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Mineral Formation on Metallic Copper in a "Future Repository Site Environment"

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SUMMARY.

Formation of copper minerals in a “future repository site environment” is discussed. Since reducing conditions are expected much effort has been concentrated on Cu-sulphides and CuFe-sulphides. However, oxidizing conditions are also discussed. A list of copper minerals are included. It is concluded that mineral formation and mineral transitions on the copper canister surface will be governed by kinetics and metastabilities rather than by stability relations. The sulphides formed are less likely to form a passivating layer, and the rate of sulphide growth will probably be governed by the rate of transport of reacting species to the cansiter surface. A series of tests are recommended, in a milieu resembling the initial repository site conditions.

SAMMANFATTNING.

Bildning av kopparmineral i en framtida slutförvarsmiljö diskuteras. Eftersom reducerande betingelser kan förväntas har Cu-sulfider och CuFe-sulfider getts stor plats, men även oxiderande betingelser diskuteras. En lista på kopparmineral är inkluderad. Slutsatsen är att mineralbildning och mineralförändring på ytan av kopparkapslarna kommer att styras av kinetik och metastabiliteter snarare än av jämviktsrelationer. Det är mindre troligt att sulfiderna kommer att bilda ett passiviserande skikt och sulfideringshastigheten kommer troligtvis att bestämmas av hur fort reagerande ämnen kan transporteras till kapselytan. En serie tester rekommenderas, i en miljö som liknar den initiala slutförvarsmiljön.

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1 INTRODUCTION.

The present report was initiated by the Swedish Nuclear Power Inspectorate. It may be regarded as a continuation of our previous report; "Stability of metallic copper in the near surface environment" (SKN 57, 1992), which dealt with geochemical aspects of copper solubility and stability in an expected future "repository site environment for spent nuclear fuel".

Here we discuss possible mineral forming processes on the surface of the copper canisters, based on the geological - geochemical literature. The advantage in using geological analogies is that nature provides us with long-term low temperature experiments on mineral behaviour, which we can never hope to copy in the laboratory. The disadvantage is that the conditions, in terms of chemical composition etc., are often ill defined.

Unfortunately, information which has a direct bearing on the present well-defined problem is missing, to a large degree. This means that we have to use circumstantial evidence and analogy reasoning, to be able to say anything about possible futures for the canisters. Partly, this problem stems from the fact that studies on ore formation - ore alteration etc., are based on stability relations of various ore minerals at elevated temperatures. Here we are confronted with the problem of predicting what to expect, in an environment (about +5 to +80^{O}C) where most ore minerals fail to equilibrate in the laboratory within reasonable times (This does not mean that the minerals fail to react at all, rather that reactions tend to follow metastable paths at low temperatures. This is true both for natural long-term - and laboratory short-term experiments, and is discussed below).

Thus, studies on mineral equilibria are of limited value, since we have to extrapolate experimental results from, say 200 - 300^{O}C, to the present environment. To add to the uncertainty, it is evident that even equilibrium Eh-pH studies, which are frequently employed to delineate mineral stabilities in the natural low-temperature environment, often show large discrepancies when confronted with reality. As exemplified in Appendix 1, Eh-pH values calculated from thermochemical data, often differ significantly from what is actually observed employing potentiometric measurements.

Since considerable uncertainty exists as to which minerals (if any!) will actually form on the copper canisters, we have listed both likely and less likely candidates in Table 1. Much of the discussion here is concerned with Cu-sulphides and CuFe-sulphides. This is partly so because we are more familiar with these phases compared with Cu-oxides and complex Cu(II)-compounds like malachite; $Cu_2(CO_3)(OH)_2$ etc., found in environments suggesting oxidizing conditions. Although measurments on deep groundwaters indicate reducing conditions, it is also of interest to analyse the behaviour of copper under oxidizing conditions. Oxidizing conditions will prevail in the repository for some time due to residual oxygen from entrapped air.

Formation and alteration of metal sulphides in nature is a question of redox processes. Some basic definitions and basic thermodynamic quantities were given in SKN 57, 1992, as well as a few examples on how to construct a Eh-pH stability diagram. This is not repeated here. Besides, in the present report we discuss qualitative rather than quantitative aspects of mineral formation on the copper canisters. Quantitative aspects depend on the environment, in terms of exact chemical composition of the groundwater and behaviour of the other barriers (bentonite, enclosing rocks). These questions are outside the scope of this report.

Much of the text below is given to exemplifications and discussion of low temperature processes observed in nature. As stated above, several of these examples are not directly applicable to the present problem. We think they merit our attention, however, since low temperature processes among metal sulphides show some common behaviour, which can be applied to the question of mineral formation on metallic copper. Also, they illustrate the complexity of the processes to be expected, as well as the difficulty confronting us when we try to make predictions about something we have little solid knowledge about.

2 FORMATION OF MINERAL PHASES ON METALLIC COPPER.

2.1 General.

As discussed by Amcoff and Holényi in SKN 57, 1992, there are two major environments in nature where metallic copper is found; (i) In meteorites, "Moon-rocks", and mantle rocks (magmatic rocks with a low SiO_2 content, crystallized at great depth), which suggest the strongly reducing environment when the Earth was formed. (ii) In the deeper parts of the oxidized zone of some Cu-rich sulphide ores (still in the upper part of the crust), where conditions are not oxidizing enough for formation of Cu-oxides etc., and not reducing enough for Cu-sulphide formation. It was also suggested that environment (ii) is more relevant when discussing the future repository site environment.

As far as we know, geochemical studies concerning the present problem are practically non-existent. This is so, because the interest has been focused more on the particulars of metallic copper *formation*, in terms of the physico-chemical milieau, than on its subsequent surface alteration characteristics. The reason for this is partly that metallic copper is a rare mineral, its very existence has been considered the most interesting discussion topic. Besides, microscale surface processes have earlier been difficult to study, they have consequently recieved little attention.

Thus, information which is of interest in the present context is of a rhapsodic and indirect character. As seen in Table 1, there exist many Cu-minerals in the low temperature environment. Some of these may be of importance here.

A number of factors influence mineral formation in the present environment. These include; (i) Temperature and pressure, (ii) Chemical environment in terms of aqueous and solid species which may participate in reactions with the metal, (iii) Stability-metastability. Again we would like to stress that the present report is concerned with qualitative aspects of mineral formation. (For example, the redox conditions in terms of Eh tell us little about the redox *capacity*, which depends on how fast redox couples which participate in reactions are replenished. This quantity is of fundamental importance when it comes to the question of long-term survival of the copper canisters).

For the sake of argument we assume that the groundwater surrounding the canisters contains a certain amount of species with the ability to oxidize metallic copper; that some sulphur is present in the form of aqueous sulphides and polysulphides (discussed below), and that some dissolved iron is present (SKB 86-03, 87-07). Also we assume a temperature below 100°C and a pH slightly on the alkaline side of neutrality. Here we will not discuss the possibility that the copper canisters might accidentally be subjected to strong oxidation "from above".

A sulphidation process is equivalent with a redox process, independant of whether it takes place in an aqueous or a dry environment. Copper in binary Cu-sulphides seems to be univalent, independent of the Cu/S ratio (Rolf Berger, Institute of Chemistry, Uppsala University, personal communications). This is the case also for CuFe-sulphides, where the valency of Fe varies (+2 - +3), depending on composition, as observed in a number of Mössbauer studies. (for example, $Cu^{1+}Fe^{3+}S_2$, in chalcopyrite, $Cu^{1+}{}_5Fe^{3+}S_4$, in bornite, and $Cu^{1+}Fe^{2.5+}{}_2S_3$, in cubanite. In idaite; approx. Cu_5FeS_6, which is often found together with CuS, it is likely that the valency of sulphur varies according to; $Cu^{1+}{}_5Fe^{3+}S^{4/3-}{}_6$. This phase has not been investigated, however.). Crystals of Cu-sulphide or CuFe-sulphide, formed on the canister surface, may be subjected to further change through *replacement,* a process discussed below. In most cases electron transfer (redox reactions) is involved in replacement among metal sulphides, but it may also be a simple ion exchange process.

Before we start to discuss mineral formation mechanisms, however, we shall take a look at the ternary Cu-Fe-S system, since phases belonging to this system are most likely to form on the canister surface. We will concentrate somewhat on the ternary phases (minerals containing *both* Cu and Fe), since aqueous Fe-species are important in most natural environments.

2.2 The Cu-Fe-S system.

This system has probably recieved more attention than any other ternary metal sulphide system (e.g. Merwin and Lombard, 1937; Brett, 1964; Yund and Kullerud, 1966; Cabri, 1973; Sugaki et al, 1975; Vaughan and Craig, 1978; Durazzo and Taylor, 1982; Kojima and Sugaki, 1987). This is so because CuFe-sulphides are almost invariably present in sulphide ores (chalcopyrite; $CuFeS_2$, is one of the most widespread metal sulphides on Earth), and because they show a great deal of complexity and interesting behaviour, especially at low temperatures.

Since our knowledge of the complicated low temperature relations in the system are based on extrapolations from experiments performed at elevated temperatures, and on studies of natural occurences, we have chosen to discuss the relations at decreasing temperatures (Figure 1). High temperature relations have no direct bearing on the present problem, but they are valuable to know anyway, because they indicate the direction towards low temperature relations (Figure 2), which are considerably more uncertain because of problems with metastabilities etc.

Our knowledge of these phases are mainly based on so called "dry experiments", i.e. pure metals and elemental sulphur in desired proportions are reacted at high temperatures in vacuum until equilibrium is achieved. Comparative studies where water is included, using pressure vessels, give similar results, at least at high temperatures. Metal sulphides are much more sensitive to temperature changes than to pressure changes. For those unfamiliar with phase diagrams, it should be noted that the lines between different phases in Figures 1 and 2 (tie-lines), connect phases which are supposed to be in thermodynamic equilibrium with each other under the specified conditions. (The so called *thermodynamic phase rule* states that a maximum of five phases can co-exist stably with one another in a ternary system, given that *both* temperature and pressure are exactly fixed. In the real world, however, both these variables vary, which gives a maximum of three co-existing phases, as seen in Figures 1 and 2).

Two things are apparent when the phase relations at different temperatures are compared; (i) The complexity increases when temperature is decreased, and (ii)

Extensive *solid solutions* are found at high temperatures, while only phases with relatively well-defined compositions are stable at room temperature in the present system. This is due to the fact that Cu and Fe atoms are randomly distributed in tetrahedral *intersticies or holes* in a close-packed sulphur structural framework at high temperature (Figure 3). In a close-packed structure the number of tetrahedral intersticies is twice the number of atoms making up the close-packed framework. These factors make it possible to vary *both* the Cu/Fe ratio and the metal/S ratio within certain limits, depending on the specific structure. At low temperature, on the other hand, Cu and Fe tend to order with respect to one another, for energetic reasons, resulting in a number of possible structures with distinct Cu/Fe - and metal/S ratios (*superstructures*).

At 600°C the system is dominated by three extensive solid solution fields; (i) a *pyrrhotite;* $Fe_{1-x}S$, series (po_{ss}), which can accomodate several wt.% Cu, (ii) an *intermediate solid solution* series (iss) which extends compositionally from about $CuFeS_2$ to $CuFe_2S_3$, on the metal-rich side of a 1:1 metal:sulphur ratio, and (iii) a *bornite solid solution* series (bn_{ss}), which extends from the Cu-S binary, at about Cu_2S - $Cu_{1.7}S$, to ternary compositions half-way towards $CuFeS_2$ (Figure 1). The only other phase which is stable at this temperature, besides the elements themselves, is *pyrite*; FeS_2.

As temperature is decreased, *chalcopyrite;* $CuFeS_2$, appears at 557°C (a superstructure of iss), *covellite*; CuS, at 507°C, and *idaite*; Cu_5FeS_6, at 501°C. The solid solution fields decrease successively in size, and bn_{ss} is split into two solid solutions at around 300°C, one Cu-rich; *digenite solid solution* (dg_{ss}) and one Fe-rich (bn_{ss}) (Craig and Scott, 1974).

Between 300°C and room temperature a large number of changes take place. The solid solutions, where the metal atoms are disordered, break down completely, and a large number of superstructures appear. For example, within the compositional field occupied by the cubic iss at high temperature, we find at least five phases with well-defined compositions; *chalcopyrite*; $CuFeS_2$, *cubanite*; $CuFe_2S_3$, *talnakhite*; $Cu_9Fe_8S_{16}$, *moohekite*; $Cu_9Fe_9S_{16}$, and *haycookite*; $Cu_8Fe_{10}S_{16}$. Tetragonal *bornite*; Cu_5FeS_4, appears in place of the cubic bn_{ss}, and dg_{ss} breaks down to *chalcocite*; Cu_2S and *digenite*; about $Cu_{1.8}S$ (possibly stabilized by a minor amount of Fe) (Figure 2). Additional phases appear along the Cu-S binary, and several varieties of *covellite* (CuS) have been found in nature. Also, *nunkundamite*; about $Cu_{11}Fe_2S_{13}$, may form in stead of *idaite*; Cu_5FeS_6 (Wang, 1984). (Note that both these phases are "covellite-like" in appearence).

2.3 "Problems" concerning low temperature relations in the Cu-Fe-S system.

Since we are here interested in what will actually happen at the metallic copper - hydrous environment interface, it seems appropriate to expand the discussion a bit, regarding low temperature mineral formation. We are confronted with large discrepancies between on the one hand laboratory results and on the other hand what we observe in nature. Below, we will give a few examples, illustrating that low temperature phases found in nature may have formed and been altered along quite different reaction paths, as compared with phases produced in the laboratory. Not all of these examples are directly relevant in the copper canister context, but we believe they are instructive in showing the problems involved in making low temperature predictions.

(1) Cubanite; $CuFe_2S_3$, is an orthorombic mineral found in many copper ores, often intimately (=crystals intergrown on the microscale) associated with chalcopyrite, and pyrrhotite. It is stable to 200-210°C, above which it rapidly transforms to cubic isocubanite (with Cu and Fe disordered), which is a member of the high temperature intermediate solid solution (iss). Although reaction rates are relatively rapid at 200°C, the cubanite $\rightarrow$ isocubanite transition has never been successfully reversed in the laboratory. In fact, it has not been possible to synthesize cubanite *under any laboratory conditions.*

According to Putnis and McConnell (1980) this enigmatic behaviour can be explained as follows: In the cubanite structure sulphur exhibits hexagonal close-packing, changing to cubic close-packing (Vaughan and Craig, 1978) in isocubanite. A change in sulphur packing is equivalent with a major transition and sulphur behaves as a relatively sluggish component in all kinds of processes taking place in metal sulphides. It is possible to bring about the cubanite $\rightarrow$ isocubanite transition since we can use excessive heat, but it is not possible to bring about its reversal since we must keep the temperature below 200°C. The interesting point is that isocubanite decreases its free energy on cooling by *exsolving* chalcopyrite; $CuFeS_2$, from the cubic matrix. In chalcopyrite sulphur exhibits cubic close-packing, and is well-ordered at variance with isocubanite. The isocubanite "motherphase" becomes correspondingly enriched in Fe during the exsolution process. This is typical metastable behaviour, and the decrease in energy which accompanies the exsolution process further decreases the tendency for isocubanite to transform to cubanite. (*Exsolution* in the solid state = precipitation of a supersaturated solid phase from a solid solution. Normally it takes place on cooling.).

Cubanite ($CuFe_2S_3$) in nature is found in environments suggesting strongly reducing conditions (see *type a* environment, page 4 in SKN 57, 1992) and a rock-forming temperature much in excess of 200°C. Textural relations (= how the mineral grains are intergrown with each other) between cubanite ($CuFe_2S_3$), chalcopyrite ($CuFeS_2$) and pyrrhotite ($Fe_{1-x}S$), suggest that cubanite has formed at quite a low temperature, however, by means of *chemical replacement* (A process where compositional and structural changes take place in a solid phase at practically constant volume. Examples are given in Figure 4.).

We can consider a hypothetic redox process:

$$3CuFeS_2(ox) + Fe^{2+} + e^- \rightarrow 2CuFe_2S_3(red) + Cu^{1+}$$

$$3FeS(red) + Cu^{1+} \rightarrow CuFe_2S_3(ox) + Fe^{2+} + e^-$$

which gives the overall process:

$$CuFeS_2 + FeS \rightarrow CuFe_2S_3$$

Among metal sulphides, such replacement processes, which are very complex in detail, take place by means of rapid electron transfer together with diffusion of metal ions through an essentially static sulphur structural framework. The reaction rate is probably increased by presence of water.

