

A GEOCHEMICAL MODEL FOR SULFIDE PARAGENESIS AND ZONING IN THE Cu–Fe–As–S SYSTEM (TSUMEB, SOUTH WEST AFRICA/NAMIBIA)

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ABSTRACT

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The Cu-bearing hypogene mineralization at Tsumeb, South West Africa/Namibia, is interpreted to have resulted from the interaction of hot circulating Cu-rich saline solutions and host dolomites. Fluids attending formation of the main sulfide stage were warm (210–280°C) and moderately saline (6–12 wt.% NaCl equivalent).

Phase relations within the Cu–Fe–As–S system suggest that the observed paragenetic sequence (chalcopyrite → bornite → chalcocite → enargite → tennantite) is consistent with a model calling for successive introduction of a single Cu-rich solution into a host dolomite. The Cu and As content of the solution decreased as it passed through the permeable dolomite precipitating Cu–As-sulfides and sulfosalts. A concomitant increase in pH created by the dissolution and buffering effect of dolomite produced sufficient changes in the fluid chemistry to shift the stable sulfide mineral assemblage.

INTRODUCTION

The Tsumeb orebody of South West Africa/Namibia consists of a pipe-like structure extending to a depth of greater than 1.5 km containing Cu–Pb–Zn mineralization. The structure follows a narrow zone of folding in the upper dolomite formations of the late Precambrian miogeosynclinal sediments of the Damari–Otavi System. Mineralization is associated with solution collapse brecciation, limited wall-rock alteration, and a “pseudoaplite” of controversial origin. For more detailed accounts of the local geology and structural controls of the deposits readers are referred to Schneiderhohn (1958), Söhngé (1961), Park and MacDiarmid (1975), and Weber and Wilson (1977). In a recent comprehensive study by Lombaard et al. (1984) it is suggested that the pseudoaplite is actually a feldspathic sandstone, correlatable with the overlying arenaceous Tschudi Formation. They further suggest that it became incorporated into the lower unit during karsting and related collapse prior to the introduction of ascending mineralizing fluids.

Mineralization, both in the oxide and hypogene sulfide zones, is extremely complex. Thirty-two distinct sulfide phases have been identified (Pinch and Wilson, 1977). This study utilizes petrographically determined sulfide paragenesis, fluid inclusion geothermometry and mineral stabilities to place limits on the solution geochemistry responsible for the hypogene Cu—Fe—As—S mineralization in the Tsumeb main ore zones.

Paragenetic relationships among the primary sulfide phases were studied in polished sections from the 16 and 30 levels. The limited vertical coverage represented by the samples of this study precludes a complete evaluation of the vertical zonation in the pipe. Instead, this paper seeks to combine petrographic observations of sulfide paragenesis with fluid—mineral equilibria to constrain temporal changes in mineral stability and solution chemistry that accompanied ore formation.

PETROGRAPHY

While galena and sphalerite occur as replacement sulfides throughout the pipe length, the majority of the early sulfide phases in the Tsumeb ores are Cu-rich. Pyrite is reported as an early phase at Tsumeb (Söhnge, 1961), but its position in the paragenetic sequence was ambiguous in the samples of this study. It is likely that pyrite was stable periodically during the mineralization event but as a minor phase. The possible significance of pyrite will be discussed later.

Chalcopyrite is the earliest Cu-bearing phase observed in the Tsumeb ores. It comprises only a few percent of the total sulfide assemblage and has been virtually completely replaced by later, more Cu-rich phases. Bornite and chalcocite were the next major sulfide phases to become stable and commonly exhibit exsolution textures, probably indicating original deposition of a chalcocite—bornite solid solution. Enargite and then tennantite are the final hypogene Cu phases encountered. The sulfosalts occur in veins and pods cutting the earlier bornite and/or chalcocite. Galena and sphalerite complete the sulfide mineral assemblage.

