

Chapter 1: Sulphide Mineralogy

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The sulphides, metal-sulphur minerals, are important hosts of metal resources e.g. iron, copper, zinc, lead, nickel, that occur in common ore deposits formed in a variety of settings.

In order to predict which ore minerals and metal resources are likely to be found in an ore deposit it is important to study their mineralogy, as this controls the behaviour and occurrence of the ore minerals. Sulphide mineralogy is also useful for mineral identification in hand specimen, outcrop, drill core as well as in microscopy, as the external features and mineral properties are related to the internal organisation of the mineral structure.

Goals:

After reading this chapter you should be able to:

- Describe the mineral structures of common sulphide minerals.
- Relate sulphide minerals to one another by similarities in mineral structure and/or composition.

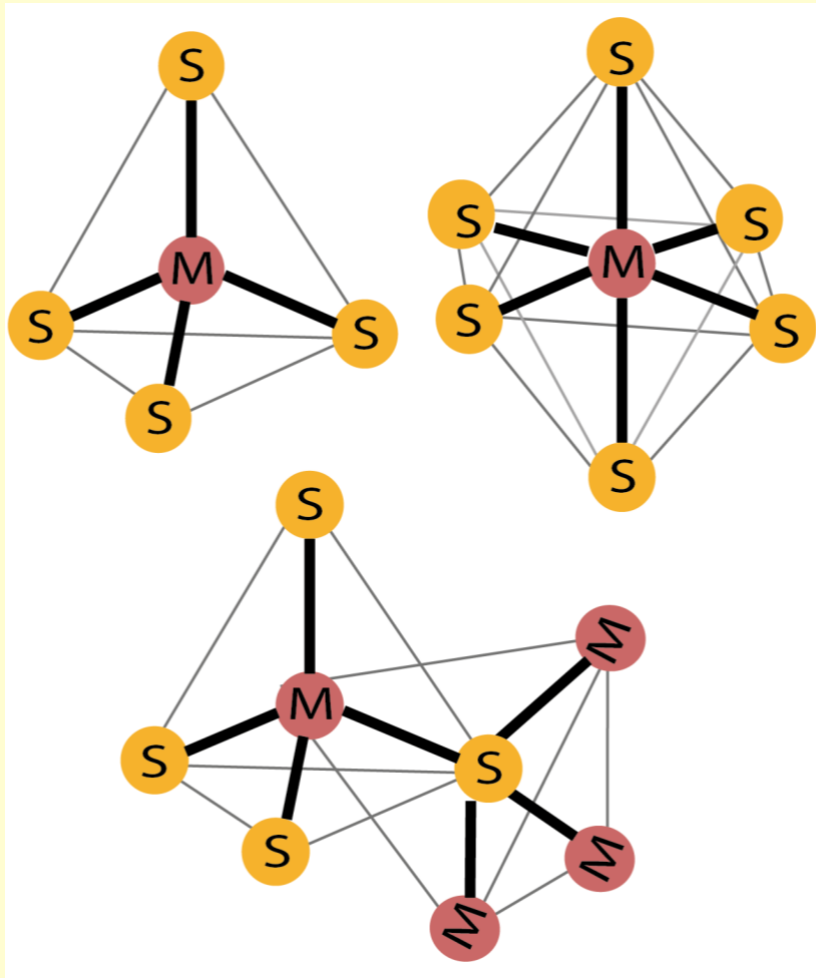
The sulphide minerals are a broad and varied mineralogical group, showing much more complexity than silicate minerals. This is in part due to the ability of sulphur to occur in several valence states e.g. S^0 , S^{-1} , S^{-2} . Although most of the bonding in sulphides is ionic between sulphur and metal atoms, covalent bonding such as the S-S bond in pyrite (FeS_2) and metallic bonding e.g. between edge or side sharing tetrahedra in pentlandites is not infrequent and influences the nature of the sulphide minerals.

This complexity in sulphide minerals makes them difficult to group for the purposes of description. Some classifications group them according to metal:sulphide ratio e.g. monosulphides, disulphides which involves various derivatives and subgroups of mineral structures. Sulphides can also be grouped by composition e.g. Cu, Fe, Ni sulphides, however each compositional group is connected to

Monosulphide = S
Disulphide = S_2

each other by substitutions such as copper and iron forming the Cu-Fe sulphides. Here a dual approach is adopted, firstly the most important monosulphides, disulphides and their derivatives are described and subsequently Ni-Fe sulphides and Cu-Fe sulphides, drawing on the connections between the groupings.