(2) Bornite; Cu_5FeS_4, is a tetragonal phase, which exhibits similar interesting behaviour. On heating to 228°C (Craig and Scott, 1974) it inverts to a cubic disordered form, which is a member of bn_{ss}. Rapid cooling of cubic bornite leads to formation of cubic superstructures (ordering takes place), whose *unit cell* dimensions are simple integers of the unit cell of the high temperature form. (*unit cell* = the smallest possible repetitive building block of a crystal. All information necessary to define the crystal structure is contained in the unit cell. For a cubic crystal, for example, it constitutes a small cube). However, at variance with cubanite, the stable tetragonal form of bornite forms on slow cooling below the transition temperature. This is so because sulphur exhibits cubic close-packing in both crystal structures, i.e. no major structural reorganization is needed to bring about the change, only ordering between Cu and Fe.

In nature, bornite is found in primary copper ores formed at low temperature in the near surface environment, as well as in ores which have been subjected to *secondary alteration* (=redox processes essentially, which take place because of interaction with groundwaters). Both environments can be considered to correspond with *environment b*, page 5 in our previous report; SKN 57, 1992. Bornite is often found together with secondary Cu-sulphides (Cu_2S, CuS etc), and chalcopyrite and digenite are commonly present as beautiful, crystallographically oriented two-phase "exsolution lamellae" in these bornites. (During exsolution the "daughter" phase commonly grows only along certain energetically favourable crystal planes in the "mother" crystal, resulting in intricate network textures. Most prominent in this respect is the so called *Widmannstätten texture* in iron meteorites (Ramdohr, 1980) where two FeNi alloys have formed on slow cooling of a single high temperature solid solution phase). Moreover, the lamellae are typically rimmed by digenite; $Cu_{1.8}S$ (Figure 4).

Indeed, cooling of experimentally produced crystals of bornite solid solution; bn_{ss}, enriched in $CuFeS_2$ compared with a nominal Cu_5FeS_4 composition, invariably results in lamellar exsolution of chalcopyrite from the "mother" bornite phase. However, at temperatures in excess of about 200°C crystallographic coherency is lost in a very short time, and the chalcopyrite lamellae recrystallize to rounded grains in the bornite host crystal (e.g. Durazzo and Taylor, 1982).

Thus, the "exsolution lamellar" texture observed in nature point to near room temperature conditions. Besides, bulk chemical analyses of bornite crystals, including exsolved phases, points to compositions well outside the boundary of the high-temperature bornite solid solution; bn_{ss}. In analogy with formation of cubanite ($CuFe_2S_3$), this indicates that these intergrown bornite - chalcopyrite - digenite (Cu_5FeS_4 - $CuFeS_2$ - $Cu_{1.8}S$) crystals have formed by means of chemical replacement, i.e. *replacement exsolution*. We can consider a simplified reaction:

$$Cu_5FeS_4(red) \rightarrow CuFeS_2+2Cu_{1.8}S(ox) + 0.4Cu^{1+} + 0.4\ e^-$$

taking place during slight oxidation at near room temperature conditions (Amcoff and Hedin, 1992). Dissolved copper ions precipitate as CuS along grain boundaries, while chalcopyrite and digenite form lamellae in the host bornite crystals.

Microscopic observations (e.g. Ramdohr, 1980) and stability considerations, suggest that chemical reactions among sulphide minerals at low temperatures to a large degree is a question of chemical replacement. For Cu- and CuFe-sulphides this means a redox process where metal atoms and electrons are rapidly exchanged through an essentially static sulphur structural framework, i.e. the reaction takes place with a minimum of structural reorganization (Amcoff, 1987; 1988; Amcoff and Hedin, 1992).

(3) Stability relations among Cu- and CuFe-sulphides at low temperature are uncertain. For example, Craig and Scott (1974) proposed that the common association of pyrite and bornite (FeS_2 + Cu_5FeS_4) at Magma Mine, Arizona, at present rock temperature of 50^oC (a long-term natural equilibrium experiment!), suggests that the two phases may co-exist stably at room temperature. In Sweden, the two minerals are found in direct grain contact, for example at Mårtansberg (Geijer, 1924).

On the other hand, Yund and Kullerud (1966) proposed that a tie-line; bornite - pyrite (Cu_5FeS_4 - FeS_2) is replaced by a tie-line; chalcopyrite - digenite ($CuFeS_2$ - $Cu_{1.8}S$), below 228°C. This was established experimentally, both by reaction; pyrite + bornite to produce chalcopyrite + digenite, slightly below 228°C, and by exsolution of the same product phases from sulphur enriched bornites at low temperature.

Moreover, hydrothermal experiments by Sugaki et al (1975), using pressure vessels, indicated a tie-line; idaite - chalcopyrite (Cu_5FeS_6 - $CuFeS_2$), at 300 - 350°C, but Kojima and Sugaki (1985) showed that a tie-line bornite-pyrite (Cu_5FeS_4 - FeS_2) exists in the Cu-Fe-Zn-S system, at least above 300°C. (Note that Zn does not enter the Cu-minerals to a large extent. Also, at these temperatures equilibrium should be achieved relatively rapidly).

Additional examples showing discrepancies among Cu-mineral stability relations could be given. These findings all suggest small differences in energy between different alternatives, and metastable behaviour is to be expected. Also, different results between anhydrous and hydrothermal experiments, suggest that H-S bonds in sulphides may play a role. Besides, the different observed results between the Cu-Fe-S and Cu-Fe-Zn-S systems (see above) suggest that trace amounts of Zn in the Cu-mineral structures may have a strong influence on the stability relations. It may be added here that a large number of elements are invariably present in trace amounts in naturally occuring metal sulphides. In fact, pure phases are absent in nature for energetic reasons.

(4) A number of metal sulphides found in nature appear to be impossible to synthesize in the "dry" system, for reasons other than discussed in connection with the "cubanite enigma" above. Several such Fe-sulphides are found in the "low temperature sedimentary environment" (stagnant basins on the seafloor, suggesting reducing conditions). Mackinawite (FeS with tetragonal PbO structure), greigite (Fe_3S_4; a thiospinel), and marcasite (orthorombic metastable FeS_2; compare with pyrite which is cubic FeS_2) are found in this milieau, as well as additional more or less well-defined phases (e.g. Berner, 1964; Rickard, 1975). These Fe-sulphides

can be synthesized in a water system of appropriate chemical composition at low temperature. According to Rickard (1969, cited in Rickard, 1975) marcasite tends to form under acid conditons and pyrite under more alkaline conditions.

According to Kullerud (1967, cited in Craig and Scott, 1974) marcasite can be inverted to pyrite down to 150°C in the presence of excess sulphur, but only above 400°C in the absence of sulphur; this suggests a slightly higher Fe/S ratio in marcasite. From his experiments Kullerud (1967) proposed that H-S bonds might stabilize the marcasite structure. (It is impossible to convert pyrite to marcasite in a "dry" experiment at any temperature.).

To add to the complexity, a large number of pyrrhotite varieties of compositions between troilite (stoichiometric FeS) and monoclinic pyrrhotite (Fe_7S_8) have been reported in the literature, all of which may be metastable with respect to the end-members, according to Putnis and McConnell (1980). The conclusion to be drawn here is, that there probably exist many more metastable Fe-sulphides in nature than the thermodynamically stable ones.

To conclude: The reason for discussing the "natural Fe-S system" here is that it is the most studied among binary sulphide systems (Fe-sulphides are most important, quantitativly). There is no reason that Cu- or CuFe- sulphides should be more simple at low temperatures. In fact, reaction rates generally increase when the Cu-content increases among phases in the Cu-Fe-S system, indicating that relations could possibly be even more complex along the Cu-S join compared with the Fe-S join. Textural interrelations (=how the mineral grains are intergrown) among bornite (Cu_5FeS_4), chalcocite (Cu_2S), digenite ($Cu_{1.8}S$) etc., are extremely diverse, suggesting a variety of possible processes, depending on the conditions. Colour variations in Cu-sulphides observed under the microscope, point to minor amounts of eg. Ag, Fe, Mn in the solid matrix. It may be noted here that in mineral samples subjected to air, tarnishing sets in immediately. The compositions of the thin films formed are little known, but Ramdohr (1980) suggested that a thin layer of $Cu_{1.8}(S,O)$ forms on Cu_2S crystals subjected to air. Instant tarnishing on synthetic crystals of bornite and chalcopyrite has also been observed by one of the present authors, indicating transport of Cu to the surface of the grain and precipitation of oxidized phases (e.g. CuS, Cu_5FeS_6, and possibly Cu-oxides). Once started, tarnishing continues for a while, even when the sample is placed under acetone!

2.4 Mechanisms of sulphide formation on metallic copper.

Whatever the subsequent history, an electron transfer from metallic copper must take place in the initial sulphidation step. Copper is oxidized from zerovalent to univalent. A suitable electron acceptor must be present at the canister surface. A number of possible alternatives are present in various groundwaters, which we will not dwell on here, but it may be noted that even aqueous sulphide species may oxidize metallic copper. Thus, aqueous polysulphide ions, the formation of which can be considered as a reaction between S^0(aq) and aqueous H_2S, HS^- or S^{2-} (depending on pH), have mean valencies between 0 and -2 (Shea and Helz, 1988), and will most likely be present in the repository environment (Nordstrom SKB 86-03). According to Nordstrom, a polysulphide zone will probably be present above a sulphide zone in a typical swedish "granitic groundwater", reflecting the somewhat higher oxidation state. From a mechanistic point of view (kinetic collision theory), it seems feasable that a polysulphide ion colliding with the canister surface, might act both as an electron acceptor and as a source of sulphur. Formation of FeS_2 from FeS by a similar process was indicated by Rickard,1975; discussed below). As the polysulphide/"simple sulphide" ratio decreases, other oxidants in the neighbourhood may oxidize "simple sulphide" to polysulphide, to maintain the reaction. Besides, also in the presence of "simple" sulphide species (H_2S, HS^-) Cu-sulphides may form, since H^+ will act as an electron acceptor leading to H_2(g) formation.

However, once a solid sulphide "layer" has precipitated on the metal surface, continuing reaction will take place by electron transfer and copper diffusion through the semiconducting metal sulphide to the surface, while aqueous sulphur species as well as other possible reactants, like ferrous iron, will diffuse through the surrounding aqueous medium to the reaction site (Figure 5). This will continue as long as reactants are available in the neighbourhood.

We do not think it is possible to show the redox process in detail at present. As already hinted at, there will probably be several alternatives among the aqueous species with the capacity to oxidize metallic copper. Furthermore, as discussed in Appendix 1, redox processes among aqueous species are often path controlled, leading to formation of metastable products. Processes involving transfer of many electrons (more than one or two) are disfavoured as are also processes where strong chemical bonds are broken. For example, the thiosulphate ion; $S_2O_3^{2-}$, acts as a metastable but persistent intermediary, in both oxidation and reduction, for the S^{2-}/SO_4^{2-} redox couple (Ohmoto and Lasaga, 1982; Sato, 1992). Also, hydrogen peroxide; H_2O_2, acts as an intermediary for reactions involving the important O_2/H_2O redox couple (Moffett and Zika, 1983; Millero et al, 1987; Sato, 1992), which defines the upper Eh boundary for the natural environment.

Regarding crystalline phases at low temperature, the discussed replacement examples above demonstrate that chemical change takes place in such a way that a minimum of structural reorganization is involved. In metal sulphides the metal atoms are typically very mobile, while sulphur acts as a sluggish component. Chemical replacement often results in formation of metastable phases and textures.

Thus, sulphidation of metallic copper in a repository site environment is a process which involves an outward diffusion of copper and precipitation on the surface of the Cu-sulphide crystal, growing into the bentonite surrounding. The details of the continuing growth process are not obvious but we think *dendritic growth* through the bentonite layer is possible (*dendrites* are single crystals which form during growth from a non-convective supersaturated solution, which can be a melt, a solid phase or a gas phase). As a *crystallite* grows by means of diffusion of solute species through the solution, the neighbourhood to the crystal will be depleted in these species and concentration gradients are formed. Since a *crystal face* will need more solute particles per unit area for a certain amount of growth, compared with a *crystal edge*, which in turn will need more solute particles compared with a *crystal corner*, the concentration gradient around the crystal will become steeper in the order; crystal face < crystal edge < crystal corner. This will favour growth in the order; crystal corners > crystal edges > crystal faces, which may result in dendritic growth. In a *saturated solution* dendrites will tend to change into normal crystals since the precipitating particles are more strongly bonded to a crystal face than to a crystal corner. Also, for the same reason, dissolution in a non-convective solution will tend to operate in such a way that corners are dissolved before faces, leading to rounded crystals. Strong *undersaturation* may lead to dissolution from dislocations etc. on the crystal faces, resulting in the appearence of *etch pits.* Since bentonite constitutes an unconsolidated mass of clay mineral grains which are only loosely connected with each other, Cu-sulphide crystals will probably grow into the space between individual clay particles and encapsulate them. This is a common process during crystal growth in nature; large single crystals filled with inclusions of other "engulfed" phases are called *poikiloblasts.* However, in this way we think growth of Cu-sulphides in a "wet" bentonite medium may resemble *open space growth* rather than arrested growth in a confined space. Experimental sulphidation by Amcoff (1987, 1988) in "open space" showed that covellite and idaite crystals, forming on the surface of the phase which was sulphidized, typically developed as single crystals which always grew outward in a direction perpendicular to the surface from where reaction started. Considering such a "single crystal" texture as well as the high solid diffusion rates involved, it does not seem likely that the forming Cu-sulphide will passivate the metal.

Cu-sulphides as well as Ag-sulphides react extremily rapid (Barton, 1970), suggesting very high diffusion rates of the metal through the solid matrix. The sulphidation experiments by Amcoff (1987, 1988) also showed, that the position of the original crystal surface (where reaction started) could still be inferred as reaction continued. The process is assymetric in a sense, since the phase which is sulphidized loses copper continuously, while sulphur does not diffuse the opposite way but reacts at the surface of growing Cu-sulphide crystals. Copper is lost from the interior and reprecipitated at the exterior. In this respect it does not seem likely that sulphidation in a water environment will differ much, compared with the discussed dry experiments.

Microscopic examination of natural low temperature Cu- and CuFe-sulphides shows that chemical alteration preferentially proceeds via chemical replacement. In this way "old" crystal shapes may survive, although the chemical composition as well as the crystal structure are changed. Chemical replacement was a popular branch of experimental sulphide mineralogy in the twenties and thirties, and it was repeatedly demonstrated that mm-sized crystals of CuFe-rich sulphides, could be altered within hours into more Fe-rich or more Cu-rich varieties, even below $100^{o}C$, by subjecting the crystals to more or less concentrated solutions of suitable copper- and iron salts (e.g. Ray, 1930; Schouten, 1934).

In the copper canister case, replacement will probably become important *if* and *when* the chemical composition of the water surrounding the canisters starts to change. For example, the entrapped groundwater may become increasingly depleted in aqueous sulphide species *if* initial Cu-sulphide precipitation is rapid compared to diffusion through the bentonite barrier to the reaction site (a small *redox capacity* because of slow replenishment). Thus, an initial Cu-sulphide with a low Cu/S ratio may be replaced by a sulphide with a higher ratio. With time a *steady state* situation will be set up where diffusion through the solution medium matches precipitation. Another possibility is that a metastable solid phase forms initially, for kinetical reasons, which is subsequently transformed into a thermodynamically more stable mineral by means of replacement.

2.5 "Oxide" formation on metallic copper.

Although the present paper is mainly concerned with sulphide phases associated with metallic copper, formation of other Cu-phases can not be excluded. Cu-oxides like *cuprite* (Cu_2O) and *tenorite* (CuO), as well as a large number of other complex Cu(II) phases, for example Cu-carbonates like *malachite*; $Cu_2(CO_3)(OH)_2$ etc. (see Table 1C, Figures 6 and 7), are found associated with metallic copper in oxidized copper ores. This natural "near room temperature" environment was discussed in our previous report; SKN 57, 1992, pp 5-6. Besides, a number of these phases are formed when copper metal is directly exposed to the atmosphere.

When oxidized copper ore is studied under the microscope (Ramdohr, 1980) a number of conclusions can be drawn which are of interest in the present context: (i) Metallic copper is often associated with chalcocite (Cu_2S) and/or cuprite (Cu_2O). It may replace these phases *or* be replaced by them. (ii) Replacement involving metallic copper; for example; $Cu \rightarrow Cu_2O$ or $Cu_2O \rightarrow Cu$, is typically *massive* in character rather than *oriented* (Figure 4). Thus, grains of metallic copper are often rimmed by *cuprite* (Cu_2O). (iii) Other oxidized phases, like *tenorite* (CuO), Cu-carbonates and *chrysocolla* ($CuSiO_3 + nH_2O$), as well as *limonite;* FeO(OH), often precipitate in concentric shells around metallic copper-Cu_2O aggregates, or occur as vein fillings. Banded oxidized copper ore is sometimes quite "massive"; *malachite*, $Cu_2(CO_3)(OH)_2$, from the Ural is famous for its use as ornamental stone. Sometimes Cu-carbonates directly replace metallic copper (Ramdohr, 1980) suggesting steep chemical gradients.