Fluid inclusions in quartz intimately associated with bornite—chalcocite and with tennantite—enargite deposition were analyzed for homogenization temperature and salinity. Temperatures of homogenization for 26 inclusions are reported in Fig. 1, and suggest a bimodal distribution with peaks at 170—200° and 220—240°C. Salinities, determined by freezing point depression methods and calculated using the regression analysis of Potter et al. (1978), are as high as 12 wt.% NaCl equivalent, and average ~8 wt.%. Based on fluid inclusion work, Lombaard et al. (1984) report a formation pressure of 500—700 bar, which would require a 30—40°C pressure correction of the observed homogenization temperatures. Thus, the peaks of formation temperatures corresponding to the filling temperatures would be 210—240° and 260—280°C, and an average temperature for sulfide deposition of 250°C is reasonable. Formation pressures of as much as 1 kbar would require a 60°C correction, and a 250°C temperature would still be reasonable.

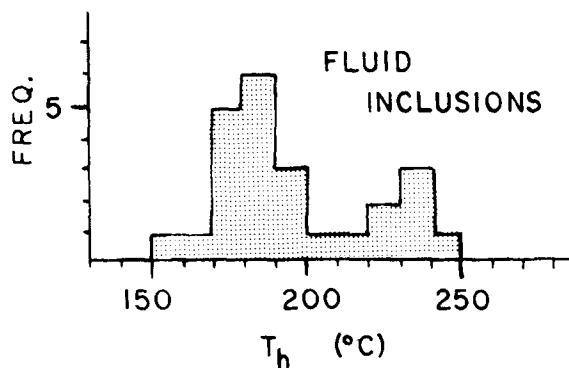


Fig. 1. Homogenization temperatures from fluid inclusions in quartz associated with sulfide deposition.

DISCUSSION

The preceding mineralogic, paragenetic and thermal knowledge can be used to approach the problems of ore genesis from a geochemical viewpoint. Unfortunately, the Cu—Fe—As—S system has too many variables to permit an exhaustive study of all possible chemical permutations. However, by fixing the $\log a_{H_2S}$ at -4 , and plotting $\log(a_{Cu^+}/a_{H^+})$ vs. $\log(a_{Fe^{2+}}/a_{H^+}^2)$ over a range of $\log(a_{H^+} \cdot a_{As(OH)_4^-})$ -values, all of the observed Cu phases can be plotted. The resulting phase diagram, modified from Brimhall (1979), is depicted in Fig. 2. The equations utilized in modifying Brimhall's work are those of Knight (1977) and thermodynamic data are also from Knight.

By coupling a steady drop in Cu and As concentrations in solution with an increasing pH accruing from the solutions' interaction with dolomite, a model can be developed that is both consistent with the observed paragenesis and geologically reasonable for the Tsumeb environs.

Acidic solutions, rich in Cu and As, ascend the brecciated pipe structure and enter the permeable and chemically receptive dolomite at temperatures in excess of 250°C . In this scenario, tennantite would be the first sulfide mineral to be precipitated [at point A in Fig. 2 and with $\log(a_{H^+} \cdot a_{As(OH)_4^-}) = -9$]. The precipitation of tennantite is accompanied by a decrease in both Cu^+ and $As(OH)_4^-$ in solution. The drop in As compounded by a rising pH causes a significant fall in the $\log(a_{H^+} \cdot a_{As(OH)_4^-})$, forcing the enargite—tennantite join to increasingly higher $\log(a_{Cu^+}/a_{H^+})$ -values until enargite becomes stable at point B [$\log(a_{H^+} \cdot a_{As(OH)_4^-})$ has now fallen to -10.5]. In addition to a steady retreat of the sulfosalt phases to higher $\log(a_{Cu^+}/a_{H^+})$ -values, a decreasing $\log(a_{H^+} \cdot a_{As(OH)_4^-})$ produces a collapse of the enargite stability region until at $\log(a_{H^+} \cdot a_{As(OH)_4^-})$ -values of -10.9 enargite is no longer stable. Covellite and tennantite become mutually compatible at $\log(a_{H^+} \cdot a_{As(OH)_4^-})$ -values below -10.9 . Covellite was not observed in this study nor is it reported in the literature, so it must be assumed that