Box 1.1 Important building blocks in ore mineralogy



Tetrahedral and octahedral co-ordination are the most common arrangement of atoms in ore minerals. Above we see a tetrahedrally co-ordinated metal atom surrounded by four sulphur atoms (top left), an octahedrally co-ordinated metal atom surrounded by six sulphur atoms (top right) and coexisting tetrahedral co-ordination of both metal and sulphur atoms (bottom). The latter tetrahedral co-ordination of cations and anions leads to a 1:1 ratio of cations and anions (M:S) when all sites are full. Whereas combinations of octahedral and tetrahedral co-ordination lead to more complex structures and M:S ratios.

1.1 Monosulphides

Monosulphides, as the name suggests, have one (mono) metal cation to each sulphur anion, producing a metal:sulphur ratio of 1:1 or 1. There are simple to complex structures of monosulphides and we will cover but a few, beginning with the simple structures, adding complexity as we go through the range of monosulphides of the most important sulphide minerals.

The simple monosulphides form two groups, based on mineral structure, following either the sphalerite or würozite structure. The sphalerite structure develops around the simple cubic rocksalt (NaCl) structural arrangement (Box 1.2). The sphalerite group has cubic closed packing (ccp) of sulphur ions with cations in tetrahedral coordination (Figure 1.1, Box 1.1 & 1.2). Substitution of Fe, Cd, Mn replace Zn in upto 50% of the tetrahedral sites, which leads to the formation of polytypes.

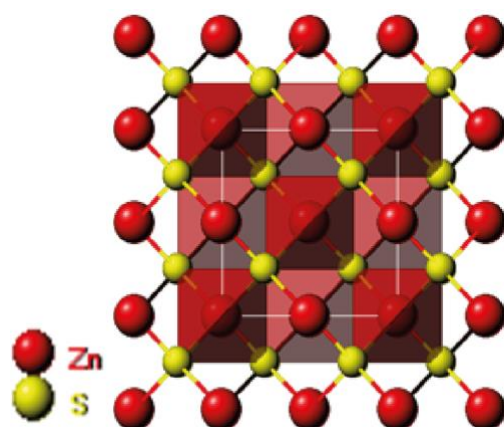


Figure 1.01 The sphalerite mineral structure. The tetrahedral coordination of Zn and S lead to a 1:1 metal:sulphur ratio. Source: Webmineral

Sphalerite is the most common sulphide with a sphalerite structure, other cadmium or mercury bearing members exist such as Hawleyite (CdS) and Metacinnobarite (HgS), a cubic high temperature variety of cinnobarite. Derivatives of the sphalerite structure include chalcopyrite (CuFeS₂) and isocubanite (CuFe₂S), the latter forming at high temperatures and only occasionally in nature. Chalcopyrite is a tetragonal superstructure of the sphalerite structure. The basic unit being two sphalerite cubes juxtaposed, one with Cu cations the other with Fe cations in the tetrahedra.