The present observations (abundant replacement, rhytmic precipitations, vein fillings, chemical disequilibrium already on the microscale, etc.) suggest a milieu of dissolution and reprecipitation. Cu^{2+} is leached from primary copper ore ($CuFeS_2$) when it is subjected to strongly acid, oxidizing solutions "from above". As sulphuric acid is neutralized by neighbouring silicates and carbonates, a whole spectrum of secondary Cu-minerals, including metallic copper, precipitate and replace each other.

Regarding the present problem it is interesting to note that metallic copper is replaced by Cu_2O as well as by $Cu_2(CO_3)(OH)_2$ in a massive manner. A process is suggested where Cu_2O "invades" the metal, i.e. "inward" diffusion of oxygen and "outward" diffusion of copper through the growing Cu_2O layer. A considerable net loss of copper is indicated, since, on a volume for volume basis, Cu_2O contains about 40% less Cu than metallic copper. Released Cu probably participates in formation of additional Cu_2O in the vicinity. At variance with *oxidation replacement* of bornite, discussed above, where bornite was replaced by a $CuFeS_2 + Cu_{1.8}S$ assemblage, a net "inward" diffusion of the anion is indicated in the present case. It is not quite obvious whether this difference reflects a fundamental difference in behaviour between oxygen and sulphur as regards solid state redox processes, or whether it simply reflects the fact that metallic copper is only involved in the $Cu \rightarrow Cu_2O$ replacement example. To get additional information we will take a look at another example involving oxides:

Since it is very important both from a geological and a technical point of view, oxidation of *magnetite* (Fe_3O_4) has been studied by numerous authors e.g . Davis et al. (1968); Colombo et al. (1868); Feitknecht and Gallagher (1970). The reaction shows some common behaviour with the sulphidation processes discussed above.

The overall redox process can be written:

$2Fe_3O_4$ (magnetite) + $1/2O_2 \rightarrow 3Fe_2O_3$ (hematite)

At low temperature oxidation takes place via intermediate formation of metastable *maghemite* (γ-Fe_2O_3; *magnetite* or *spinel* structure with hematite composition. A portion of the iron atoms are missing compared with normal magnetite), or of a magnetite - maghemite solid solution (Fe_3O_4 - γ-Fe_2O_3):

Fe_3O_4 (magnetite)$\rightarrow$ $Fe_{3-x}O_4$ - γ-Fe_2O_3 (solid solution) $\rightarrow$ Fe_2O_3 (hematite).

From a mechanistic point of view, this oxidation process takes place via outward diffusion of Fe^{2+} ions to form Fe_2O_3 (maghemite or hematite) on the surface. With time hematite (Fe_2O_3) also nucleates along (111)-planes in the metastable magnetite-maghemite host crystal, resulting in a typical *martitic* intergrowth texture (Figure 4). The *oxidation replacement* process can be written:

$3Fe_3O_4 \rightarrow 4Fe_2O_3 + Fe^{2+} + 2e^-$

illustrating that oxygen behaves as an immobile component within the crystal. Note the similarity with *oxidation replacement* of bornite discussed above:

$Cu_5FeS_4 \rightarrow CuFeS_2 + 2Cu_{1.8}S + 0.4Cu^{1+} + 0.4e^-$

Martitization is a very common process during oxidation of iron oxide ores (for example Kiruna), and is also a characteristic feature during oxidation of Fe -Ti - oxide ore where *ilmenite* ($FeTiO_3$) and *hematite* (Fe_2O_3) precipitate in lamellar form along (111)-planes in the host Fe_3O_4 - Fe_2TiO_4 (*magnetite* - *ulvospinel* solid solution) crystal (e.g. Haggerty, 1976a and 1976b; Lindsley, 1976; Reynolds, 1985 a and 1985b; Amcoff and Figueiredo, 1990).

The important point is that the *martitization* process which is thus an example of *oxidation replacement* very much resembles oxidation of bornite (Figure 4). Additional examples from the Cu-Fe-S system could be given. Thus, no fundamental difference in behaviour between oxides and sulphides is suggested. It is possible that the diffusion rate of copper in a "dense" Cu_2O crystal is lower compared with a Cu_2S crystal, but we do not have actual figures to corroborate such a statement. (The *martitization* process is a more sluggish process compared with oxidation of CuFe-sulphides). Thus, we do not know whether Cu_2O will *passivate* metallic copper.

Initial oxide formation: There is a possibility that Cu-oxide(s) may have formed on the canister surface before sulphidation starts. During construction of the repository it is inevitable that some oxygen will be entrapped, and also a thin oxide coating is likely to have formed already during manufacturing of the canisters. Here it might be added that oxygen and sulphide species are mutually exclusive in a hydrous environment. According to Berner (1981) they react within minutes at room temperature. (Recently; 5/6 1993, the "dead" H_2S-rich bottomwaters of Gotlandsdjupet, due east of Gotland, were rapidly oxygenated because of influx of O_2-rich heavy "Northseawater", 300 km^3 of which was "spilled" into the Baltic during the strong winterstorms. Since then the O_2 concentration has gradually decreased again, probably because of release of accumulated H_2S from the bottom sediments).

A fresh copper surface typically becomes reddish (Cu_2O?) in a day or so if subjected to the atmosphere. According to Hägg (1966) a slight heating of copper in pure air leads to oxidation to Cu_2O (yellow-red) and then CuO (black). Subsequently, other compounds may form if the air contains species like sulphuric acid and chlorine compounds etc. Hägg (1966) observed that a copper roof first becomes black from Cu-sulphides. McNeal and Little (1990) observed that Cu-sulphides (the whole spectrum from Cu_2S to CuS) may form on a Cu_2O layer on copper metal in an oxidizing environment, because of anaerobic, sulphate-reducing bacteria, forming a surface film. These bacteria are diverse and can be isolated from many aerobic environments, but their principal habitats are seawater and soil. According to Hägg (1966), subsequent processes involving oxidation, result in formation of greenish Cu(II)-compounds; especially $Cu_4(OH)_6SO_4$, but also malachite; $Cu_2(OH)_2CO_3$ etc. Near the coast, $Cu_2(OH)_3Cl$ may become important. From a mechanistic point of view, this reaction sequence seems logical, since formation of Cu_2O or Cu_2-S is a relatively straightforward redox process, while formation of e.g. $Cu_2(CO_3)(OH)$ is a complex process involving many individual reaction steps.

However, an initial thin coating of Cu_2O or CuO on the copper canister surfaces will affect subsequent sulphidation at the repository site. (Unless the repository is accidently subjected to *strong* oxidation for a long period of time, a case which we have not considered here, we do not believe complex Cu(II)-compounds will form). As discussed above, it is not quite clear whether the presence of Cu_2O could inhibit sulphidation to any significant degree. If Cu_2O behaves like a persistent phase, in the repository site milieau, it seems likely that initial reaction with sulphur on the Cu_2O crystal surface will be followed by an outward diffusion of Cu^+ through the crystal to the reaction site on the surface, a process not much different from diffusion of Cu^+ through a Cu-sulphide. (The rate may differ, however). If, on the other hand, Cu_2O does not persist in a sulphidic water environment, it will simply be replaced by Cu-sulphide, i.e:

$$Cu_2O + H_2S \rightarrow Cu_2S + H_2O$$

Such a process is probably quite feasible, although it may be characterized by outward diffusion of copper ions and inward diffusion of protons rather than diffusion of anions through the oxide crystal. Even phases persisting well outside their stability fields are subjected to simple exchange processes (see Appendix 1). Observations from nature have shown *sulphidation replacement* to be extremely common. According to Bastin et al (1931); " Sulphides replace all rock minerals, all gangue minerals (vein fillings etc.), and all sulphides." This shows that these processes are mechanistically favoured.

2.6 What phase(s) will form on the canister surface?

Since we can expect metastable behaviour it is neither possible to answer in detail which redox processes will be in operation nor which phase(s) will form. Besides, we do not know the exact composition of the groundwater, nor of the enclosing bedrocks. However, in general terms we can relate low temperature metal sulphide behaviour, observed in the experimental Cu-Fe-S system and in nature, to the present problem.

In minor or trace amounts, metal sulphides are almost always present in crystalline bedrocks. Pyrite and pyrrhotite, the two most important iron sulphides, strongly dominate. In sedimentary rocks and in loose sediments, forming at low temperature in reducing environments, other Fe-sulphides like mackinawite; FeS_{1-x}, may be present as well (e.g. Rickard, 1975). Also, in the bentonite clay a certain amount of iron sulphides may be present. There is a general tendency that more oxidized iron sulphides (FeS_2, pyrite) are common in granitic rocks (high SiO_2 content), while more reduced iron sulphides ($Fe_{1-x}S$, pyrrhotites) dominate in gabbroic rocks (low SiO_2 content). Both types are common in Swedish bedrocks. In magmatic rocks, low in SiO_2 (ultramafic rocks), even troilite (stoichiometric FeS) is found. (This is the meteoritic environment discussed above.). These differences reflect increasingly oxidizing conditions in the order; ultramafic rocks → gabbroic rocks → granitic rocks.

A considerable amount of data have been collected on groundwater chemistry. For the sake of argument, however, we assume that the composition of the groundwater to which the copper canisters will be subjected, in some way will reflect the composition of the neighbouring bedrock (influx of water which has reacted with sediments from a larger distance, organics and microbial activity affecting the sulphate : sulphide ratio etc., may, of course, also be important). This does not neccessarily mean that the groundwater has equilibrated with respect to iron sulphides in the neighbourhood. However, we will discuss initial sulphide formation on the canisters in terms of an "iron sulphidic water environment".

Since we do not know whether the environment will be "pyritic" or "pyrrhotitic" or a mixture of both we will discuss both cases. (From Figure 2 it can be seen that neither FeS_2 nor $Fe_{1-x}S$ are in thermodynamic equilibrium with metallic copper at room temperature. On the other hand, troilite; FeS, may probably co-exist with metallic copper at low temperatures. Troilite is not expected in the present environment, however).

(1) *Metallic copper subjected to a "pyritic environment":* In this case we think the chemical composition of the groundwater will be characterized by a relatively low dissolved iron : aqueous sulphide ratio. From Figure 2a it is apparent that FeS_2 may coexist thermodynamically with different Cu-rich sulphide assemblages, i.e. with decreasing sulphur activity; (i) $CuS + Cu_5FeS_6$, (ii) $Cu_5FeS_6 + Cu_{1.8}S$, (iii) $Cu_{1.8}S + Cu_5FeS_4$, and (iiii) $Cu_5FeS_4 + CuFeS_2$. A further decrease in sulphur activity would destabilize pyrite. Note that Figure 2b would yield different assemblages.

(2) *Metallic copper subjected to a "pyrrhotitic environment":* In this case we think the chemical composition of the groundwater will be characterized by a higher dissolved iron: aqueous sulphide ratio. From Figure 2a and b it is appearant that $Fe_{1-x}S$ may only co-exist thermodynamically with Fe-rich CuFe-sulphides. With decreasing sulphur activity we have the alternatives: (i) $FeS_2 + CuFeS_2$, (ii) $CuFe_2S_3 + CuFeS_2$, (iii) $CuFe_2S_3 + FeS$. Thus, pyrrhotite is not thermodynamically stable in the presence of simple Cu-sulphides at room temperature. A further decrease in sulphur activity would destabilize pyrrhotite

We have given these examples just to illustrate the complexity of the present problem. It should also be noted that we have here assumed thermodynamic equilibrium. In the real case we must rather assume path-dependant processes, leading to formation of metastable phase assemblages.

Metallic copper will be present in large excess, compared with reactive aqueous species. This means that the groundwater will be depleted in aqueous species, a situation which is quite the opposite the *pyritic* and *pyrrhotitic* environments above, where we assumed aqueous species (resulting from interactions with FeS_2 and $Fe_{1-x}S$, respectively) in excess. Moreover, if we think of the sulphidation process in terms of kinetic theory (collision rate of reactive aqueous species with the canister surface), it seems likely that chalcocite; Cu_2S, will be the first phase to form, independently of the exact composition of the water. Copper is already present at the reaction site, and a lower collision frequency of sulphide species is neccessary for Cu_2S formation, compared with S-richer Cu-sulphides. Also, initial formation of a CuFe-sulphide (e.g. Cu_5FeS_4) is unlikely, because *both* Fe and S have to be present simultaneously at the reaction site. This is equivalent with a higher activation energy, or a more sluggish reaction.

The subsequent pathway is more difficult to predict. We will discuss two cases; *high* and *low* sulphur activity conditions, respectively. (This thermodynamic quantity depends on the total concentration of available sulphide species).

2.6.1 *High sulphur activity conditions.*

In this case Cu_2S will be transformed into S-richer Cu-sulphides on the surface of the growing crystals. Also, if the groundwater is not depleted in sulphide species, it seems likely that a *steady-state* process will be set up, where originally formed Cu_2S will survive at the "old" metallic copper - water interface, a whole spectrum of Cu-sulphides will form across the growing crystals, and CuS might be present at the sulphide crystal - water interface (Figure 5). As long as sulphidation continues, we can expect solid state diffusion of copper to determine the phase apparence of the "sulphide layer", where the neighbourhood to metallic copper determines the "stability" of Cu_2S, while the composition of the surface Cu-sulphide is controlled by the composition of the water phase.

This state of affairs becomes obvious when $CuFeS_2$ crystals are experimentally subjected to a sulphur atmosphere (anhydrous experiment) at elevated temperatures, leading to formation of Cu- and S-richer minerals on the crystal surface (Amcoff, 1987, 1988). If the reaction is arrested, while in progress, and the crystal subsequently examined under the microscope a remarkable relationship becomes apparent between the phases. Initially, covellite crystals (CuS) grow outward from the original $CuFeS_2$ grain, while "islands" or clusters of small FeS_2 crystals grow around formed "holes" in the $CuFeS_2$ grain. When all sulphur has been consumed, further reaction between CuS and $CuFeS_2$ results in a FeS_2 + Cu_5FeS_4 assemblage, replacing the original crystal, while CuS is replaced by Cu_5FeS_4 only. The interesting point is, that new phases only exhibit physical boundaries towards "older" phases with which they can be in thermodynamic equilibrium under the experimental conditions, i.e. $CuFeS_2$ + Cu_5FeS_4 + FeS_2 in the interior of the "old" crystal, and CuS + sulphur atmosphere on the surface. "Intermediate" phases, for ex. Cu_5FeS_6, also form in an intermediate position. Another point of interest here is that the "old" crystal becomes progressively porous with continuing reaction, showing that the redox process is characterized by outward diffusion of copper ions essentially, while sulphur from the original $CuFeS_2$ remain "behind" to form FeS_2, a similar process as suggested for natural low temperature bornite (Cu_5FeS_4) replacement above.

2.6.2 *Low sulphur activity conditions.*

If the groundwater is depleted in sulphide species (a small redox capacity), the various Cu-sulphides, which have formed on the canister surface, will start to reequilibrate with respect to each other and to metallic copper. Since dissolved iron species are also expected in the groundwater, it seems likely that this element will also, at least to a degree, be incorporated in the forming sulphides. Assuming an initial formation of "pure" Cu_2S, a subsequent process involving iron will almost certainly be a chemical replacement process; i.e. Fe atoms will replace Cu atoms in the solid matrix. This does not mean a 1:1 process, since Fe has a higher valency (+2 - +3) compared with Cu (+1) in the solid matrix, but the sulphur structural framework will most probably remain more or less unchanged (see bornite replacement, above). Thus, we can expect a process where Cu rapidly diffuses outward through the growing sulphide crystals, while, at the same time, Fe diffuses inward. Since the supply of Cu will be practically unlimited, it seems likely that the forming sulphides will be low in Fe *as long as aqueous sulphide species are in abundance.* However, if the sulphur supply is depleted while the activity of reactive Fe remains high in the groundwater Cu_2S will continue to incorporate Fe through replacement, and "try to equilibrate" with regard to both metallic copper and the water phase. Possibly, the net result will be a Cu_2S + $Cu_{1.8}S$ + Cu_5FeS_4 assemblage, where the Cu-richer phases border the metal. Although thermochemical data on ternary Cu-Fe-S phases are missing, formation of one or several such phases might be inferred from Figure 2.