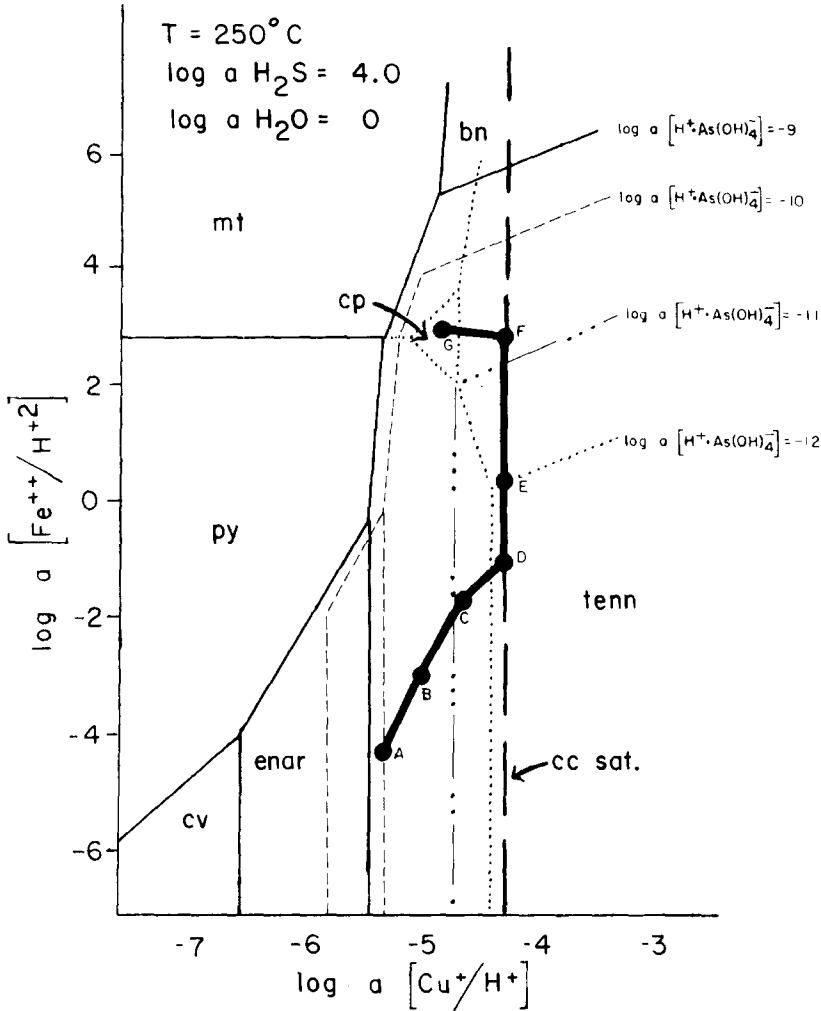


Fig. 2. Log activity ($\text{Cu}^{+}/\text{H}^{+}$) vs. log activity ($\text{Fe}^{2+}/\text{H}^{+2}$) at a fixed temperature of 250°C , activity $\text{H}_2\text{O} = 1$, and activity $\text{H}_2\text{S} = -4.0$. The phase relations are shown at variable activity ($\text{H}^{+} \cdot \text{As}(\text{OH})_4^{-}$) values.

before the product of the As and H^{+} concentrations reached the limit of enargite stability the solution composition had left the univariant tennantite–enargite surface into the divariant tennantite field at point C, where $\log(a_{\text{H}^{+}} \cdot a_{\text{As}(\text{OH})_4^{-}}) = -11$. Such an assumption is reasonable in an environment like Tsumeb where pH is probably climbing as the host dolomites are consumed.

As the solutions continue to migrate upward and outward, $\log(a_{\text{H}^{+}} \cdot a_{\text{As}(\text{OH})_4^{-}})$ and H^{+} continue to decrease. The competing effects of decreasing

Cu^+ and decreasing H^+ preclude major fluctuations in the $\log(a_{\text{Cu}^+}/a_{\text{H}^+})$; the ratio changes less than one log unit over the entire proposed ore-forming process. However, since chalcocite is observed, the solution composition must impinge upon the chalcocite saturation surface; this can be easily accomplished at point D if the pH effect slightly overrides the Cu^+ decrease and the $\log(a_{\text{Cu}^+}/a_{\text{H}^+})$ is allowed to increase a small amount.