Polytype

A compound that differs in composition from the pure mineral structure



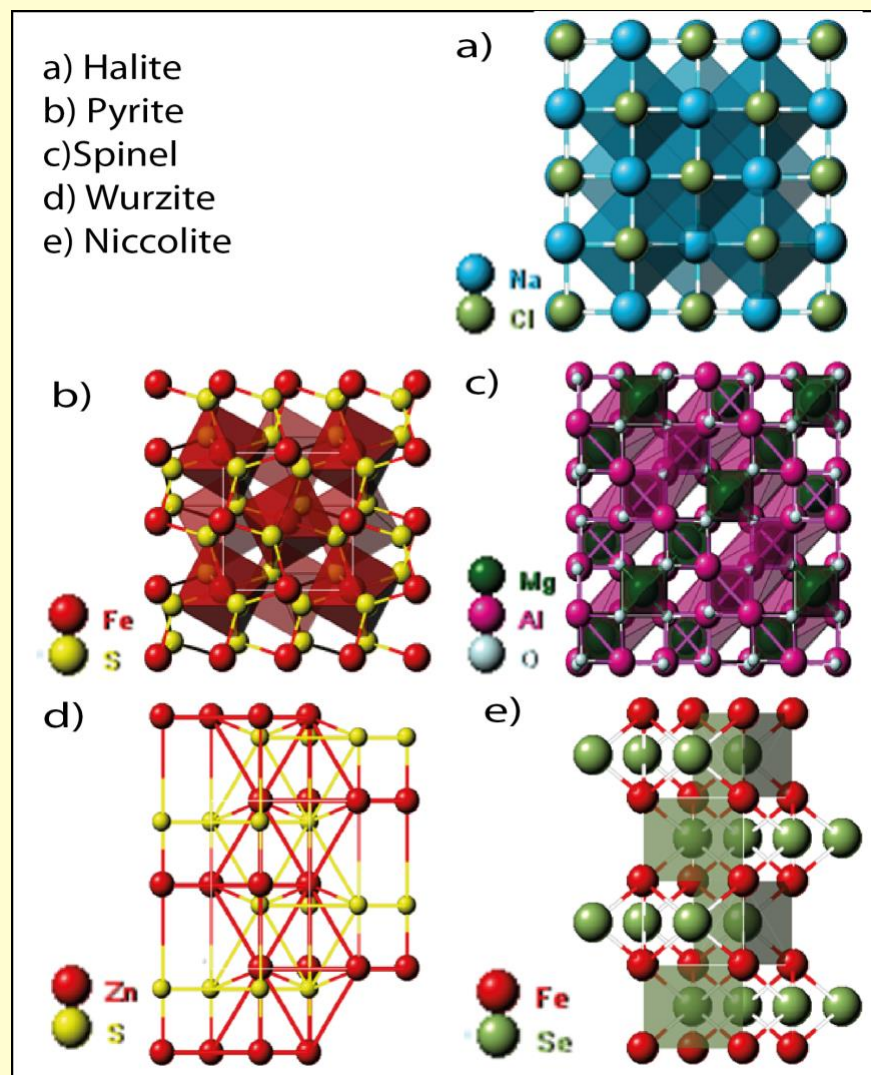
Superstructure

A related mineral structure, where differences in cations, or cation, vacancy ordering modify the mineral

Sphalerite is the primary ore mineral of zinc, i.e. the mineral in which zinc is most commonly found and can be economically extracted from. Cadmium and mercury substitute into sphalerite to form solid solutions with sphalerite and are considered pollutants during the smelting process.

Solid solution (SS)
Cation substitution allows mixing between different elements in a mineral site

Box 1.1 Basic mineralogical structures occurring in ore mineralogy



The ore minerals form around five basic mineral structures. The simpler ones have structures like (a) rock salt (NaCl, halite) with a close-cubic packing (ccp) arrangement and tetrahedral co-ordination of the cations. Complexity adds with covalent bonds between sulphur in the pyrite structure (b). The spinel structure exhibits layers of alternately tetrahedrally and octahedrally arranged atoms (c). Hexagonal symmetry is found in the wüurzite and niccolite structures (d, e), with the latter hosting cations in octahedral co-ordination (See Box 1.1). Source: Webmineral

Galena has a related structure to sphalerite, also forming a cubic rocksalt (NaCl) type structure, but some important differences including substitutions by Group V elements such as Ag, As as well as Se, Te for the sulphur anions set the galena group apart. The galena group consists of sulphosalts that are derivatives of the sphalerite or rocksalt mineral structures. The Pb cations occur in octahedral co-ordination (Box 1.1; Fig 1.2). Substitution of sulphur by Group V elements to form the sulphosalts lead to distortion of the mineral lattice from the idealised cubic rocksalt structure. Galena is the most common mineral in the galena group and the primary ore mineral of Pb. Related sulphosalts include clausthalite (PbSe), altainite (PbTe), alabandite (MnS), marrite (PbAgAsS₃) and miargyrite (AgSbS₂).

Galena, PbS
VMS, MVT

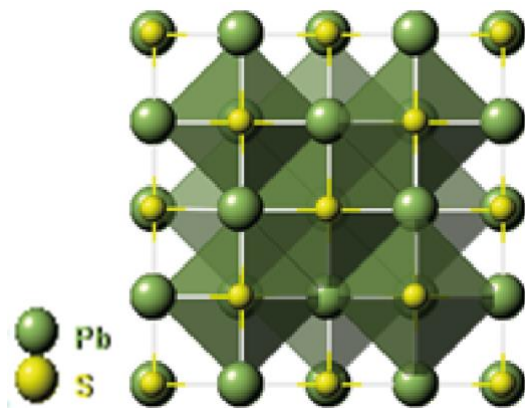


Figure 1.02 The galena mineral structure. Source: Webmineral

The **würtzite** structure, in contrast to the sphalerite structure has hexagonal symmetry, with metal cations in tetrahedral co-ordination and only 50% of the tetrahedral sites are occupied (Box 1.2; Fig 1.03).