In the present context, it should be mentioned that there are indeed indications that formation of CuFe-sulphides may be kinetically retarded, compared with simple Cu-sulphides. This was suggested by Shea and Helz (1988) who studied the solubility of copper in a reduced sulphidic environment. Besides, they suggested that the solubility of copper decreases strongly in water in contact with CuFe-sulphides compared with water in contact with simple Cu-sulphides. In general, solubilities of metastable phases are higher compared with thermodynamically stable phases (Snoeyink and Jenkins, 1980).

Because of the discussed unknown factors, the present discussion on mineral formation on metallic copper is somewhat speculative. The future histories of path-controlled processes can not be predicted based on theory alone, they can only be inferred from relevant experiments. For example, we would like to draw attention to chlorine, which is expected to be present in the future repository environment. Unfortunately we have found no data on the behaviour of Cl^- during sulphidation processes, but we have a strong feeling that it may still be important because of the chemical similarities with sulphur. F^- commonly substitutes for OH^- in mineral structures, by analogy we would expect Cl^- to substitute for HS^- in sulphide structures. Thus, we think that HS-bonds will form, at least to a degree, in all solid sulphides in a hydrous environment, because of simple protonization processes. There is also a possibility that Cl^- may substitute directly for S^{2-} in the sulphide structure, the charge being balanced by Cu^{1+} vacancy formation, i.e.: $S^{2-} + Cu^{1+} = Cl^- +$ *vacancy.* Besides, even more possibilities exist since sulphur in some structures has a negative charge less than 2.

2.7 Rate of sulphidation on metallic copper.

Whatever the exact mechanisms it seems safe to assume that formation of metal sulphides on the surface of metallic copper in a reducing environment will be a rapid process. In fact, high temperature crystalline modifications of Cu-sulphides, Ag_2S (the only known silver sulphide) and members of the ternary Cu-Ag-S system invert so rapidly to low temperature modifications that they are impossible to "freeze". Direct sulphidation experiments also show that copper, like silver, is instantly blackened when put in contact with elemental sulphur, and replacement experiments show that mm-sized crystals of Cu-sulphides and CuFe-sulphides can be inverted into one another within hours below 100°C, if the crystal, is subjected to a suitable concentrated solution (e.g. Schwartz, 1931; Schouten, 1934). These authors did not much consider the mechanisms of the processes, however.

Apparently simple and straightforward sulphidation processes are actually quite complex, when studied in detail, and may involve a number of different steps, where the most sluggish one will determine the rate. Rickard (1975) studied low temperature sulphidation of FeS (approximate formula) to form FeS_2 in an aqueous medium, containing sulphide species and S^o. (This is considered a typical reducing sedimentary environment). The overall process can be written:

$$FeS + S^o \rightarrow FeS_2$$

However, this reaction tells us virtually nothing about the mechanism, since sulphur at low temperature will be present as puckered eight-membered rings (S_8). Thus:

$$8FeS + S_8 \rightarrow 8FeS_2$$

Such a process is obviously mechanistically impossible as written (a reaction of the 9th order), since it would require simultaneous reaction of all eight sulphur atoms in a ring. Rickard (1975) performed his rate studies at 40°C, and considered a process involving dissolution of FeS to form Fe^{2+}(aq) and aqueous sulphide species, and recombination to form FeS_2:

$$Fe^{2+} + S_5S^{2-}\text{(polysulphide)} + HS^- \rightarrow FeS_2\text{(pyrite)} + S_4S^{2-} + H^+$$

Note that polysulphide ions form through reaction between S^o and e.g. S^{2-}, and that the aqueous sulphide species here participate in both oxidation and reduction. Thus, considering the mean valency of sulphur:

$$Fe^{2+} + S_5S^{2-}(-1/3) + HS^-(-2) \rightarrow FeS_2(-1) + S_4S^{2-}(-2/5) + H^+$$

Rickard(1975) also showed that formation of pyrite at 5°C, in a sedimentary environment containing 1% FeS (particle size around 0.001 mm), 0.01% S^o and P_{H_2S}=0.001, would be 2 mgxcm^{-3}x year^{-1}. Sulphidation of Cu-sulphides under similar conditons would probably take place at a much higher rate, since they typically react many magnitudes faster than Fe-sulphides (Barton, 1970).

Besides, Rickard (1975) showed that the rate of "pyritization" was two orders of magnitude higher at 40°C, than at 5°C. Assuming a similar activation energy for sulphidation of metallic copper, this might mean that an initial copper canister temperature of some 80°C (heat produced by decay processes) would be equivalent with a 10 000 times faster process, compared with a 5-10°C milieau.

The examples discussed indicate that the major rate determining factor will not be the sulphidation process itself, but rather the rate of transport of aqueous species to the reaction site on the cansiter surface, i.e. the redox *capacity* of the groundwater. However, questions like; rate of transport of species through the bentonite barrier, whether the bentonite will survive intact etc., are outside the scope of this report.

3 CONCLUSIONS AND RECOMMENDATIONS.

The discussion above has been much focused on path-controlled processes and metastabilities. Several of the examples given are not directly applicable to the problem of mineral formation on metallic copper in a future repository environment. It is necessary, however, to use analogies when studies which have a direct bearing on the problem are missing.

In the geochemical literature it is stressed that low temperature processes seldom result in formation of the chemically most stable product. As indicated by McNeal and Little (1990) and Sato (1992, see Appendix 1), Cu-sulphides may both form and persist, well outside their stability fields. For this reason, and also in view of the chemical complexity of the natural environment, it is quite impossible to predict in detail which chemical reactions will take place and which solid compounds will form. Also, there is some uncertainty regarding a possible formation of Cu-oxides on the canisters. (Perhaps this question has recieved too little attention in the present report.).

However, we think we have indications showing that metallic copper will be subjected to rapid sulphidation *if* reactice aqueous sulphur species are present in the neighbourhood. Iron may also be of importance, as well as other species (Cl^-) which we have not considered. The point is, that the rate of copper "destruction" will depend on the rate with which reactive sulphur species etc. are transported to the canisters. In turn, this depends on the surrounding barriers.

In this report we have not considered factors like; species present in and long-term fate of the bentonite barriers, diffusion rate of reactive species through the bentonite, concentration of species, flow rate of groundwater through neighbouring rocks, microbial activity etc. Here it might be added that microbial life, not dependent on solar energy and photosynthesis, may be widespread at depth in the crust. According to Gold (1992), it may be comparable in mass and volume with *all* surface life. For the sake of argument, however, we will briefly outline two hypothetic situations, which should cover the whole spectrum of possible futures in a reduced environment: (1) The surrounding rocks do not allow appreciable groundwater flow, and the bentonite barriers act as expected. This means a very small transport of reactive species to the copper canisters. (2) The bentonite- and rock barriers do not act as expected and/or reactive species are released from the bentonite (dissolution of iron sulphide) leading to a high concentraton of reactive sulphur species. (Here we do not consider the possibility that the milieau might accidently become strongly oxidizing.).

(1) After initial reaction with reactive sulphur species etc. in entrapped groundwater, very little will happen (SKBF 83-24). It is a fact that "fresh dense" rocks, free of cracks, can act as very efficient barriers against chemical change. For example, in glacial boulders of *quartzite* untarnished highly reactive metal sulphides and even metallic copper can be found within centimetres from the surface (Quartzite is a rock with a very low porosity, made up of quartz; SiO_2, crystals. Quartz is resistent against chemical weathering). This means that a barrier, of a few cm of quartzite, has prevented attack from the highly corrosive atmosphere for about 10 000 years.

(2) Since we do not find it likely that forming metal sulphide will form a passivating coating on the canister surface, we believe that the rate of sulphidation will be governed by the rate of transport of aqueous reactants to the canister surface. Besides, since sulphidation experiments suggest a one-way outward diffusion of copper, the canister will simply corrode, and copper in the form of sulphides will reprecipitate on the surface. Nord et al. (1993), who investigated a copper alloy compass ring from *SS Kronan*, wrecked in the Baltic Sea in 1676, observed that the artefact was covered with a thick crust *and that it had no remaining metal core*. The crust consisted mainly of *spioncopopite* ($Cu_{39}S_{28}$) with traces of *covellite* (CuS). Diffusion experiments between copper and nickel (Birchenall, 1974) show that metallic copper typically developes pores when one-way outward diffusion takes place. Thus, penetration of the canisters might take place long before all copper has been transformed into sulphide (or been dissolved in the groundwater). Besides, as observed during replacement processes the rate is increased when a loss of volume is

involved (Schouten, 1934). Important in this respect are factors like; grain size of the metal, crystal defects, the "quality" of welded joints, texture and initial porosity(?), foreign alloyed elements etc. These factors depend on the mode of manufacturing. Should copper loss be concentrated to a few "high energy points" there is a potential for rapid penetration of the canisters.

In light of a large number of reports by SKB on the expected properties of the surrounding rocks and on the bentonite barrier, it seems likely that formation of metal sulphide on the canisters will be limited. However, considering the uncertainties regarding the chemical reactions involved and the mode of copper loss from the canisters, we would recommend a series of simple sulphidation experiments to be undertaken on metallic copper, in a chemical environment and at a temperature similar to the expected future repository milieau. A better understanding of the mechanisms and rates of mineral formation should hopefully increase our confidence in the use of metallic copper as a technical barrier. Such experiments were outlined in our report SKN 57, 1992. Also, if copper is alloyed, it is important to investigate how this may affect its resistivity against chemical attack. For example, based on numerous observations of low temperature behaviour of Ag-minerals, we have a strong feeling that this element might have an adverse effect on the stability of the canisters.

Parallel with the laboratory experiments we would recommend a series of tests, using nature itself as a laboratory. This means that a number of small copper cylinders, manufactured in exactly the same way, and of identical composition, as the future copper canisters, should be placed in a "future repository site environment", i.e. artificial heating at about 80°C, a bentonite surrounding etc. Such an experiment could be monitored for several decades, and the copper cylinders could be taken out one at a time, after suitable periods of time, and examined for signs of mineral formation and internal corrosion. Even if 10-30 years is a short period of time in the present context, it is not insignificant, because the expected drop in temperature around the canisters will result in a corresponding rapid decrease in reaction rates.

Thus, if copper remains undamaged during the first decades we can be more confident that it will survive as a technical barrier for a long time to come.

4 **Table 1**

Low temperature copper minerals; 1A: Cu-sulphides, 1B: CuFe-sulphides, and 1C: other Cu-phases. Data used here are based on the following references: Bridge,P.J. et al (1978), Burns,P.C. and Hawthorne,F.C. (1993), Chao,G.Y. (1981), Craig,J.R.,and Scott,S.D. (1974), Giuseppetti,G. et al (1989), Goble,R.J. (1981), Goble,R.J.,and Robinson,G. (1980), Graedel,T.E. et al (1988), Groat,L.A. and Hawthorne,F.C. (1987), Jambor,J.L. et al (1964),JCPDS (1980), Mumme,W.G. et al (1988), Nickel,E.H. (1973), Pollard,A.M. et al (1989) and (1990), Potter,R.W. (1977), O'Keeffe,M. and Bovin,J.O. (1978), Ridkosil,T. et al (1982), Robertsson,B.E. et al (1967), Rösler,H.J. (1984), Ruotsala,A.P.and Wilson,M.L. (1977), Sieber,N.H.W. et al (1987), Van Oosterwyck,G. (1977), Wan,C. et al (1978), Wang,N. (1982), Woods,T.L. et al (1986). Further information on mineral stability fields can be obtained from Fig.6 and Fig.7. (Pollard,A.M. et al:1990).

1 A

Mineral	**Composition**	**Structure**	**Th. Stability** C°		**Remarks**
			Min	**Max**	
<u>Cu-sulphides</u>					
Chalcocite	Cu_2S	Monoclinic		103	
	Cu_2S	Hexagonal	103	435	
Djurleite	$Cu_{1.97}S$	Orthorombic		93	
Digenite low	Cu_9S_5	Cubic		83	stab. by Fe
high	$Cu_{9+X}S_5$	Cubic	83	1129	
Anilite	Cu_7S_4	Orthorombic		70	
Roxbyite	$Cu_{1.74-1.82}S$	Monoclinic		65-70	stab. by Fe
Geerite	$Cu_{1.60}S$	Pseudocubic			ass. with sphalerite
Blaubl.covellite	$Cu_{1+X}S$			157	
I:Yarrowite	$Cu_{1.1+0.1}S$	Hexagonal			
II:Spionkopite	$Cu_{1.4}S$	Hexagonal			(metastable with regard to covellite+anilite)
Covellite	CuS	Hexagonal		507	

1 B

Mineral	Composition	Structure	Th. Stability C° Min	Max	Remarks
CuFe-sulphides					
Digenite	$(Cu,Fe)_9S_5$	Cubic		83	
	$(Cu,Fe)_9S_5$	Cubic	83	1129	
Bornite	Cu_5FeS_4	Tetragonal		228	
	Cu_5FeS_4	Cubic			metastable forms
x-Bornite	$CuFeS_{4.05}$	Tetragonal		125	
Idaite	$Cu_{5.5}FeS_{6.5}$	Hexagonal		501	
Nunkundamite	$Cu_{5.5}FeS_{6.5}$				
Fukuchilite	Cu_3FeS_8	Cubic		200	stable at high P
Chalcopyrite	$CuFeS_2$	Tetragonal		557	
Cubanite	$CuFe_2S_3$	Orthorombic		200-210	
Interm.sol.sol.		Cubic	20-200	960	
Talnakhite	$Cu_9Fe_8S_{16}$	Cubic		186	
Interm ph.1	$Cu_9Fe_8S_{16}$?	??	186	230	
Mooihoekite	$Cu_9Fe_9S_{16}$	Tetragonal		167	
Interm ph.A	$Cu_9Fe_9S_{16}$	??	167	236	
Haycockite	$Cu_4Fe_5S_8$	Orthorombic		?	low T
Prim.cub.ph.	Wide range	Cubic?	20	200	
??	$Cu_{0.12}Fe_{0.94}S_{1.00}$	??		????	
Valleriite	$CuFeS_2 * 1.53(Mg,Al)(OH)_2$	Hex		250	
Djerfisherite	$K_3Cu_3(FeNi)_{11}S_{14}$	Cubic			ass. with talnakhite, pentlandite and cubanite

1C

Mineral	Composition	Structure	Th. Stability C° Min	Max	Remarks
Carbonates					
Malachite	$Cu_2(CO_3)(OH)_2$	Monoclinic			common on artifacts in soil
Azurite	$Cu_3(CO_3)_2(OH)_2$	Monoclinic			
Nakauriite	$Cu_8(SO_4)_4(CO_3)(OH)_6$	Orthorombic			
Chalconatronite (synthetic)	$Na_2Cu(CO_3)_2{*}3H_2O$	Monoclinic			corrosion product
Chlorides					
Nantokite	$CuCl$	Cubic			
Tolbachite	$CuCl_2$	Monoclinic			unstable in air, hygroscopic
Eriochalcite	$CuCl_2{*}2H_2O$	Orthorombic			ass. with atacamite
Botallackite	$Cu_2(OH)_3Cl$	Monoclinic			
Paratacamite	$Cu_2(OH)_3Cl$	Trigonal		40	
Atacamite	$Cu_2(OH)_3Cl$	Orthorombic			
Claringbullite	$Cu_8(OH)_{14}Cl_2{*}H_2O$				
Calumetite	$Cu(OH,Cl)_2{*}2H_2O$	Orthorombic			
Anthonyite	$Cu(OH,Cl)_2{*}3H_2O$	Monoclinic			
Connellite	$Cu_{37}Cl_8(SO_4)_2(OH)_{62}{*}8H_2O$	Hexagonal			
Buttgenbachite	-------(SO_4,NO_3)----	Hexagonal			
Mitscherlichite (synthetic)	$K_2CuCl_4{*}2H_2O$	Tetragonal			synthesized at room temp.