The migrating solutions are now saturated with chalcocite and the $\log(a_{\text{Cu}^+}/a_{\text{H}^+})$ is buffered at -4.35 for an $a_{\text{H}_2\text{S}} = -4$. pH will continue to increase and since H^+ is squared in the denominator of the ordinate variable [$\log(a_{\text{Fe}^{2+}}/a_{\text{H}^+} = 2)$], the solution composition will migrate up the chalcocite saturation surface and will encounter the bornite field at point E [$\log(a_{\text{H}^+} \cdot a_{\text{As}(\text{OH})_4^-})$ -values now depressed to -12]. Bornite and chalcocite (or a solid solution which later exsolves) will continue to be the stable assemblage until point F. At this point the solution composition must leave the chalcocite saturation surface to reach the small triangular stability region of chalcopyrite. Such a departure is reasonable; by this time it is conceivable that the acidic character of the solution is nearly spent and the decrease in pH may be reduced. The loss of Cu^+ and Fe^{2+} in solution inherent in the precipitation of bornite and chalcocite may become the influencing factors, and the solution composition can migrate to point G, where the final Cu^+ in solution is consumed by the precipitation of chalcopyrite.

The total effect of this *migrating solution* can be visualized in Fig. 3A. Early tennantite–enargite deposition near the source of the fluids gives way to a bornite + chalcocite zone as the solution migrates further into the dolomite. Finally, the nearly-spent solutions deposit chalcopyrite before reaching equilibrium, with respect to sulfides, with the dolomite host.

The effects of subjecting these mineralized zones to subsequent fluids of similar initial composition are illustrated in Fig. 3B. The solutions would pass through the sulfosalt portions of the earlier mineralized zone unchanged since they would be in equilibrium with tennantite–enargite. Upon reaching the bornite–chalcocite zone the solutions would be too high in Cu^+ and $\text{As}(\text{OH})_4^-$ and too low in pH to be in stability with bornite and chalcocite. Tennantite and enargite would be stable and would form as replacements and along veins in the earlier Cu–Fe-sulfides. Upon contacting the chalcopyrite zone, it is likely that these temporally intermediate solutions would be sufficiently depleted in $\text{As}(\text{OH})_4^-$ and H^+ to no longer be in stability with sulfosalt phases, but the solutions could still be saturated with bornite and chalcocite with the result: bornite and chalcocite replacing chalcopyrite. Still later fluids of similar composition would allow tennantite to be stable farther outward, perhaps to a point where initial solutions had precipitated chalcopyrite. The entire sequence, chalcopyrite \rightarrow bornite + chalcocite \rightarrow tennantite + enargite, would be expected in this zone (Fig. 3C).

In review, the observed paragenetic relationships are all consistent with a model of upward and outward moving chemical fronts. The paragenetic sequence related to the Cu phases can be produced from a single Cu-rich fluid,