Würtzite, ZnS
Sedimentary deposits,
low temperature
deposits

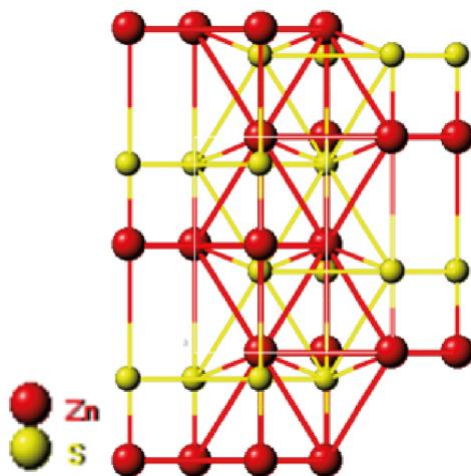


Figure 1.03 The würtzite mineral structure. Source: Webmineral

The würtzite and sphalerite structures can be regarded as polytypes, with differences in stacking associated with the cubic and hexagonal symmetries. The basic member of the würtzite structure is würtzite (ZnS), and derivatives lead to the formation of **cubanite** (CuFe₂S₃). Würtzite is associated with low temperature, sedimentary deposits where it can be found intergrown with sphalerite. Cubanite is an important source of copper in Ni-Cu ultramafic deposits.

Cubanite, CuFe₂S₃
Ni-Cu ultramafic deposits

The **covellite** (CuS) mineral formula gives the impression of a simple monosulphide structure but is in fact quite complicated. Two types of layers are formed: 1) Tetrahedrally co-ordinated copper, where the tetrahedra share corners to form a layer and 2) Cu in trigonal interstices forming a layer between tetrahedral layers (Fig 1.4). Thus covellite has a sheet-like structure of CuS₃ triangles and double layers of CuS₄ tetrahedra.

Interstitial sites
Spaces in the mineral structure

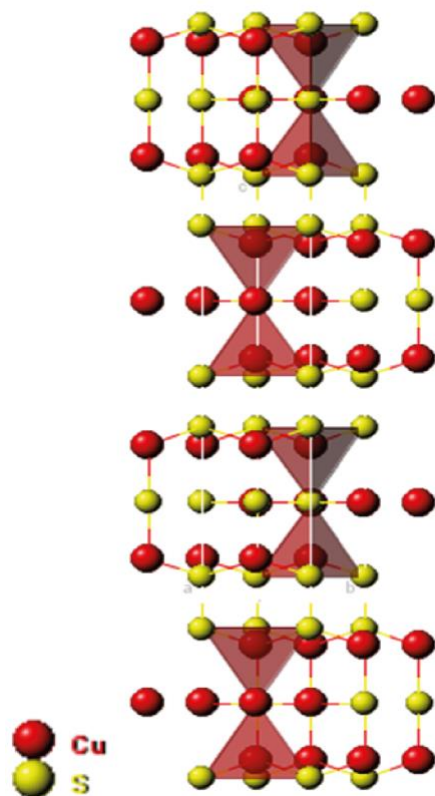


Figure 1.04 The covellite mineral structure. Source: Webmineral 1



1.1 Disulphides

In turn, the disulphides have two sulphur anions to each metal cation, giving a sulphur:metal ratio of 2:1. **Pyrite** (FeS₂) and derivatives define the disulphides. They have cubic symmetry based on the rocksalt (NaCl) structure. The cations, iron in pyrite, are octahedrally

arranged around each S₂ pair, leading to covalent S-S bonding. Sulphur in turn is co-ordinated by three cations (Fe) and one anion (S) forming a distorted tetrahedron (Fig 1.5). At low temperatures FeS₂ occurs in an orthorhombic polymorph, forming the mineral **marcasite** (Fig 1.5).

The **arsenopyrite** group result from a further derivative of the pyrite mineral structure, or more accurately marcasite. Sulphur in the arsenopyrite group is substitutes for a Group V element such as As. The As:S ratio can range between 0.82 and 1.22. The structure becomes monoclinic (Fig 1.5).