1C

Mineral	**Composition**	**Structure**	**Th. Stability C^o**		**Remarks**
			Min	**Max**	
Oxides and Hydroxides					
Cuprite	Cu_2O	Cubic			
Paramelaconite	Cu_4O_3	Tetragonal			ass. with tenorite
Tenorite	CuO	Monoclinic			
Delafossite	$CuFeO_2$	Trigonal			
Cuprospinel	$CuFe_2O_4$	Tetragonal		700-800	stable with hematite
		Cubic	700-800		stab. by Mg at room temp.
Spertiniite	$Cu(OH)_2$				
Gerhardtite	$Cu_2(OH)_3NO_3$	Orthorombic		140	ass. with malachite, cuprite
Phosphates					
Cu-pyrophosph.	a-$Cu_2P_2O_7$	Monoclinic		70-100	
	b-$Cu_2P_2O_7$		70-100		
Sampleite	$Cu_3(PO_4)_2*H_2O$	Orthorombic			ass. with atacamite, corrosion product on artifacts
Libethenite	$Cu_2PO_4(OH)$	Orthorombic			ass. with malachite
Cornetite	$Cu_3PO_4(OH)_3$	Orthorombic			
Reichenbachite	$Cu_5(PO_4)_2(OH)_4$	Monoclinic			ass. with ps.malachite
Pseudomalachite	$Cu_5(PO_4)_2(OH)_4$ $(*H_2O)$	Monoclinic			
Tagilite	$Cu_2(PO_4)OH*H_2O$?	Monoclinic			ass. with libethenite.and ps.malachite.
Hentschelite	$CuFe_2(PO_4)_2(OH)_2$	Monoclinic			
Chalcosiderite	$CuFe_6(PO_4)_4(OH)_8$ $*4H_2O$	Triclinic			(Cornwall)
Likasite	$Cu_6(NO_3)_2PO_4(OH)_7$	Orthorombic			ass. with gerhardtite

1C

Mineral	Composition	Structure	Th. Stability C°		Remarks
			Min	Max	
<u>Silicates</u>					
Chrysocolla	$Cu_2H_2Si_2O_5(OH)_4$ $*nH_2O$	Orthorombic			
Dioptase	$CuSiO_2(OH)_2$	Trigonal			
Shattuckite	$Cu_5(SiO_3)_4(OH)_2$	Orthorombic			
Plancheite	$Cu_8(Si_4O_{11})_2(OH)_4$ $*nH_2O$	Orthorombic			ass. with dioptase, malachite,cuprite
(Bisbeeite)					=plancheite+chrysocolla
(Katangite)					=microcryst. variety of plancheite(?)
Kinoite	$Cu_2Ca_2Si_3O_{10}*2H_2O$	Monoclinic			in skarn and in basalt ass. with native copper
Papagoite	$CaCuAlSi_2O_6(OH)_3$	Monoclinic			ass. with ajoite
Litidionite	$KNaCuSi_4O_{10}$	Triclinic			(Vesuvius)
Ajoite	$(K,Na)Cu_7AlSi_9O_{24}$- $(OH)_6*3H_2O$	Triclinic		425	

1C

Mineral	**Composition**	**Structure**	**Th. Stability C°**		**Remarks**
			Min	**Max**	
<u>Sulphates</u>					
Chalcocyanite (=Hydrocyanite)	$CuSO_4$	Orthorombic			
Poitevinite	$CuSO_4*H_2O$	Monoclinic			theoretical formula
Bonattite	$CuSO_4*3H_2O$	Monoclinic			
Chalcanthite	$CuSO_4*5H_2O$	Triclinic			
Boothite	$CuSO_4*7H_2O$	Monoclinic			
Antlerite	$Cu_3SO_4(OH)_4$	Orthorombic			
Brochantite	$Cu_4SO_4(OH)_6$	Monoclinic			ass. with cuprite, also common on artifacts
Posnjakite	$Cu_4SO_4(OH)_6*2H_2O$	Monoclinic			
Langite	$Cu_4SO_4(OH)_6*2H_2O$	Orthorombic			
Wroewolfeite	$Cu_4SO_4(OH)_6*2H_2O$	Monoclinic			
Dolerophanite	$Cu_2O(SO_4)$	Monoclinic			converts to antlerite(?) in water at room temp.
Guildite	$CuFe(SO_4)_2(OH)*4H_2O$	Monoclinic			
Cuprocopiapite	$CuFe_4(SO_4)_6(OH)_2*20H_2O$	Triclinic			
Devillite	$Cu_4Ca(SO_4)_2(OH)_6*3H_2O$	Monoclinic			
Natrochalcite	$NaCu_2(SO_4)_2OH*H_2O$	Monoclinic			
Krohnkite	$Na_2Cu(SO_4)_2*2H_2O$	Monoclinic			
Cyanochroite(s)	$K_2Cu(SO_4)_2*6H_2O$	Monoclinic			(s)=synthetic sample
Leightonite	$K_2Ca_2Cu(SO_4)_4*2H_2O$	Triclinic (Pseudoorthorombic)			
Chlorothionite	$K_2CuSO_4Cl_2$	Orthorombic			water soluble

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Appendix 1.

6 CONSTRAINTS ON THE USE OF Eh-pH STABILITY DIAGRAMS TO PREDICT FORMATION OF SULPHIDE MINERALS.

6.1, General.

Much of the discussion below is based on Sato (1992). When discussing sulphide mineral relations in a natural water environment at low temperature, diagrammatic presentations of phase stability fields in terms of two or more *intensive* variables (*intensive v.* = thermodynamic v. not related to mass), such as temperature, pressure, and *chemical potentials* (related to activities), are of great help. Most common is the use of Eh-pH diagrams. However, when these equilibrium diagrams are confronted by the real world, large differences frequently become apparent. For example, as discussed at length by Sato (1992); large discrepancies are observed, when phase relations in the Cu-Fe-S-O system at room temperature, constructed by Mckinstry (1959) from field- and microscopic observations of supergene sulphide - and oxide ore, are compared with phase relations in the same system, as calculated from thermochemical data (reproduced after Garrels and Christ, 1965).

As discussed above, this can partly be explained by the fact that many mineral phases which have experienced changes at low temperature in nature, owe their present appearence to metastable processes. However, it has been observed, as well, that redox processes between aqueous species, where several electrons are exchanged, and/or where a considerable structural reorganization of the molecule takes place, are very sluggish at low temperatures. As a result of this, direct potentiometric measurements often give results that differ strongly from values calculated from thermodynamic equilibria. (Perhaps most well-known in the present context is reaction between SO_4^{2-} and S^{2-}, the kinetics of which have been investigated by Ohmoto and Lasaga, 1981, who used exchange of ^{34}S - ^{32}S between the oxidized and reduced species, and who reported insignificant rates below 200°C in a non-bacterial environment). Below, we will give a few examples of redox disequilibria, which may have a bearing on the present problem.

According to Sato (1992), the reaction between oxygen and water is the most striking example of redox disequilibrium that persists for geological time in the Eh range of subareal waters, especially ocean water. This very important redox process defines the upper Eh boundary of the natural environment. Under standard conditions the equilibrum between oxygen and water is given by:

$$O_2 + 4H^+ + 4e^- = 2H_2O$$

$$\mathbf{Eh} = 1.229 + 0.0148\mathbf{log}a_{O_2} - 0.0591\mathbf{pH} \qquad (A1)$$

At the atmosphere - water boundary ($p_{O_2} \sim 0.21$ atm.) this becomes:

$$\mathbf{Eh} = 1.22 - 0.059\mathbf{pH} \qquad (A2)$$

Measured potentials of various aerated waters are all about 0.4 volt lower than predicted from this equation (Garrels and Christ, 1965). Thus, another control mechanism must be in effect. According to Sato (1960, cited in Sato, 1992) the observed persistent non-equilibrium is due to the high activation energy needed to break the strong bonds in molecular oxygen to form "atomic" oxygen. A number of authors, including Sato (1992), have considered an alternative reaction:

$$O_2 + 2H^+ + 2e^- = H_2O_2$$

$$\mathbf{Eh} = 0.682 - 0.0591\mathbf{ph} + 0.0295\mathbf{log}a_{O_2}/a_{H_2O_2} \qquad (A3)$$

The details of hydrogen peroxide formation in natural waters, which are complex, have been investigated by Millero et al (1987). It has also been shown to be of importance for the Cu^{1+}/Cu^{2+} redox couple, i.e. for the persistence of Cu^{1+}(aq) in seawater (Moffet and Zika, 1983).

However, according to Sato (1992), reduction of hydrogen peroxide takes place through:

$H_2O_2 + 2H^+ + 2e^- = 2H_2O$

$$\mathbf{Eh} = 1.772 - 0.0591\mathbf{pH} + 0.0295\mathbf{log}a_{H_2O_2} \qquad (A4)$$

As seen in these reactions, the Eh at which H_2O_2 is reduced to H_2O is much higher than its oxidation Eh under identical conditions, which means that H_2O_2 is unstable with respect to decomposition into $H_2O + O_2$. This process can be catalyzed by redox couples with intermediate E^o values, for example Fe^{3+}/Fe^{2+}, with $E^o = 0.77$ volt, where Fe^{2+} is oxidized and Fe^{3+} reduced by H_2O_2, leading to little net change in the Fe^{3+}/Fe^{2+} ratio.

If Eh of a solution containing ions of multivalent elements, like Fe and Mn, is lower than in equation A3, both O_2 and H_2O_2 can act as oxidizers, resulting in a rapid increase in Eh. When Eh exceeds that of equation A3, however, O_2 ceases to be an effective oxidizer, because H_2O_2 starts to decompose into O_2 and H_2O as soon as it forms. This means that H_2O_2 no longer contributes to the net oxidation, while equation A2 is blocked by a high energy barrier. According to Sato (1992) the empirical upper limit of Eh of aerated waters, containing elements like Fe and Mn corresponds to a $a_{O_2}/a_{H_2O_2}$ ratio of 10^6 in equation A3, which gives:

$$\mathbf{Eh} = 0.86 - 0.059\mathbf{pH} \qquad (A5)$$

Highly oxidized minerals can form, however, in spite of the discussed constraint on Eh by the O_2/H_2O_2 process. This is so, because solid oxides containing mixed valency elements (Fe, Mn) can disproportionate if the chemical environment is suitable. According to Sato (1960), simple acidification can bring about disproportionation of intermediate Mn-oxides to Mn^{2+} ions plus "higher" oxides. For example:

$Mn_2O_3 + 2H^+ = MnO_2 + Mn^{2+} + H_2O$

where Eh is finally controlled by the MnO_2/Mn^{2+} redox couple:

$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$

$$\mathbf{Eh} = 1.228 - 0.1182\mathbf{pH} - 0.0295\mathbf{log}a_{Mn^{2+}} \qquad (A6)$$

At variance with oxides, metal sulphides behave in a complex manner when subjected to changing redox conditions. This is so, because both metal atoms and sulphur may participate in electron exchange processes. This property leads to stability relations, which, at first glance, may seem contradictory. For example, when metallic copper is oxidized in an environment where reactive sulphur species and water are present, copper sulphides form in order of increasing oxidation; $Cu^0 \rightarrow Cu_2S \rightarrow .....\rightarrow CuS \rightarrow ......Cu_2S \rightarrow Cu^0$ (see for example, Figure 5, page 60-61 in SKN 59, 1992). For simplicity we have ignored all copper sulphides of composition intermediary between Cu_2S (chalcocite) and CuS (covellite). If we assume that copper is univalent in all copper sulphides (personal communications with Rolf Berger, Institute of Chemistry, University of Uppsala) the average valency on sulphur changes according to: $Cu^0 \rightarrow Cu_2S(-2) \rightarrow.....\rightarrow CuS(-1) \rightarrow...\rightarrow Cu_2S(-2) \rightarrow Cu^0$. This is explained by the fact that we assume SO_4^{2-}(aq) to be in perfect equilibrium with the copper sulphides and with the present aqueous sulphide species. This is *not* the case at low temperature.

The present example is instructive in showing that the chemical milieau, in terms of Eh, can not be inferred from valencies of metal atoms and sulphur in metal sulphides. Moreover, as already mentioned above, metal sulphide relations observed in nature often differ significantly from what is expected from equilibrium considerations. This is the topic under the next heading.

6.2 Persistency field Eh-pH relations.

The discussion below is to a large degree based on Sato (1992) and references therein. Persistency field Eh-pH relations differ from thermodynamic equilibrium relations in that observed metastability fields are included. Thus, persistency relations should resemble more closely what actually takes place in nature, and, hence, be of value in predicting reaction paths.

Direct potentiometric measurements are employed to deliniate the metastability fields of semiconducting metal sulphides. The solid sulphide electrode is connected via an external circuit to an inert metal electrode (Pt, Au), and both electrodes are immersed in the solution. When Eh of the solution is higher than that of the solid sulphide, the latter will release electrons which are transported via the external circuit to the inert metal electrode, where reduction takes place; e.g. $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$. When Eh of the solution is lower than that of the metal sulphide, the latter will be reduced and recieve electrons via the external circuit etc.

It is important to note that in the "natural system" the solution is in most cases regarded as having a much larger redox *capacity* than the metal sulphide, i.e. it is continually replenished from outside. (If we assume that the technical barriers function as expected, the situation will be the opposite as regards the copper canisters, thus, the solution Eh will change. This is not discussed here).

Now, the actual reaction is identified by a comparison of the observed phase-boundary electrode potential (=potential where the solid phase is oxidized and reduced, respectively) with computed potentials of various possible electrode reactions. Thus, it is observed that oxidation takes place via release of electrons and metal ions, resulting in formation of a sulphide with a lower metal to sulphur ratio. If such a phase does not exist, elemental sulphur may form.

For example, for a Cu_2S electrode in an acid, slightly oxidizing solution, the reversible phase-boundary reaction observed is in good agreement with the following model:

$CuS + Cu^{2+} + 2e^- = Cu_2S$

$$Eh = 0.578 + 0.0295\log a_{Cu^{2+}} \quad (A7)$$

and for a CuS electrode:

$S^o + Cu^{2+} + 2e^- = CuS$

$$Eh = 0.591 + 0.0295\log a_{Cu^{2+}} \quad (A8)$$

Electrode reactions of copper sulphides with compositions intermediate between Cu_2S and CuS should fall between these values. In a near-neutral to weakly basic solution, $a_{Cu^{2+}}$ becomes a function of pH because of hydroxide or oxide formation. Hence for the Cu_2S and CuS oxidation:

$CuS + CuO + 2H^+ + 2e^- = Cu_2S + H_2O$

$$Eh = 0.753 - 0.0591pH \quad (A9)$$

and:

$S^o + CuO + 2H^+ + 2e^- = CuS + H_2O$

$$Eh = 0.812 - 0.0591pH \quad (A10)$$

On the other hand, reduction of copper sulphide is observed to proceed via a release of sulphur as sulphide ions into the solution and formation of a sulphide with a higher metal to sulphur ratio, according to the *stability* Eh-pH diagram (finally metallic copper will form).

Thus, for reduction of CuS in the S^{2-}, HS^-, and H_2S predominance fields, respectively:

$2CuS + 2e^- = Cu_2S + S^{2-}$

$$\mathbf{Eh} = -0.538 - 0.0295\mathbf{log}a_{S^{2-}} \qquad (A11)$$

$2CuS + H^+ + 2e^- = Cu_2S + HS^-$

$$\mathbf{Eh} = -0.124 - 0.0205\mathbf{log}a_{HS^-} - 0.0295\mathbf{pH} \qquad (A12)$$

$2CuS + 2H^+ + 2e^- = Cu_2S + H_2S$

$$\mathbf{Eh} = 0.083 - 0.0591\mathbf{pH} - 0.0295\mathbf{log}a_{H_2S} \qquad (A13)$$

(again ignoring intermediary copper sulphides).

To summarize; observed oxidation of metal sulphides leading to a release of metal ions is path-controlled and results in metastable equilibria. On the other hand, reduction reactions, where sulphur is released as sulphide ions, are in concordance with the stability Eh-pH relations.