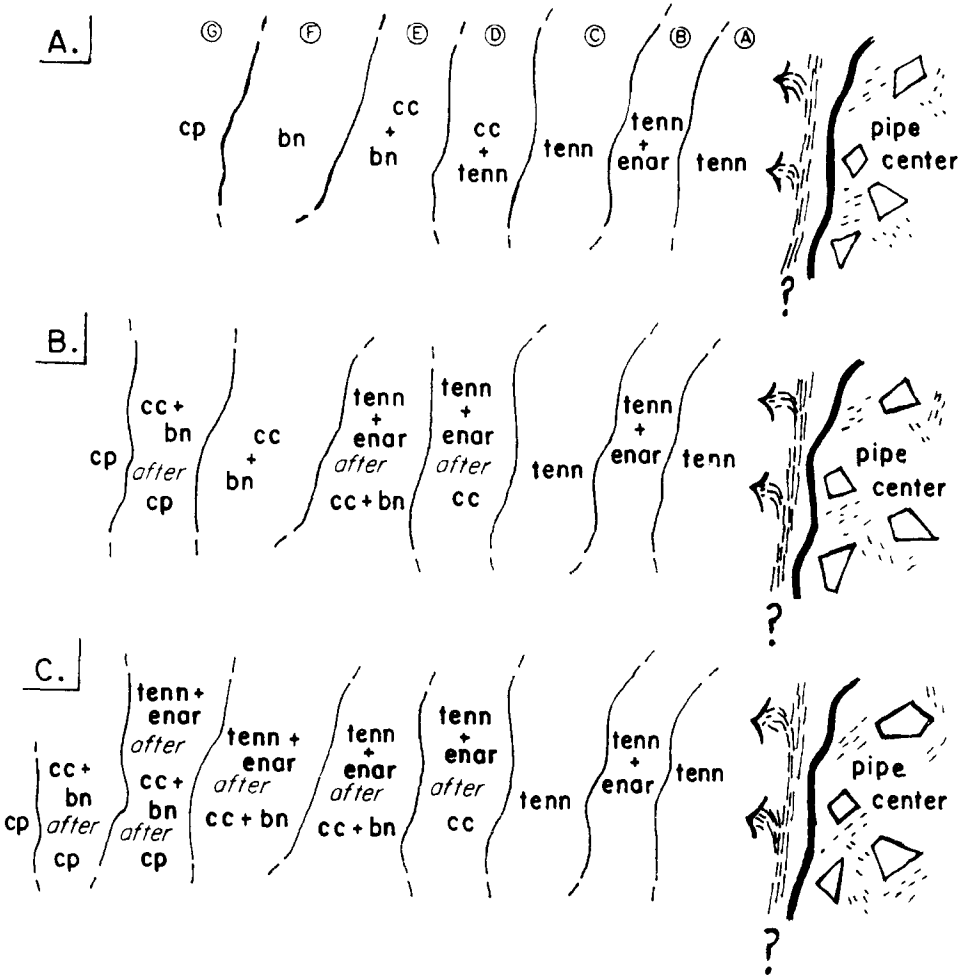


Fig. 3. Spatial and temporal distribution of copper sulfide phases predicted by the model. A. Early spatial zoning created by initial fluids. *Circled letters* correspond to points along the solution path as depicted in Fig. 2. B. Later fluids of similar composition create "moving" chemical fronts. The predicted replacement mineralogies are shown. C. Final results after considerable fluid-rock interaction.

simply by passing the fluid through chemically receptive dolomites over a period of time. No changes in the original concentrations of Cu, As, S, Fe or H⁺ in the solution are needed.

At this point it is worth returning to the possible chemical significance of pyrite in the Tsumeb ores. The stability field of pyrite in Fig. 2 is large and although the described path never intersects the pyrite divariant stability field, the field is never too distant from the proposed path. Small fluctuations, either of local or deposit-wide extent, of a_{H₂S}, a_{Fe²⁺}, or pH could

easily thrust this path into the pyrite field at any time during the system's evolution. The occurrence of limited amounts of pyrite at Tsumeb, especially deep in the system (Lombaard et al., 1984), suggest that these fluctuations did occur. However, a more detailed study of accurately located samples would be required to document the nature and extent of such fluctuations.

The preceding analysis precludes the incorporation of galena and sphalerite in the geochemical model. Their presence in structures cutting earlier Cu-rich assemblages has been attributed to the introduction of Pb—Zn-rich solutions into earlier massive Cu replacement ores (Geier and Otteman, 1973; Lombaard et al., 1984). The validity of such a proposal cannot be evaluated by the preceding geochemical model introduced in this paper.

CONCLUSIONS

(1) Textural evidence from isolated samples from Tsumeb, South West Africa/Namibia, suggest a sulfide paragenesis of early chalcopyrite, intermediate bornite and chalcocite, and late tennantite and enargite.

(2) Fluid inclusion data derived from quartz associated with sulfide mineralization indicate that temperatures of 210–280°C attended formation of the complex ores and that fluids were of moderate salinity (6–12 wt.% NaCl equivalent).

(3) The observed paragenetic sequence is consistent with a model of upward and outward migrating fronts of sulfide stabilities produced by changing solution chemistry. The decrease in Cu^+ , Fe^{2+} and $\text{As}(\text{OH})_4^-$ in solution and the increase in pH, all required in the model, are geologically reasonable in the Tsumeb environment.

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