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Article for Elements Magazine on 'Sulphides' (Kiseeva and Edmonds, editors)

Mineralogy of Sulphides

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Metal sulphides are the most important group of ore minerals. As shown in this brief introduction, much is known about their compositions, crystal structures, phase relations and paragenesis. Much less is known about their surface chemistry and, in particular, about their biogeochemistry, and about the formation and behaviour of 'nanoparticle' sulphides, whether formed abiotically or biogenically. These are large and complex topics which can only be touched upon in this article which also serves to direct readers to more comprehensive accounts.

KEYWORDS: metal sulphides, crystal structures, paragenesis, surface chemistry, biogeochemistry

INTRODUCTION

Sulphide minerals are compounds in which sulphur is combined as an anion with a metal (or semi-metal) cation or cations. The definition is commonly widened to include minerals in which the anion is As or Sb, sometimes together with S, and to include Se and Te minerals. The sulphosalts are a special subset of the sulphide minerals that have a general formula $A_mT_nX_p$ and in which the common elements are $A = \text{Ag, Cu, Pb}$; $T = \text{As, Sb, Bi}$; $X = \text{S}$. They generally contain pyramidal TS_3 groups in their structures. Although several hundred sulphide minerals are known, only five are sufficiently abundant as accessory minerals in rocks to have been categorized as 'rock forming' (see Bowles et al. 2011). They are pyrite, pyrrhotite, galena, sphalerite and chalcopyrite. Of these, it is the iron sulphides (pyrite and pyrrhotite) which are dominant. The very fine particle iron sulphides found in reducing environments beneath the surfaces of some sediments and soils are also volumetrically important. Formally known as 'amorphous iron sulphides', they are now known to be comprised of fine particle mackinawite (tetragonal FeS) and, to a lesser extent, the thiospinel mineral greigite (Fe_3S_4), and to be metastable compared to pyrite and pyrrhotite.

Above all, however, the sulphides are the most important group of ore minerals, responsible for the concentration of a wide range of metals as mineable ore deposits. They are also potential sources of pollution, of the air and of surface waters and soils. Pollution of the air may arise not only from the smelting of sulphide ores, but also from the burning of coal which contains sulphur mainly as sulphide impurities. The breakdown of sulphides exposed by weathering at the Earth's surface generates sulphuric acid as well as releasing potentially toxic metals into waters and soils. This very common form of pollution may arise from minewastes (and termed acid mine drainage) or sulphide-containing natural rocks (acid rock drainage).

The literature on sulphide minerals is extensive, and a number of overview textbooks and monographs have been published; earlier work is reviewed in Ribbe (1974), Vaughan and Craig (1978) and Kostov and Mincheeva-Stephanova (1981). The most recent comprehensive review is that of Vaughan (2006). The present article provides a brief overview of the compositions and crystal structures of the major sulphide minerals, aspects of their chemistries (bulk and surface) and their occurrence. In addition to the sulphides mentioned above, pentlandite ($(\text{Fe,Ni})_9\text{S}_8$) and its alteration product violarite (FeNi_2S_4) are important as the major ore minerals of nickel, bornite (Cu_5FeS_4) as a major copper mineral, and molybdenite (MoS_2) as the source of world supplies of molybdenum. Tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) is notable because of the large range of metals, silver in particular, which can substitute at percent levels for copper or antimony in its structure. In contrast, arsenopyrite (FeAsS) is the major natural source of arsenic, an extremely toxic pollutant.

CRYSTAL STRUCTURES AND THE CLASSIFICATION OF SULPHIDES

The structures of nearly all mineral sulphides are described by Makovicky (2006), who also provides a detailed account of structural classification schemes. This extensive review provides much more detail than we require here, where we categorize the most important sulphides into a series of groups based on major structure types or having key structural features in common, as shown in Table 1 (modified after Vaughan and Craig, 1978). Commonly, these are the structures exhibited by a much larger group of crystalline solids, such as the rocksalt structure of the galena group (Fig. 1a), the sphalerite and wurtzite forms of ZnS (Fig. 1b,c), or the nickel arsenide structure (Fig. 1d).

The disulphides contain dianion units (S-S, S-As, As-As etc); here, in the pyrite structure, FeS_6 octahedra share corners along the c-axis direction, whereas in the marcasite form of FeS_2 , the

octahedra share edges to form chains of octahedra along the c-axis. Loellingite (FeAs_2) and arsenopyrite (FeAsS) have variants of the marcasite structure with, respectively, shorter or alternately long and short metal-metal distances across the shared octahedral edge.