The situation becomes more complex, when we try to define the electrode potential of a metal sulphide in the Eh-pH region where it can be in equilibrium with the solution. Sato (1966) derived a theoretical expression for a simple binary sulphide, with the stoichiometric formula; M_2S_j, which dissociates in the solution into M^{j+} and S^{2-} ions, as:

$$\mathbf{Eh} = \mathbf{E^o} + 2.303(\mathbf{RT/4jF})\mathbf{log}[(a_{M^{j+}})^2(a_S)^j/(a_{S^{2-}})^j(a_M)^2] \qquad (A14)$$

(see Appendix in SKN 57, 1992, for definitions)

E^o can be computed using:

$$\mathbf{E^o} = (1/4j\mathbf{F})[2\Delta \mathbf{G}^o{}_f(M^{j+}) + j\Delta \mathbf{G}^o{}_f(S^{2-})] \qquad (A15)$$

where $\Delta G^o{}_f(M^{j+})$ is the Gibbs free energy of formation of M^{j+} at 25°C and 1 atm., etc. The relation between Gibbs free energy and the equilibrium constant was discussed in our report SKN 57, 1992. The activity of the metal ion; a_Mj+, and the sulphide ion; a_S2-, are related to each other through the solubility product (K_S):

$$M_2S_j = 2M^{j+} + jS^{2-}, \qquad \mathbf{K_S} = (a_Mj+)^2(a_S2-)^j \qquad (A16)$$

where:

$$\mathbf{logK_S} = -[2\Delta \mathbf{G}^o{}_f(M^{j+}) + j\Delta \mathbf{G}^o{}_f(S^{2-}) - \Delta \mathbf{G}^o{}_f(M_2S_j)]/2.303\mathbf{R\,T} \qquad (A17)$$

The activities of metal and sulphur in the metal sulphide; a_M and a_S, are related to each other by means of the *solid state activity product* (K_a):

$$M_2S_j = 2M + jS \qquad \mathbf{K_a} = (a_M)^2(a_S)^j \qquad (A18)$$

where:

$$\mathbf{logK_a} = \Delta \mathbf{G}^o{}_f(M_2S_j)/2.303\mathbf{R\,T} \qquad (A19)$$

It is important to note that the components in the solid; M and S, are *not* equivalent with the the ionic species; M^{j+} and S^{2-}, in the solution. Also note that the solid state solubility product (which is not often used, since it is difficult to calculate activities in solid compounds) is derived from the Gibbs-Duhem relation. Thus, for a binary compound:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \qquad (A20)$$

where μ_1 and μ_2 are the chemical potentials and n_1 and n_2 are the number of moles, of components 1 and 2, respectively, in a binary solid solution (Klotz and Rosenberg, 1986).

The chemical potential can be related to the activity:

$$\mu_i = \mu_i^o + RT\ln a_i \quad \rightarrow \quad d\mu_i = RTd\ln a_i \qquad (A21)$$

Where μ_1 is the chemical potential of component i in the solid solution, $\mu^o{}_i$ is the chemical potential of component i in the pure phase i, and a_i is the activity of component i in the solid solution.

substitution yields:

$$n_1 d\ln a_1 + n_2 d\ln a_2 = 0 \qquad (A22)$$

Integration yields:

$$n_1\int d\ln a_1 = -n_2\int d\ln a_2$$

$$n_1\ln a_1 = -n_2\ln a_2 + C$$

or:

$$\ln[(a_1)^{n_1}(a_2)^{n_2}] = C \qquad (A23)$$

or:

$$(a_1)^{n_1}(a_2)^{n_2} = e^C = \mathbf{K_a} \text{ (solid state solubility product)} \qquad (A24)$$

However, for CuS; **log**a_{Cu} varies from -6.62 to -8.60 and **log**a_S from -1.98 to 0. (It is assumed that the most sulphur-rich CuS is in equilibrium with pure sulphur at 25°C, 1 atm.). For Cu_2S, **log**a_{Cu} varies from 0 to -6.62 and **log**a_S from -15.22

to -1.98 (It is assumed that the most copper-rich Cu_2S is in equilibrium with pure metallic copper). Again, intermediary copper sulphides have been ignored.

In one important aspect, the oxidation trend observed in potentiometric measurements contrasts with the trend expected from thermodynamic stability considerations. Thus, the latter trend indicates that formation of SO_4^{2-} directly from a metal sulphide, gives the lowest computed oxidation potential among alternative possible oxidation paths, at a given pH. This means that "SO_4^{2-} forming" reactions define *the lowest possible upper boundary of sulphide stability fields*, regardless of whether these reactions really take place at the solid surface. Also, these reactions predict that the oxidation potential of a sulphide should become more positive as the SO_4^{2-} activity in the solution increases.

In reality, however, the potential of a metal sulphide is not directly affected by $a_{SO_4^{2-}}$ (unless solid metal sulphate is precipitated, in which case the activity of the metal in solution is affected).

The reason for the observed behaviour of semiconducting metal sulphides during oxidation is that a *direct formation of* SO_4^{2-} *is inhibited by a high activation energy*, while release of metal as an aqueous ion is a much simpler process. It may also be noted that thiosulphate ions; $S_2O_3^{2-}$, act as a metastable intermediary at low *temperatures. (Incidently, if we consider the metastable redox process;* $S^o \rightarrow S_2O_3^{2-}$, which has been indicated by thiobacterial oxidation; Zajic, 1969, cited in Sato, 1992, elemental sulphur will also have a metastable extension towards higher Eh values, although it can not be directly measured potentiometrically, since sulphur is an insulator).

When a persistency field Eh-pH diagram for a copper sulphide is compared with a corresponding stability field it is obvious that the solid phase may persist under higher Eh conditions than expected from purely thermodynamic considerations (Figure 8). Besides, CuS can persist at higher Eh than Cu_2S, which is also at variance with what we would expect from equilibrium considerations. Within the persistency field, the metal sulphide can survive for long periods of time at room temperature, at least as regards redox reactions. *However, processes that do not require destruction of the solid sulphur structural framework are possible, such as cation exchange and other replacement processes including redox processes involving sulphur.*

7 FIGURE CAPTIONS.

Figure 1: Phase relations in the central parts of the "dry" Cu-Fe-S system at decreasing temperatures. Note the increase in complexity (compare with Figure 2), and the decrease in extents of solid solutions, with decrease in temperature. The tie-lines connect phases which are believed to be in thermodynamic equilibrium under the specified conditions (temperature specified, total pressure equivalent with the sum of all partial vapor pressures, for a specific phase assemblage). In the diagrams we can distinguish one-phase, two-phase, and three-phase assemblages, depending on bulk composition. *Abbrevations*: dg_{ss}: digenite solid solution, bn_{ss}: bornite solid solution, cv: covellite (CuS), id: idaite (Cu_5FeS_6), cp: chalcopyrite ($CuFeS_2$), iss: intermediate solid solution, po_{ss}: pyrrhotite solid solution, py: pyrite (FeS_2). Based on a number of authors, referred to in the text.

Figure 2: Tentative room temperature relations in the Cu-Fe-S system. Two possibilities are shown: (a) tie-line digenite - pyrite ($Cu_{1.8}S$ - FeS_2), (b) tie-line idaite - chalcopyrite (Cu_5FeS_6 - $CuFeS_2$). *Note that other possibilities exist as well.* The diagrams are simplified along the binary joins Cu-S and Fe-S. *Abbrevations*: cc: chalcocite (Cu_2S), dg: digenite ($Cu_{1.8}S$), an: anilite ($Cu_{1.75}S$), cv: covellite (CuS), id: idaite (Cu_5FeS_6), bn: bornite (Cu_5FeS_4), cp: chalcopyrite ($CuFeS_2$), t: talnakhite ($Cu_9Fe_8S_{16}$), m: moohekite ($Cu_9Fe_9S_{16}$), h: haycookite ($Cu_8Fe_{10}S_{16}$), cb: cubanite ($CuFe_2S_3$), tr: troilite (FeS), po: monoclinic low-temperature pyrrhotite (Fe_7S_8), py: pyrite (FeS_2).
Based on a number of authors, referred to in the text.

Figure 3: The *chalcopyrite* ($CuFeS_2$) structure, which can be considered a typical metal sulphide structure where the metal atoms in a regular way occupy tetrahedral intersticies between cubic close packed sulphur atoms. The packing arrangement is identical with that of *sphalerite* (ZnS). Instead of the simple rows of Zn atoms in ZnS the cation positions are occupied alternatively by Cu and Fe atoms. The result is that the unit cell of $CuFeS_2$ corresponds to two unit cells of ZnS stacked one on top of the other. Note that although the symmetry is tetragonal the basic packing arrangement is still face-centered cubic.

At 557°C (P = 0) the $CuFeS_2$ structure transforms to a "true" *sphalerite* structure since the Cu and Fe atoms are now statistically distributed among the cation positions.

Figure 4: Examples of *solid state replacement* as seen through the microscope.

(a) *Massive replacement* where Cu_5FeS_4 has formed as a result of solid state diffusion between Cu_2S and $CuFeS_2$. The simplified overall process can be written:

$CuFeS_2 + 2Cu_2S \rightarrow Cu_5FeS_4$

However, to illustrate that the process takes place via cation diffusion:

$2CuFeS_2 + 3Cu^+ + e^- \rightarrow Cu_5FeS_4 + Fe^{2+}$, and

$4Cu_2S + Fe^{2+} \rightarrow Cu_5FeS_4 + 3Cu^+ + e^-$

Note that a chemical gradient develops through the growing Cu_5FeS_4 zone; it is Cu-rich at the Cu_2S boundary and Cu-poor at the $CuFeS_2$ boundary, resulting in a change in colour from bluish (Cu-rich) to brownish (Cu-poor). After Amcoff (1988).

(b) *Oriented replacement* or *replacement exsolution* with lamellae of the replacing phase(s) growing in the host grain. In the text two examples of oxidation are discussed, both of which result in a similar texture, i.e:

(i) $Cu_5FeS_4 \rightarrow CuFeS_2 + 2Cu_{1.8}S + 0.4Cu^+ + 0.4\ e^-$, and

(ii) $3Fe_3O_4 \rightarrow 4Fe_2O_3 + Fe^{2+} + 2\ e^-$

In (i) duplex lamellae of $CuFeS_2 + Cu_{1.8}S$ form along (111)-planes in a Cu_5FeS_4 host crystal, and in (ii) lamellae of Fe_2O_3 form along (111)-planes in a Fe_3O_4 host crystal (the *martitization* process).

Note that Cu^+ ions precipitate as CuS and Fe^{2+} ions as Fe_2O_3, respectively, *outside* the grains which are being replaced! This is due to the "inertness" of sulphur and oxygen, respectively, compared with the cations as regards solid state diffusion.

Figure 5: Hypothetic sulphidation of metallic copper in an environment containing aqueous sulphide species, e.g. HS^-, H_2S, polysulphide ions.

(a) Initial conditions.

(b) Polysulphide ions may act as electron acceptors and release S^{2-} at the metal surface.

(c) Chalcocite; Cu_2S, is formed initially. Outward diffusion of Cu^+ through the metal and the growing metal sulphide is followed by combination with S^{2-} to form Cu_2S. For the overall redox process e.g: $2Cu^o + S_5S^{2-} \rightarrow Cu_2S + S_4S^{2-}$.

(d) With continuing reaction S-richer Cu-sulphides are formed, depending on the total concentration of dissolved sulphide species. A mineralogical *steady state* gradient may be set up, with Cu_2S in contact with the metal and S-rich Cu-sulphide in contact with the water-rich environment. Pores develop and grow in the metal, because of preferential copper depletion along defects etc.

(e) If the solution is depleted in reactive species the sulphide crystal layer will equilibrate with respect to both metallic copper and solution chemistry. If Fe(aq) species are present CuFe-sulphides may form through replacement of "simple" Cu-sulphides.

Figure 6: Eh-pH diagram for some "oxidized" copper minerals

(a) with $a_{SO4^{2-}}(aq)=10^{-3}$ and $a_{CL^-}(aq)=10^{-1.75}$

(b) with $a_{SO4^{2-}}(aq)=10^{-2}$ and $a_{CL^-}(aq)=10^{-1.75}$

Note that in (b) only minerals whose stability fields have been changed are named.

Figure 7: Stability field diagram for the copper(II)halide minerals. ($\log a_{Cl^-}$ as a function of pH)

(a) in the abscence of CO_2

(b) $CO_2(g)$ with a partial pressure of $10^{-3.5}$ (Normal atmospheric conditions).

(c) $CO_2(g)$ with a partial pressure of $10^{-1.36}$

In all three diagrams the sulphate activity is equal to 10^{-3}

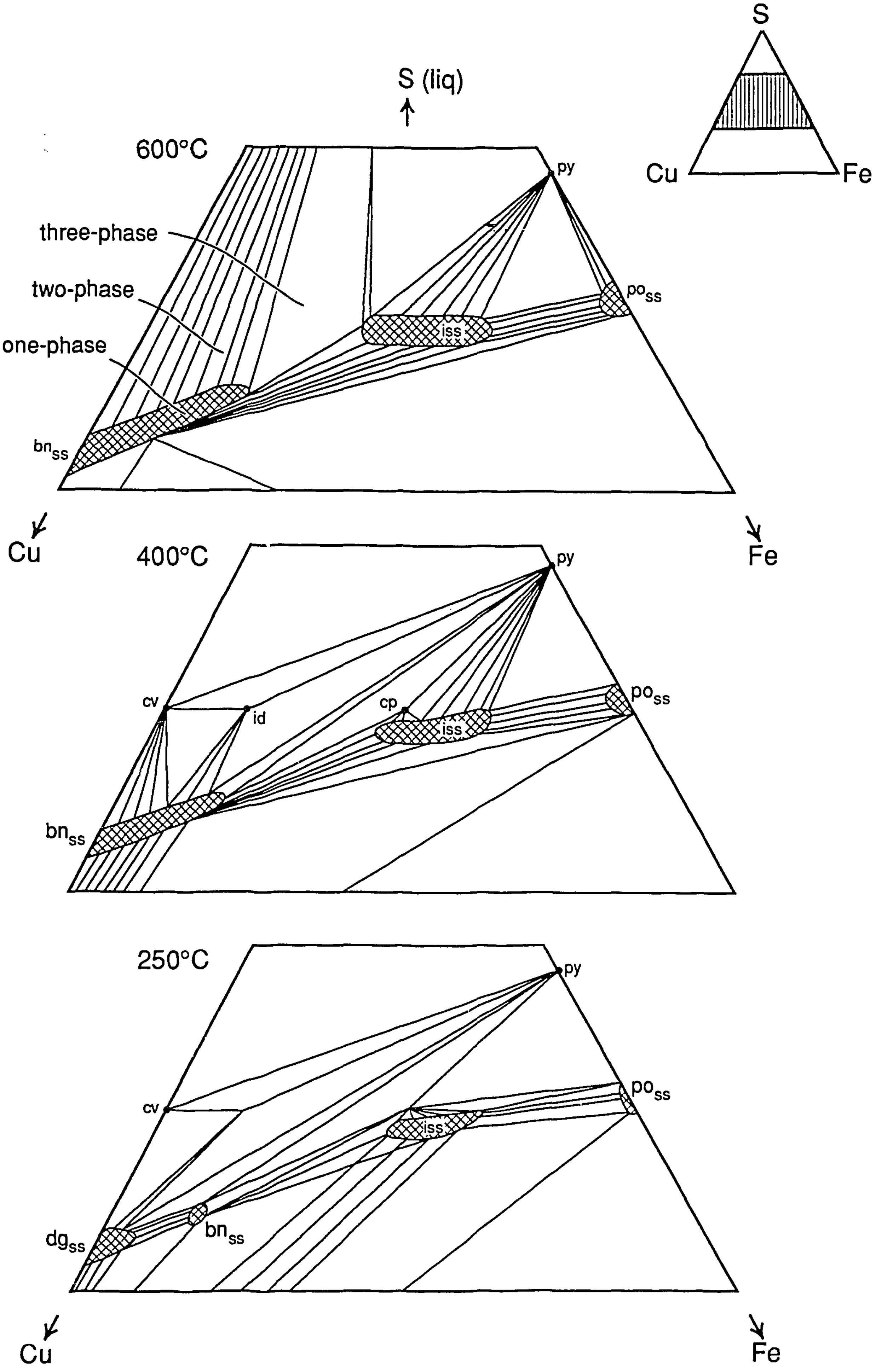
Note that in (b) and (c) only minerals whose stability fields have been changed are named.

Figure 8: Persistency fields for CuS (a) and Cu_2S (b). Cu-sulphides of intermediate compositions have been neglected for simplicity. Note that reduction reactions ($CuS \rightarrow Cu_2S$; $Cu_2S \rightarrow Cu^o$) correspond with equilibrium processes (the lower persistency boundaries in the diagrams), while the oxidation reactions are path-controlled, and correspond with a release of copper and formation of more S-

rich phases ($Cu_2S \rightarrow CuS$; $CuS \rightarrow S^o + Cu^{2+}$). See the text for details. Thus, a significant overvoltage is needed to "destroy" Cu-sulphides (like other metal sulphides!), once they have formed.

Total concentration of dissolved sulphur species: 10^{-1} molar. Note that this is only of importance for the lower persistency boundaries!

Simplified after Sato (1992).