Pyrite, FeS₂
All deposit types

Marcasite, FeS₂
Low temperature deposits, oxidation product

Arsenopyrite, FeAsS
Mesothermal, hydrothermal deposits

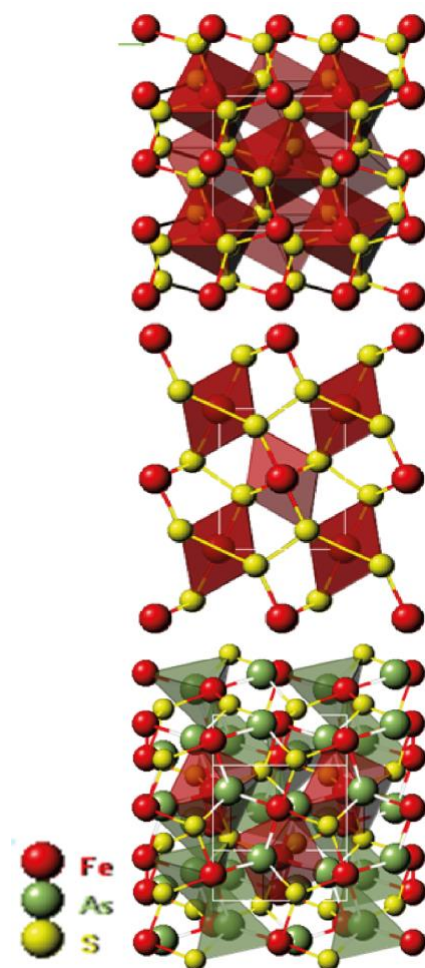


Figure 1.05 Mineral structures for pyrite (top), marcasite (centre) and arsenopyrite (bottom). Notice the covalent S-S bond in pyrite causing a distorted tetrahedron. Marcasite is a low temperature polymorph of pyrite. Arsenopyrite is a derivative of marcasite with As substituting for sulphur. Source: Webmineral



1.2 Nickel-iron sulphides

The Ni-Fe Sulphides are represented by the ternary Ni-Fe-S system, where pure iron sulphides plot along one axis (left) and pure nickel sulphides along another (right) (Fig 1.6). This allows the relationships, sulphur:metal ratios and solid solutions to be depicted.

Nickel-iron sulphides form around three basic structures; pyrite, spinel and niccolite structures. Additional derivatives lead to distortion and more complex nickel-iron sulphides. Nickel-sulphide minerals such as **Vaesite** (NiS_2) feature the pyrite structure and essentially form a solid solution with pyrite by iron-nickel substitution (Fig 1.6). The spinel structure involves layers of tetrahedrally and octahedrally co-ordinated metal cations (Box 1.2; section 2.1), typically with different cations or different valencies in the different sites, giving a formula of XY_2O_4 such as in the nickel sulphide **polydymite** (Ni_3S_4).