Sulphides such as covellite (CuS ; Fig. 1f) and molybdenite (MoS_2) have layer structures, and a number have structures best described as having rings or chains of linked atoms (such as realgar, As_4S_6). A diverse group, have been defined as the metal-excess group by Vaughan and Craig (1978); they have metal:sulphur ratios greater than 1:1 and structures of the type well illustrated by pentlandite ($(\text{Ni,Fe})_9\text{S}_8$), the major ore mineral of nickel (see Fig. 1g).

In many of these groups, as well as several minerals exhibiting the actual structure type (see Table 1), there are other minerals that have structures based upon these ‘parent’ structures and that can be thought of as being ‘derived’ from them. The relationship between derivatives and parents can involve:

- (1) **distortion** as in the troilite form of FeS which is simply a distortion of the parent NiAs structure (Fig. 2a);
- (2) **ordered omission** as in monoclinic pyrrhotite (Fe_7S_8) which is derived from the NiAs structured FeS by removal of Fe atoms leaving holes (vacancies) that are ordered (see Fig. 2a);
- (3) **ordered substitution** as in the structure of chalcopyrite (CuFeS_2) which is derived from that of sphalerite (ZnS) by the alternate replacement of Zn atoms by Cu and Fe resulting in an enlarged (tetragonal) unit cell (see Fig 2b). Stannite ($\text{Cu}_2\text{FeSnS}_4$) results from further ordered substitution of half of the Fe atoms in chalcopyrite by Sn (Fig. 2b);
- (4) a **stuffed derivative** (Fig. 2c) as in talnakhite ($\text{Cu}_9\text{Fe}_8\text{S}_{16}$), mooihoekite ($\text{Cu}_9\text{Fe}_9\text{S}_{16}$) and haycockite ($\text{Cu}_4\text{Fe}_5\text{S}_8$) which are derived from chalcopyrite by the occupation of additional, normally empty, cavities in the structure.

The structural relationships involved may be more complex in other cases. For example, some sulphosalts are comprised of slabs or other units of the parent structure.

CHEMISTRY OF SULPHIDES

Bulk Chemistry

The chemical compositions of the sulphide minerals have been well characterized as a result of numerous analyses of natural samples and laboratory investigations of phase equilibria (see Table 1

for names and formulae of all common, and many less common, sulphides). Although most sulphide minerals can ideally be regarded as simple binary or ternary compounds, natural sulphides always contain impurities ranging from trace (ppm) to minor (<5 wt %) amounts. Such impurities may include toxic elements such as arsenic, cadmium and mercury. The more extensive substitutions associated with solid solution are also found in the sulphides; for example, the complete solid solution between pyrite (FeS_2) and vaesite (NiS_2) to give the intermediate composition mineral bravoite ($(\text{Fe,Ni})\text{S}_2$) which can also have a cattierite (CoS_2) component.

Certain metal sulphides also exhibit nonstoichiometry and, in some cases, the deviation of the formula from a simple ratio is considerable. For example, pyrrhotite is commonly given the general formula Fe_{1-x}S where $0 < x < 0.125$; here, the varying compositions correspond to varying concentrations of vacancies in sites that would otherwise be occupied by iron atoms. However, in systems such as these, ordering of the vacancies occurs at low temperatures, and the result may be a series of stoichiometric phases of slightly different compositions. Although Fe_7S_8 has a (monoclinic) superstructure resulting from vacancy ordering (see Fig. 2a), the situation in the so-called ‘intermediate’ or ‘hexagonal’ pyrrhotites is more complex. Some of these pyrrhotites may represent ordered phases with clearly defined compositions (Fe_9S_{10} , $\text{Fe}_{11}\text{S}_{12}$ etc.), but more complex and partial ordering in these systems may occur. One problem is that free-energy differences between a series of phases resulting from vacancy ordering are very small, making a successful investigation of the relationships between synthetic products very difficult. Further examples of nonstoichiometry in sulphides may involve only small deviations from the simple ratio. For example, galena (PbS) exhibits a range of nonstoichiometry of 0.1 atomic%. Apparently, galena is stable over a wide range of values of a_{S_2} (activity of sulphur), and at high a_{S_2} it has lead vacancies, whereas at low a_{S_2} there are sulphur vacancies; the presence of Pb-vacancies in galena has been reported to confer enhanced oxygen adsorption, which has important implications for the oxidative dissolution of this mineral (Lan et al., 2012).