S
Cu
Fe
S (liq)
600°C
py
three-phase
two-phase
one-phase
po_{ss}
iss
bn_{ss}
Cu
Fe
400°C
py
cv
id
cp
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bn_{ss}
250°C
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po_{ss}
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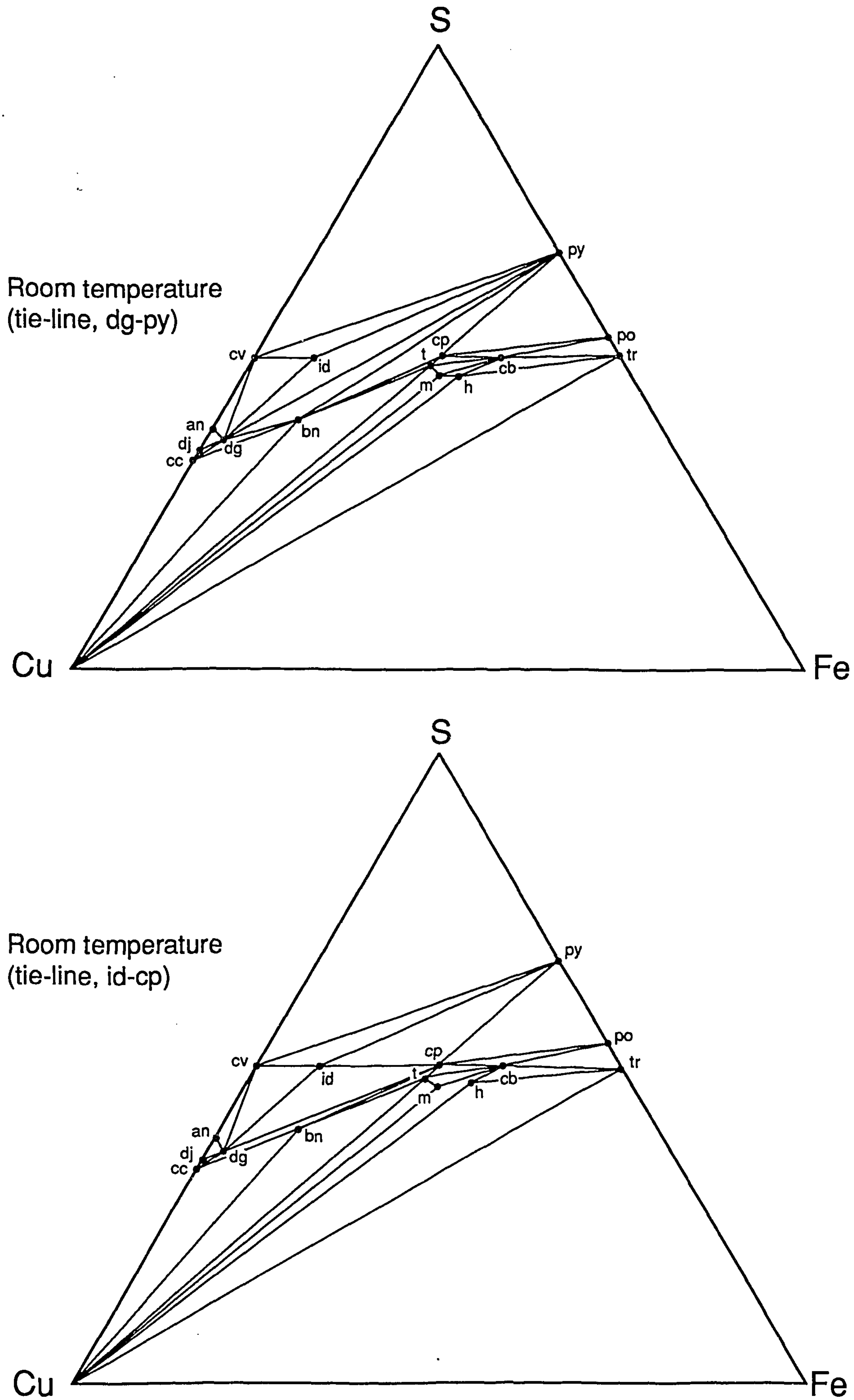
dg_{ss}
bn_{ss}
Cu
Fe

Fig. 1


S
Room temperature
(tie-line, dg-py)
py
cv
id
cp
t
po
tr
cb
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h
an
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Cu
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Room temperature
(tie-line, id-cp)
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dj
cc
dg
bn
Cu
Fe

Fig. 2

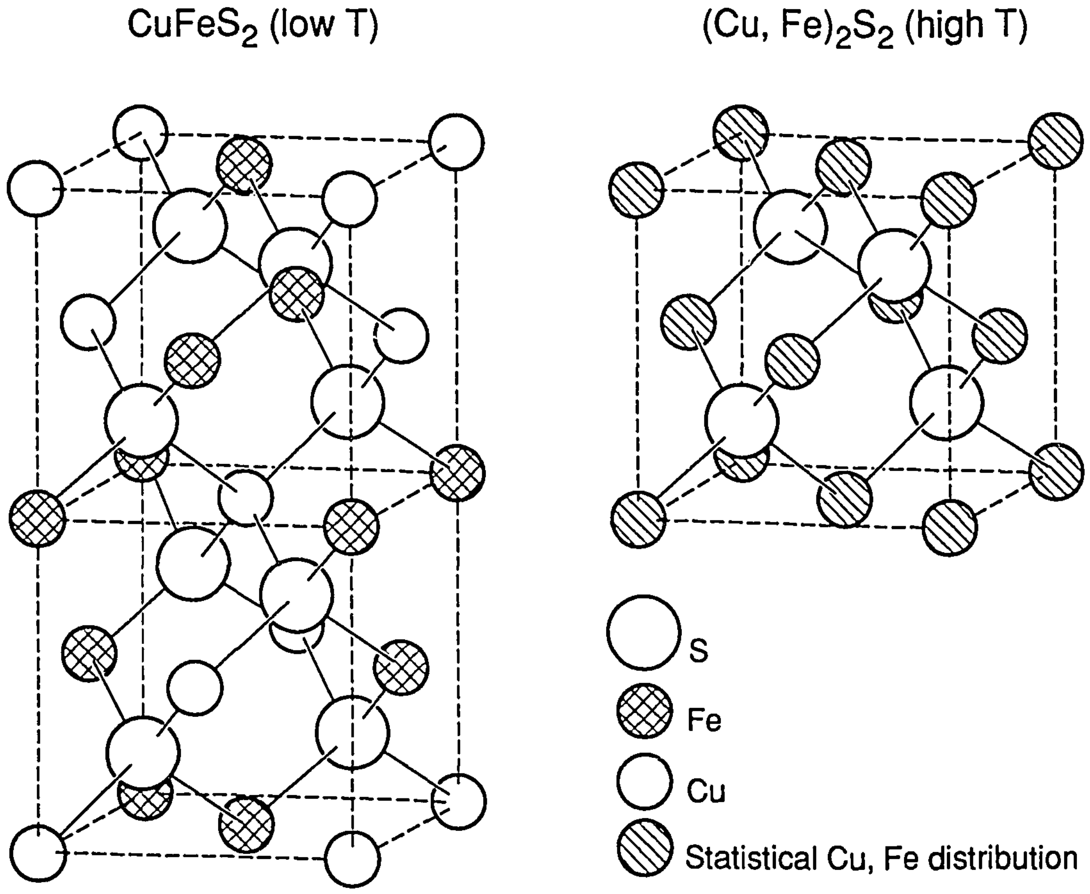

CuFeS$_2$ (low T)
(Cu, Fe)$_2$S$_2$ (high T)
S
Fe
Cu
Statistical Cu, Fe distribution

Fig. 3

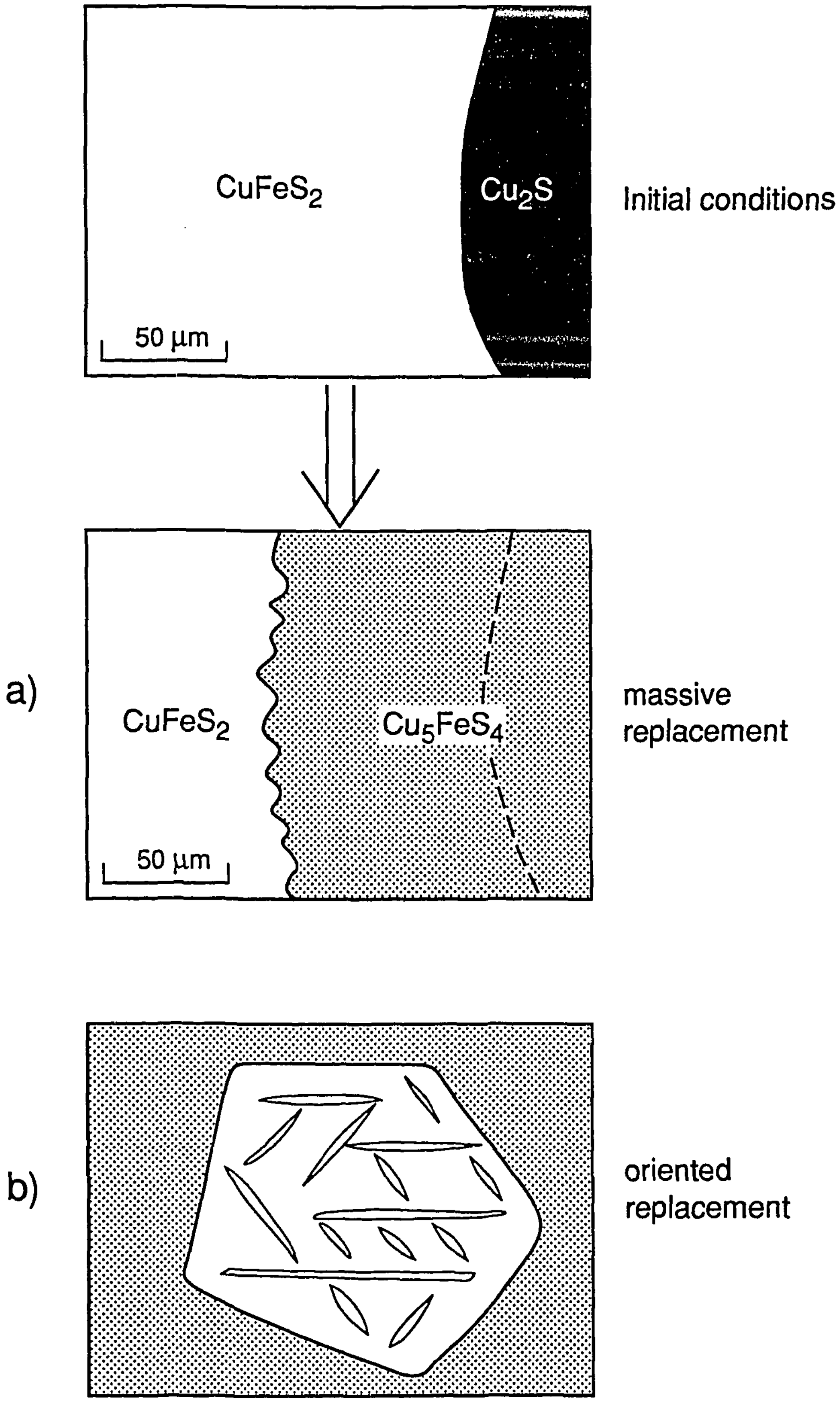

CuFeS2
Cu2S
Initial conditions
50 µm
a)
CuFeS2
Cu5FeS4
massive replacement
50 µm
b)
oriented replacement

Fig. 4

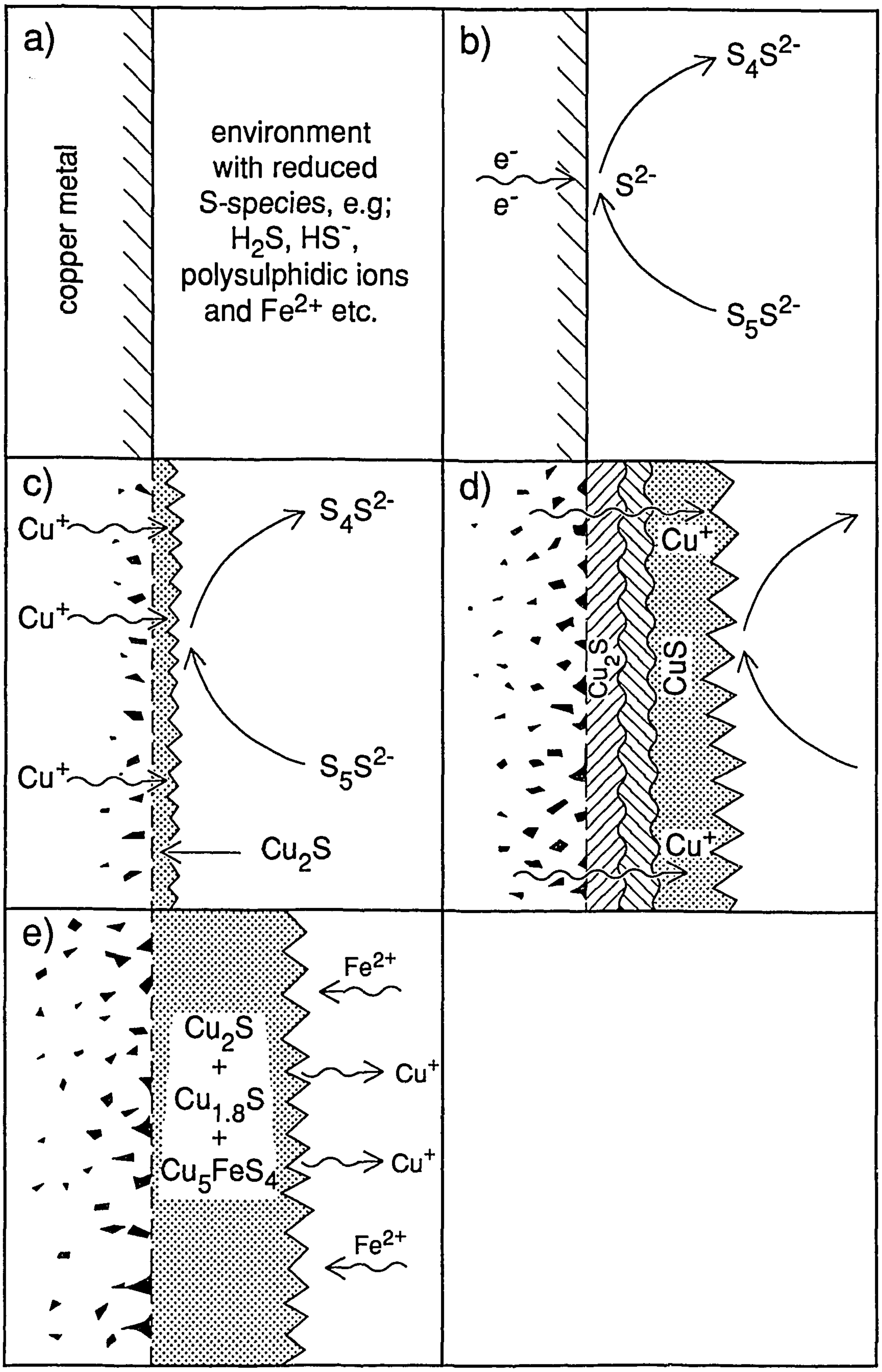

a)
copper metal
environment with reduced S-species, e.g; H_2S, HS^-, polysulphidic ions and Fe^{2+} etc.
b)
e^-
e^-
S^{2-}
S_4S^{2-}
S_5S^{2-}
c)
Cu^+
Cu^+
Cu^+
S_4S^{2-}
S_5S^{2-}
Cu_2S
d)
Cu^+
Cu_2S
CuS
Cu^+
e)
Fe^{2+}
Cu_2S + $Cu_{1.8}S$ + Cu_5FeS_4
Cu^+
Cu^+
Fe^{2+}