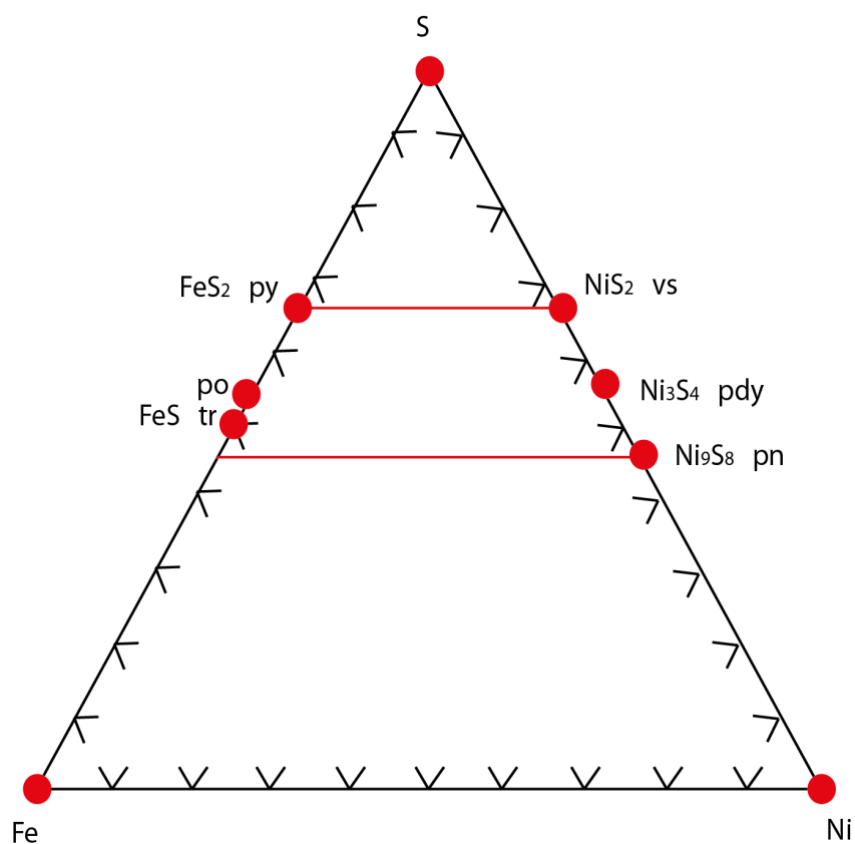


Figure 1.06 The Ni-Fe-S ternary system.

The niccolite structure is defined by the NiAs structure as having hexagonal symmetry, with the anions such as S or As (Group V element) in a hexagonal close packing structure and the metals in octahedral co-ordination (Box 1.2). **Troilite** (FeS) occurring in meteorites, is the ideal iron monosulphide end-member. **Pyrrhotite** (Fe_{1-x}S) forms a more complicated derivative of the niccolite structure, by distortion of the iron perpendicular to the c-axis and sulphur parallel to the c-axis (Fig 1.7). Moreover, the non-stoichiometry of Fe_{1-x}S leads to vacancies, which are ordered in alternating layers of the octahedral sites.

Troilite, FeS
Meteorites

Pyrrhotite, Fe_{1-x}S
High temperature igneous deposits



Non-stoichiometry
Deviates from ideal by cation or anion deficiency



Pentlandite $(\text{Fe, Ni})_9\text{S}_8$
Ni-Cu ultramafic

Vaesite, NiS_2
Ni-Cu ultramafic

Polydymite, Ni_3S_4
Ni-Cu ultramafic

py – pyrite
po – pyrrhotite
tr – troilite
vs – vaesite
pdy – polydymite
pn – pentlandite

Further non-stoichiometry and Ni-Fe substitution forms the **pentlandites** (Fig 1.7). The increasing departure from stoichiometry produces increasing distortion of the mineral structure and increased vacancies. The pentlandites have a formula of M_9S_8 , where the metal cations M can be Ni, Fe or Co. The sulphur ions are arranged in tetrahedral co-ordination with trigonal distortion leading to pseudo cubic symmetry. The cations are arranged in octahedral sites (1/8) and tetrahedral interstices (1/2). The pentlandites are effectively sulphur deficient forming a non-stoichiometric solid solution with pyrrhotite.

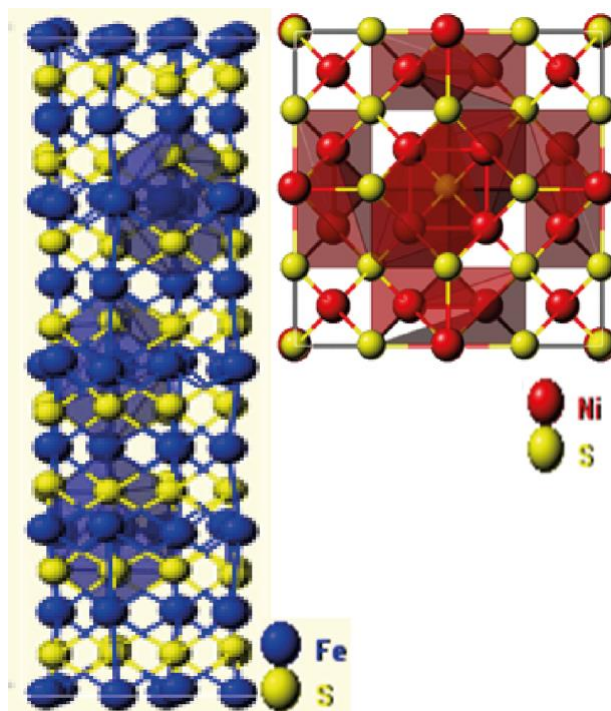


Figure 1.07 Pyrrhotite (left) and pentlandite (right) mineral structures. Source: Webmineral

1.3 Copper-iron sulphides

The Cu-Fe Sulphides are represented by the ternary Cu-Fe-S system, where pure iron sulphides plot along one axis (right) and pure copper sulphides along another (left) (Fig 1.8). Thereby relating the iron sulphides e.g. pyrite, pyrrhotite, that we have already discussed to the Cu sulphides. Furthermore the Fe-S axis can be thought of as the end-members of the Ni-Fe sulphide system.