Experimental studies of the phase relations in sulphide systems have done much to inform our understanding of the crystallization of sulphides from melts and high temperature fluids. Key binary systems that have been studied include Fe-S, Cu-S, Ni-S and ternary systems include Fe-Cu-S, Fe-Ni-S, Fe-Zn-S, Fe-As-S. A few quaternary systems are particularly important, notably the Fe-Zn-As-S system. Details of the work done in these areas can be found in Vaughan and Craig (1978, 1997) and Fleet (2006). In Figure 3 are shown phase diagrams derived using experimental data for the Fe-Cu-S system at 700°C and 300°C (after Vaughan and Craig, 1997). Even at 700°C, melts have all

crystallized, but notable are the extensive solid solution fields; the intermediate solid solution (iss) which includes chalcopyrite and other phases close to CuFeS_2 in composition and another field at, and around, bornite (bn). Further cooling to 300°C sees the shrinking of these fields, with the associated separation by solid state diffusion that produces the exsolution textures observed using reflected light microscopy (see Fig. 3). In the example illustrated in Figure 3, exsolved chalcopyrite (yellow) occurs as laths in host bornite (brown); the orientation of the laths is crystallographically controlled by the bornite host. The blue-grey phase is chalcocite formed by later alteration of the bornite.

In another example, experimental work on the Fe-As-S system has shown that the As content of arsenopyrite, when formed in equilibrium with pyrite and pyrrhotite, varies as a function of temperature and, hence, can be used as a geothermometer. On the other hand, work on the Fe-Zn-S system has demonstrated that increasing pressure reduces the iron content of sphalerite and this can be used, under favourable circumstances, as a geobarometer.

Surface Chemistry

Sulfide surface chemistry is particularly important because of its relevance to the oxidation and breakdown of sulfide minerals, and to industrial processing of as-mined ores using froth flotation or leaching. Investigations have ranged from spectroscopic and imaging studies of very clean surfaces in ultra-high vacuum (UHV) conditions providing information on structure and reactivity at atomic resolution, to micron resolution studies of reacted surfaces and reaction products. Comprehensive reviews are provided by Rosso and Vaughan (2006a,b).

The most studied sulfide as regards surface chemistry is pyrite; here, the major surface planes are (100), (111), (110) and (210), with the (100) surface being considered the most stable. At the (100) surface, a complex microtopography has been observed in UHV, defined by flat, stepped terraces, commonly with a high step density (Figure 4a, b) (Rosso et al. 1999). Spectroscopic studies of this surface in vacuum indicate that, upon cleavage, disulphide bonds break to form monosulphide species (Nesbitt et al. 1998; Schaufuss et al. 1998). However, sulphur-deficient defects have also been observed (Guevremont et al. 1998). The diverse properties of sulphide surfaces are exemplified by the electronic structure of pyrite, a 0.9 eV band gap intrinsic semiconductor; by contrast, the (100) surface can be considered as nearly metallic, with a band gap of < 0.04 eV (Rosso et al. 1999). The redox chemistry of pyrite in aqueous solution involves further complexities. Rimstidt and Vaughan (2003) note that oxidation of a disulfide such as pyrite to release sulfate requires transfer of seven electrons and, hence, up to seven elementary reaction steps. Furthermore, pyrite, like most sulfides,

is a semiconductor so the reactions are electrochemical in nature. It has been suggested that this electrochemical reaction involves three distinct steps: (1) cathodic reaction, (2) electron transport, and (3) anodic reaction, and that the cathodic reaction is the rate-determining step. It seems that the rate of pyrite oxidation depends on the concentration of O_2 or another oxidant such as Fe^{3+} .