Fig. 5

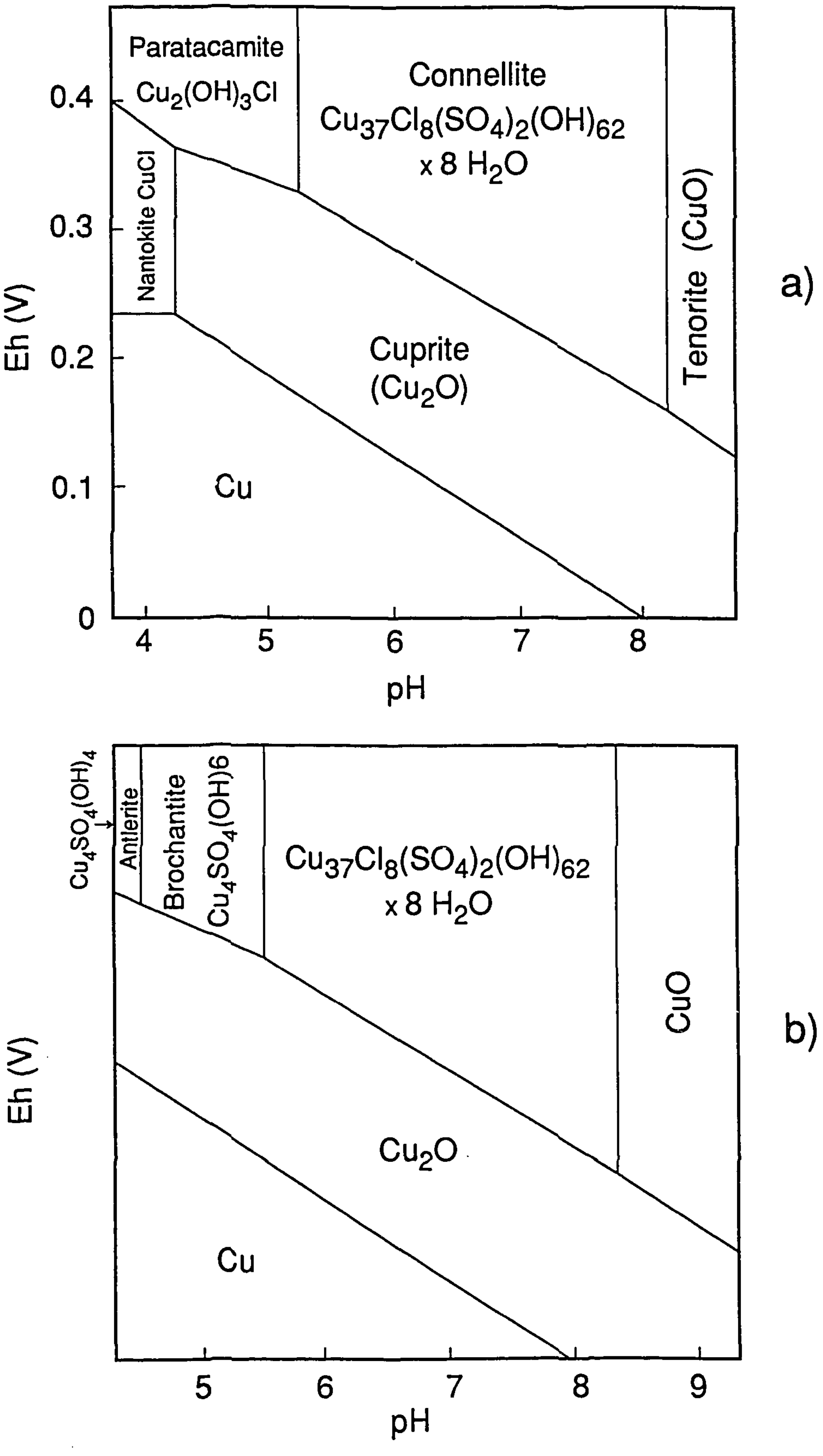

Paratacamite
$Cu_2(OH)_3Cl$
Connellite
$Cu_{37}Cl_8(SO_4)_2(OH)_{62}$
x 8 H_2O
Nantokite CuCl
Tenorite (CuO)
Cuprite
(Cu_2O)
Cu
Eh (V)
0.4
0.3
0.2
0.1
0
4
5
6
7
8
pH
a)
$Cu_4SO_4(OH)_4$
Antlerite
Brochantite
$Cu_4SO_4(OH)6$
$Cu_{37}Cl_8(SO_4)_2(OH)_{62}$
x 8 H_2O
CuO
Cu_2O
Cu
Eh (V)
5
6
7
8
9
pH
b)

Fig. 6

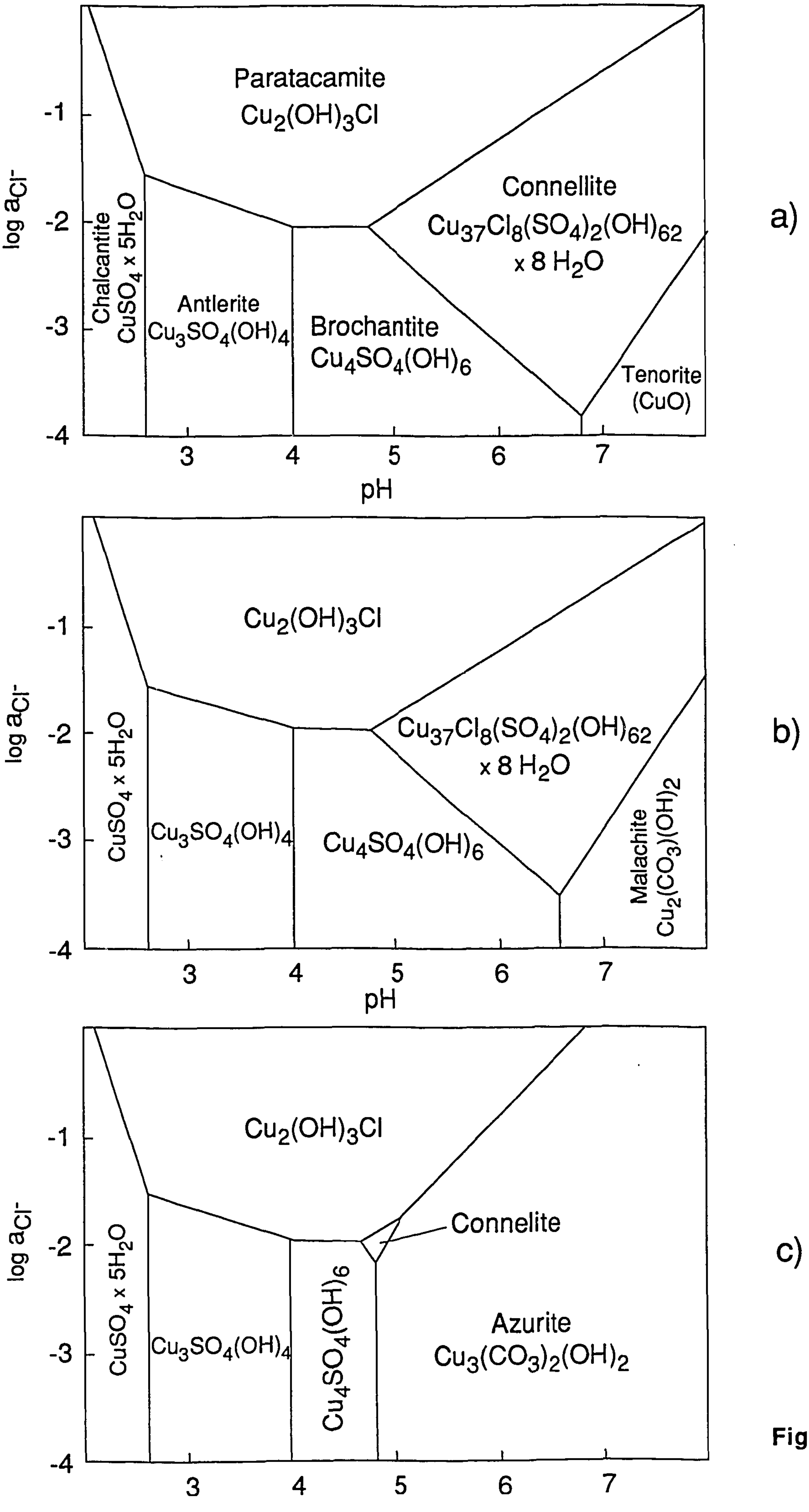
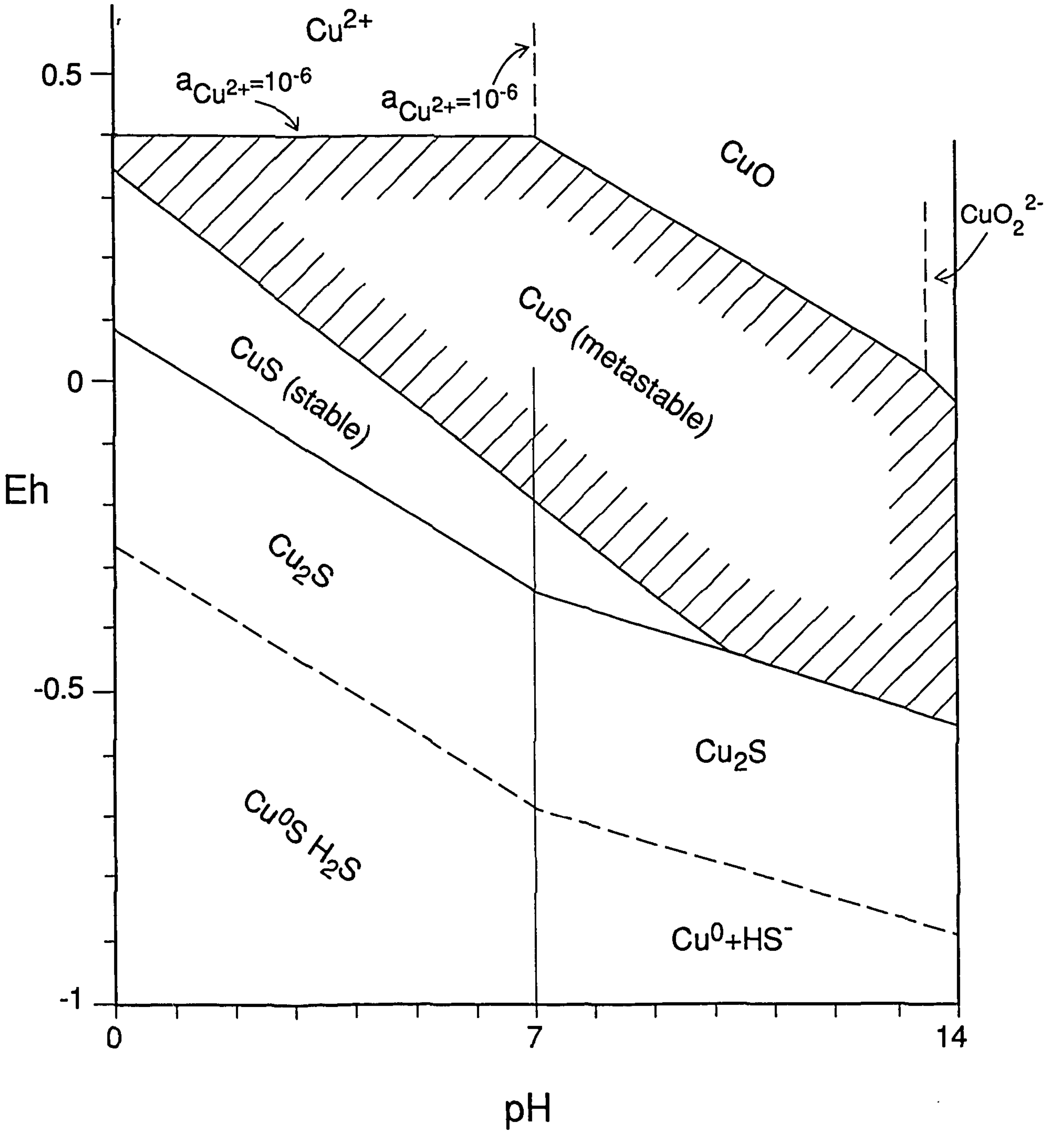
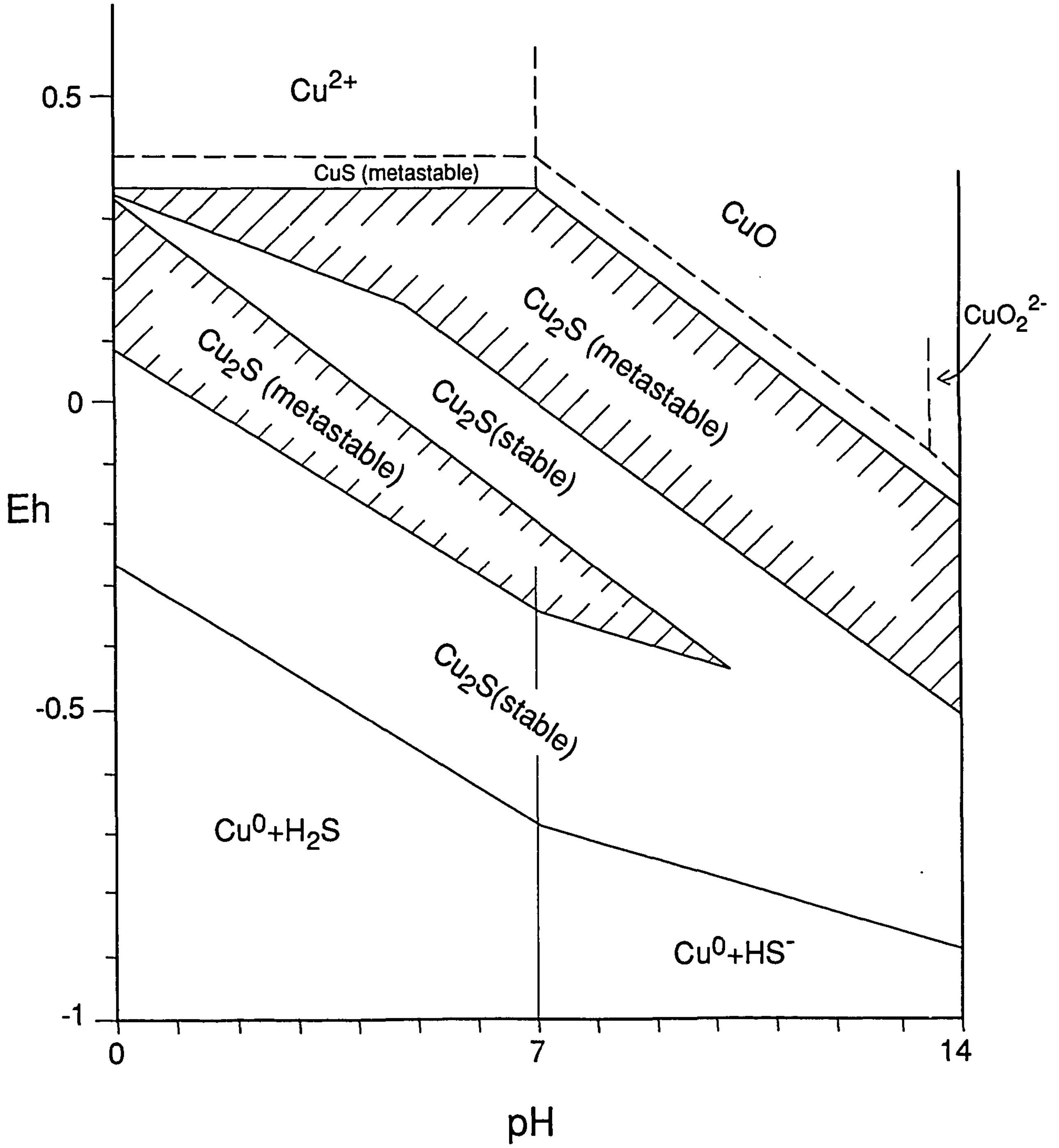

a)
Paratacamite
$Cu_2(OH)_3Cl$
Connellite
$Cu_{37}Cl_8(SO_4)_2(OH)_{62}$
x 8 H_2O
Chalcantite
$CuSO_4 \times 5H_2O$
Antlerite
$Cu_3SO_4(OH)_4$
Brochantite
$Cu_4SO_4(OH)_6$
Tenorite
(CuO)
log a_{Cl^-}
-1
-2
-3
-4
3
4
5
6
7
pH
b)
$Cu_2(OH)_3Cl$
$Cu_{37}Cl_8(SO_4)_2(OH)_{62}$
x 8 H_2O
$CuSO_4 \times 5H_2O$
$Cu_3SO_4(OH)_4$
$Cu_4SO_4(OH)_6$
Malachite
$Cu_2(CO_3)(OH)_2$
log a_{Cl^-}
-1
-2
-3
-4
3
4
5
6
7
pH
c)
$Cu_2(OH)_3Cl$
Connelite
$CuSO_4 \times 5H_2O$
$Cu_3SO_4(OH)_4$
$Cu_4SO_4(OH)_6$
Azurite
$Cu_3(CO_3)_2(OH)_2$
log a_{Cl^-}
-1
-2
-3
-4
3
4
5
6
7

Fig. 7



Cu2+
0.5
aCu2+=10-6
aCu2+=10-6
CuO
CuO2 2-
CuS (metastable)
CuS (stable)
0
Eh
Cu2S
-0.5
Cu2S
Cu0S H2S
Cu0+HS-
-1
0
7
14
pH

Fig. 8(a)



0.5
0
-0.5
-1
Eh
0
7
14
pH
Cu^{2+}
CuS (metastable)
CuO
CuO_2^{2-}
Cu_2S (metastable)
Cu_2S (metastable)
Cu_2S(stable)
Cu_2S(stable)
Cu^0+H_2S
Cu^0+HS^-

Fig. 8(b)

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