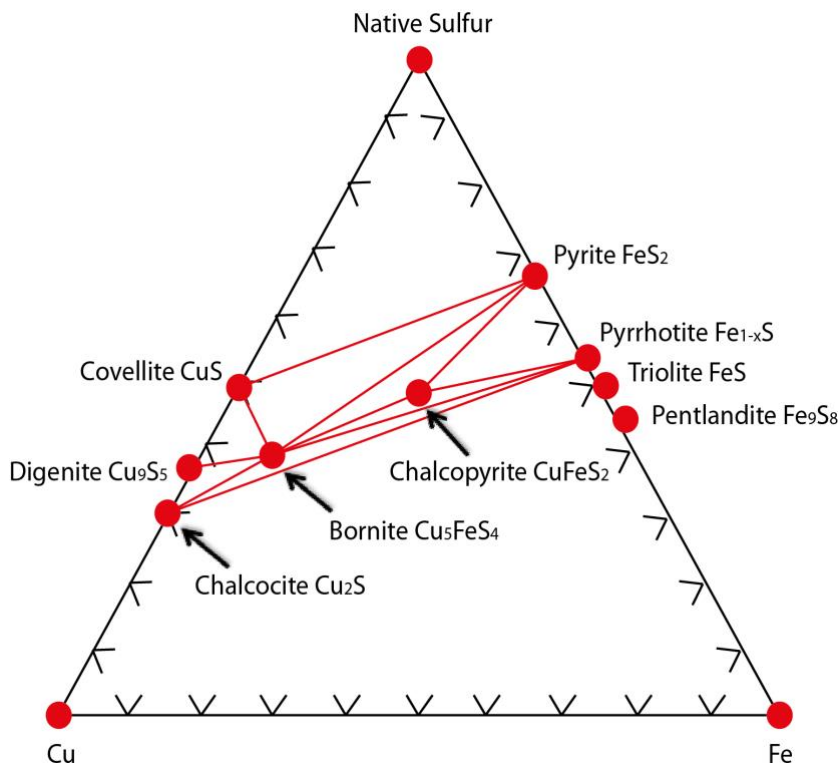


Figure 1.08 The Cu-Fe-S ternary system.

The copper sulphides typically have Cu in tetrahedral or triangular co-ordination. The monosulphide **Covellite** (CuS), as described before, has tetrahedral and trigonal layers (Fig 1.4). **Chalcocite** (Cu₂S) has a very complex monoclinic structure, based on a pseudo-hexagonal arrangement of sulphur anions (Fig 1.9). Trigonal sheets are formed by 1/3 of the Cu residing in triangular spaces and the other 2/3 of the Cu is found in triangular interstitial sites between sulphur anions. At low temperatures (<104°C), chalcocite becomes hexagonal, with the Cu transferring between triangular, tetrahedral and two co-ordinated sites. Above 350°C there is a phase transition to **digenite** (Cu₉S₅), which is cubic (Fig 1.9).

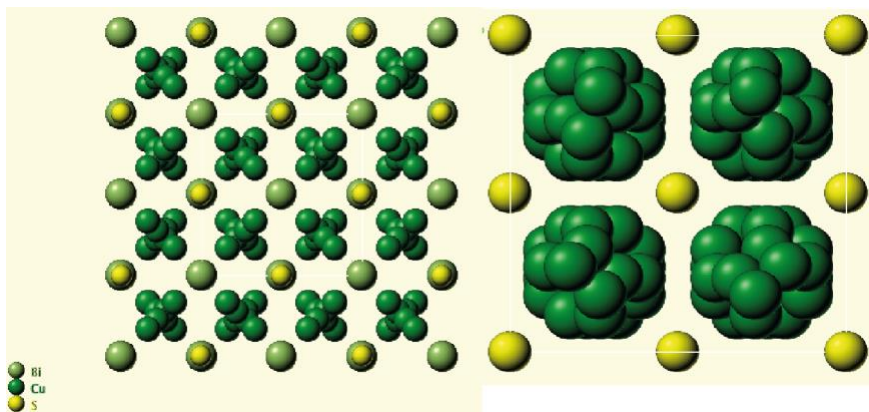


Figure 1.09 The chalcocite (left) and digenite (right) mineral structures. Source: Webmineral