Other sulphides, such as monoclinic pyrrhotite (Fe_7S_8), also have complex surfaces. Superstructures within the pyrrhotite family arise from vacancy ordering in layers parallel to the basal plane (Fig. 2a). In the most Fe-deficient end-member, Fe vacancies occur in every other Fe atom layer, and in alternate rows within that layer. Furthermore, in every S atom layer, one in four S atoms relaxes into an Fe vacancy. The (001) surface of monoclinic pyrrhotite was observed in UHV by STM to comprise flat terraces separated by steps $\sim 2.9\text{\AA}$ in height (Fig 4c), which is one quarter of the unit cell in the c direction, or the separation between two consecutive Fe or S layers (Becker et al. 1997). Although the features appear to have an atomic arrangement suggestive of Fe vacancies, it was ascertained that they were S atoms with an ordering induced by the Fe vacancies. Such complex surfaces give rise to different oxidation mechanisms. For example, due to the deficiency in Fe atoms at the pyrrhotite surface, oxidation proceeds via the formation of a sulphur rich layer, composed of disulphide, polysulphide and elemental sulphur (Chirita and Rimstidt, 2014), while for the Fe-rich surface layers of pyrite, ferric oxyhydroxide forms during the initial oxidation.

Given the environmental relevance, understanding the reactions at the surface of arsenopyrite during aqueous oxidation has received much attention in the literature; as reviewed by Corkhill and Vaughan (2009). Like the pyrite oxidation processes described above, these are complex, multi-stage electrochemical reactions. It has been proposed that the initial oxidation of arsenopyrite surfaces occurs rapidly, with As being oxidized more quickly than Fe. Spectroscopic studies (Schaufuss et al. 2000; Corkhill et al. 2008) have shown that oxidation of As proceeds via a series of one-electron transfer steps, from As^{-1} to As^{5+} , while S oxidation can be considered as a 7-step reaction, transforming disulphide (S^{2-}) to sulphate sulphur (S^{6+}) with a number of intermediate products. These oxidation products, which also include ferric-(oxy)hydroxides, form an oxidized surface layer controlled by diffusion of species from the bulk (Schaufuss et al. 2000; Costa et al. 2002). Oxidative leaching of arsenopyrite in the presence of common acid mine drainage bacteria such as *Leptospirillum ferrooxidans*, greatly enhances the release of As from the surface compared with abiotic dissolution; a combination of direct leaching, as evidenced from cell-shaped etch pits (Fig. 4d), and indirect dissolution, through cycling of Fe^{2+} within a thick layer of extra-cellular polymeric substances were the determined mechanisms (Fig. 4e).

The uptake of metal ions by sulphide surfaces has received significant interest, due to the importance of this process in the transport and mobility of metals in the subsurface, ore formation, and the mobility of contaminants and other pollutants. Once again, in this aspect of sulphide surface chemistry, pyrite is the most studied phase, with other significant contributions on the readily studied galena cleavage surface and, environmentally important, mackinawite (Rosso and Vaughan, 2006b). Investigation of the sorption of heavy metals (e.g. As, Mo, Hg) and radionuclides (U, Tc) by pyrite surfaces has identified a number of complex reactions that lead to sorption. For example, in the sorption of Cd^{2+} , surface reconstruction and disproportionation occurs, leaving a mixture of sulphide and oxide products (Bostick et al., 2000). The problematic radionuclide, ^{99}Tc , was found sorb to framboidal pyrite present in a clay formation used as host rock for geological disposal of nuclear waste, through an oxidation-reduction mechanism, forming Tc(IV)-sulphur type phases (Bruggeman et al. 2007).

PARAGENESIS OF SULPHIDES

Sulphides in Ore Deposits

In Table 2 are shown the main types of ore deposits that contain significant amounts of sulphide minerals, along with their major ore minerals, the metals extracted from them, and some specific ore deposits as examples (after Cox and Singer, 1987, Craig and Vaughan, 1990; see also Craig and Vaughan, 1994). Pyrite is abundant in nearly all of these deposits. Notable exceptions are those ores found in association with intrusive ultramafic and mafic rocks, particularly the so-called ‘sulphide nickel deposits’ where the dominant sulphide mineral is pyrrhotite and is associated with pentlandite and chalcopyrite. These minerals are regarded as having formed via crystallization from an immiscible sulphide melt that separated from the main silicate melt following injection. In the best known of all layered intrusions, the Bushveld Complex, the dominant sulphides are pyrrhotite, pentlandite and chalcopyrite with particular horizons, notably the so-called ‘Merensky Reef’, also enriched in Platinum Group Minerals (PGM).

