around the focus of the subsequent earthquake dilates in response to an increase in tectonic shear stress. Dilatation occurs due to the opening of tensile fractures normal to the least principal compressive stress. The development of such a fracture porosity causes a decrease in fluid pressure and induces inward migration of fluids from the surrounding terrain. The decreasing fluid pressure causes a rise in frictional resistance against shear, dilating the fractures. As the migrating fluids fill the cracks, fluid pressure rises, and frictional resistance drops, eventually resulting in seismic failure. Rapid relief of shear stress, accompanying earthquake faulting, allows the fractures within the dilatant zone to relax. Thus the contained fluids are expelled rapidly upwards in the direction of easiest pressure relief. The effect is especially associated with strike-slip and high-angle normal faults, where strongest compression is sub-horizontal and the fractures can be expected to be arranged sub-vertically. Uplift from such a collapsing dilatant zone generally takes place along the fault, fractures and all permeable layers.

During sub-Recent supergene phases of metal enrichment percolating meteoric waters probably utilized faults, shear zones, breccias and fractures and penetrated mineralized and unmineralized strata to considerable depths. Supergene minerals such as native Ag, native Cu, cuprite and hematite, are found at Klein Aub Mine in the vicinity of faults down to more than 600 m below surface. The less obvious, possibly also supergene Ag enrichment of the chalcocite ores at Klein Aub Mine affected the ore bodies to a depth of approximately 400 m below the present surface and with decreasing influence to even deeper levels. These meteoric waters preferentially utilized zones of tectonic permeability to penetrate the rock sequence.

Thermodynamic Constraints on the Ore Fluids

The discussion of thermodynamic constraints on the possible ore fluids focuses on the epigenetic phase of mineralization, since this thermal event produced most of the presently known mineral paragenesis at Klein Aub Mine. The calculations are based on several assumptions which are necessary since no detailed data, e.g., from fluid inclusion studies, are available. Thermodynamic calculations are normally based on constant temperature, a requirement that presents some problems in case of the Klein Aub area. Stable fields were calculated for a temperature of 80°C, based on the available local temperature data (listed overleaf).
Illite crystallinity: 350°C (Ahrendt et al., 1978).
- Pumpellite stability: 200°-300°C (Henrich en and Schurmann, 1969).
- Quartz, muscovite, Mg Chlorite, kaolinite, calcite assemblage without any biotite; 350°C.
- Minor amounts of digenite; 90°C.
- Decrepitometer analysis; peaks at 160°C and 350°C (Schmidt Mumm, pers. com., 1985).
- Fluid inclusion study, 175°C, but from a later generation of fractures (Schneider, pers. com., 1987).

Since stratigraphic controls and the mineral paragenesis from the Klein Aub area do not allow for the establishment any particular pressure, the calculations were based on a constant pressure of 500 bar. Many of the data given for this value and the pressure dependence of the stability fields is regarded as negligible (Helgeson, 1969). The total sulphur concentration was assumed to be 0.01 mole. This value is 20% of that found in porphyry copper deposits and was chosen since the sulphur activity in the Klein Aub deposit appears to have been exceptionally low. Total Cl concentration was assumed to be 1 mole and the activity of K was assumed as 0.05, values which are often associated with natural systems and found in fluid inclusions. The Ca activity was assumed to be 0.01 since this value is commonly found to be between 10% and 20% of the K activity. For the calculations it was further assumed that the activity coefficients are 1, thus the activities are equal to the ionic concentrations of the elements.

![Diagram](image-url)

**Fig. 7.14:** Diagram of fO₂ at φ defining the maximum range of CO₂ activities of the possible ore fluids. **hem** = hematite; **mag** = magnetite; **ca** = calcite; **wol** = wollastonite; **C₅₀⁻** = graphite.
The activity of solid end-members was also regarded as 1. The thermodynamic data was taken from Robie and Waldbaum (1968), Helgeson (1969), Barton (1973), Crecar and Barnes (1976), Seward (1976), and Casadevall and Ohmoto (1977). No data for the equilibrium constants of chalcocite were available.

In the fO2/fCO2 diagram of Figure 7.14, boundaries for the stability fields of hematite, magnetite, calcite, wollastonite and graphite are shown. This diagram allows for the establishment of the maximum range of possible CO2 activities. Such a compositional range is limited by the wollastonite and the graphite field since none of these minerals occurs and must be near the hematite/magnetite boundary, because traces of magnetite occur besides abundant hematite. The possible CO2 activity ranges from log aCO2 = -0.75 to log aCO2 = 5.9.

In the fO2/fS2 diagram (Fig 7.15) the characteristics of the possible fluid can be limited to a rather small field. The diagram shows the boundaries between the stability fields of native Cu, chalcocite, digenite, hematite, magnetite, pyrrhotite, and pyrite Superimposed are the stability fields of calcite, calcite and graphite shown for both maximum and minimum CO2 activities.

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Fig. 7.15: Diagram of fS2/fO2 illustrating the stability fields of some indicative mineral phases. The probable composition of the ore fluids is shown as shaded area and their maximum range is outlined by a dashed line for the Klein Vlaardingen ore paragenesis consisting of chalcocite, digenite, hematite with minor magnetite (martitized) and digenite. (ccc = chalcocite, dig = digenite, po = pyrrhotite, py = pyrite; see Fig 7.13 for other abbreviations)
The paragenesis of chalcocite, minor hematite and traces of both magnetite and digenite defines the shaded area in this figure. The boundaries of the calcite field might give a maximum range of possible fluid compositions. The fact that many magnetite crystals are replaced by hematite could imply that the original compositions were located more towards the magnetite field within this diagram.

![Diagram of pH showing the stability fields of various mineral phases and sulphur species. The compositional range of the probable ore fluids at Klein Aub (shaded area) is defined by the paragenesis of hematite (with minor magnetite) and muscovite (with minor kaolinite). (cp = chalcopyrite, bn = bornite; see Figs. 7.13, 7.14 for other abbreviations)](image_url)

The probable pH range can be determined from the diagram in Figure 7.16, where a variety of different stability fields is shown in a pH-Ti diagram. Indicated in solid lines are the fields for pyrrhotite, pyrite, magnetite and hematite. Short dashed lines indicate the fields of the different sulphur species. The lines consisting of dashes and points define the stability fields for chalcopyrite and bornite plus pyrite; the latter represents a field where no chalcopyrite can be present. Further fields outline the stability fields of kaolinite, muscovite and K-feldspar, and the calcite-wollastonite boundary at about 0°C. The pH range for the possible ore fluids, since the rock contains muscovite as well as minor amounts of kaolinite, this boundary, together with the hematite-magnetite boundary defines the pH range approximately between 3.5 and 4.5, calculated for diff...
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