Bornite, Cu₅FeS₄
Hydrogene
sedimentary ores

Chalcopyrite, CuFeS₂
Porphyry, VMS

Covellite, CuS
Low T deposits

Chalcocite, Cu₂S
Low temperature
supergene ores

Digenite, Cu₉S₅
(High temperature)
supergene ores

The copper-iron sulphide **bornite** (Cu_5FeS_4) has a high temperature form with cubic symmetry from sulphur arranged in a face-centred cube (fcc), with Cu and Fe in tetrahedral co-ordination. At low temperatures disordering leads to defects (Fig 1.10). **Chalcopyrite** (CuFeS_2) is the most common copper-iron sulphide occurring as the primary copper ore mineral in porphyry copper deposits. Chalcopyrite is a derivative of the sphalerite structure (Box 1.2; section 1.1; Fig 1.10).

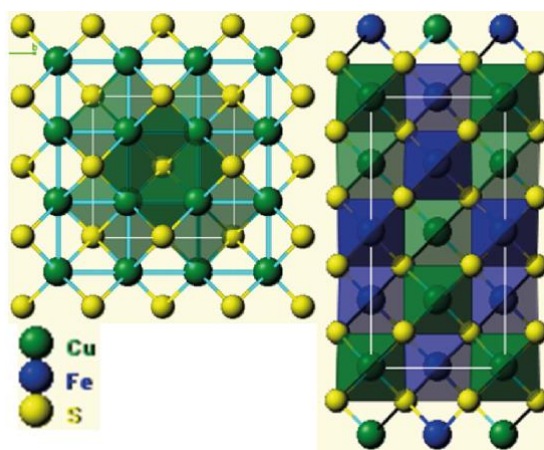


Figure 1.10 The bornite (left) and chalcopyrite (right) mineral structures. Source: Webmineral

1.3 Low temperature sulphides

In low temperature sedimentary environments sulphides are also formed and deposited. The low temperature system involves acidic fluids and a range from oxidising to reducing (brines, bogs) conditions.

Pyrite (FeS_2) occurs under a wide variety of conditions, as does the low temperature derivative **marcasite** (FeS_2). In a fluid saturated reducing system **mackinawite** (FeS) and **greigite** (Fe_2S_4) can also be (meta)stable (Fig 1.11). In mackinawite sulphur is tetrahedrally coordinated by Fe, which allows Fe-Fe bonds across tetrahedral edges (Fig 1.11). Mackinawite is poorly crystalline to amorphous occurring in sediments and sedimentary deposits. Greigite has a spinel structure and is a ferromagnetic sulphide found in sediments and associated deposits (Fig 1.11).

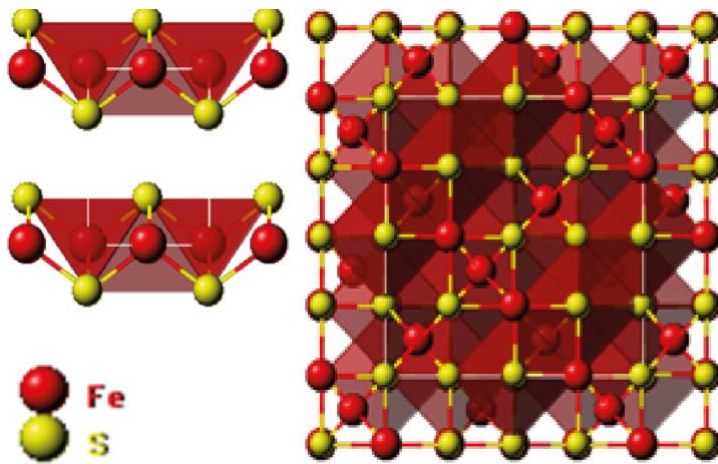


Figure 1.11 Mineral structures of mackinawite (left) and greigite (right). Source: Webmineral

The previously describes copper sulphides covellite, chalcocite, digenite and bornite as well as würtzite also occur in low temperature settings such as sediments, zones of supergene enrichment, reducing fluids such as brines and low temperature hydrothermal mineralization and veins, which often (re)concentrate resources via zone refining.

Study Questions

- 1) Give examples of monosulphides and disulphides.
- 2) Describe the structure of galena.
- 3) Describe the following mineral structures:
 - a. Sphalerite
 - b. Pyrite
 - c. Pyrrhotite
- 4) Explain the connection between non-stoichiometry, vacancies and distortion.

Sources and Further reading

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Webmineral: Credit is due to www.webmineral.com for illustrations of mineral structures.