Pyrite, in addition to its occurrence as a secondary mineral in a wide range of felsic igneous rocks, is the dominant sulphide in porphyry copper deposits, where chalcopyrite is the most important ore mineral, along with bornite and various binary copper sulphides. In the closely related porphyry molybdenum deposits, it is molybdenite that dominates as the most important ore mineral. The sulphides in such deposits occur as veinlets or disseminated grains in host intrusions ranging in composition from quartz diorite to quartz monzonite. Pyrite, along with sphalerite, galena or

chalcopyrite, also occurs in large masses in the 'skarn' deposits formed by contact metamorphism, and as a major phase in many hydrothermal vein deposits, and in those deposits that can be broadly described as 'volcanogenic'. Included here are ores that occur in thick volcanic sequences, such as the Kuroko-type deposits of Japan in which the so-called 'black ore' contains irregular masses of galena intergrown with sphalerite, chalcopyrite and pyrite.

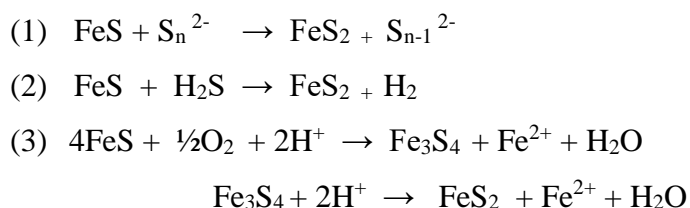
In the Japanese Besshi-type deposits, the sulphides (pyrite, chalcopyrite, sphalerite, galena) are found in predominantly sedimentary sequences. Sulphide ores in volcano-sedimentary sequences, such as those associated with ophiolite complexes (as in the Troodos Complex, Cyprus) are dominated by pyrite and chalcopyrite. Our understanding of the formation of such deposits has been revolutionized by the study of present day volcanic and hydrothermal activity on the seafloor. Disseminated to massive stratiform sulphide ores are often conformable within sedimentary sequences, and grade into volcanic deposits of the kind discussed above. Pyrite again dominates the sulphide mineralogy in deposits such as those of the Copperbelt of Zambia and Zaire which have a range of copper-iron sulphides (chalcopyrite, bornite) and copper sulphides (chalcocite, Cu_2S ; covellite, CuS) and also significant amounts of cobalt in cobaltian pyrite and in the thiospinel mineral carrollite (CuCo_2S_4).

In the ores associated with sedimentary rocks, sulphides (galena, sphalerite, pyrite) are major phases in the lead-zinc-barite-fluorite ores which occur mainly in limestones, most famously in the Mississippi Valley region of the USA. Pyrite and various copper sulphides occur in the vanadium-copper ores associated with sandstones in areas such as the Colorado Plateau (USA), and in the gold-uranium deposits associated with conglomerates in regions such as the Witwatersrand, South Africa. Pyrite and to a lesser extent other sulphides such as marcasite (FeS_2), are significant minor components in coals and occur as accessory minerals in black shales.

Biogenic Formation of Sulphides

Sulphide minerals can also form under conditions at or near Earth's surface through the activities of a group of bacteria known as dissimilatory-sulphate reducing prokaryotes (SRP). The SRP occur in many anaerobic environments including lakes, swamps and soils and, most importantly, in marine sediments. As part of their metabolic processes, these organisms reduce sulphate ions in solution to sulphide which can react with any available dissolved metal ions to form highly insoluble sulphides. Other organisms may contribute to these processes through the microbial reduction of metals, particularly iron. Iron sulphide minerals generated in this way are ubiquitous in modern anoxic (particularly marine) sediments and the pathways leading to their formation are illustrated in Figure

5. When the dissolved sulphide produced by SRP reacts with Fe^{2+} , a very fine particle black precipitate now known to be poorly crystalline mackinawite (FeS) or a mixture of mackinawite and greigite (Fe_3S_4) is formed. However, these iron minerals are metastable and with time transform to pyrite. Three possible pathways for this transformation have been suggested (see Figure 5): (1) FeS oxidation by a polysulphide; (2) FeS oxidation by H_2S , and (3) conversion via a greigite phase, with the main reactions involved being:



Attention is now also being focused on the formation and transformation of metal sulfide ‘nanoparticles’. For example, it has been shown that FeS nanoparticles produced using SRP have a primary size of 1-2nm; however, they are not stable and re-assemble and transform into highly crystalline nanorods with the structure of mackinawite within 48 hours (Hochella, pers comm). In other work, Xu et al (2016) have compared ZnS nanocrystals formed by biological and abiotic pathways. Those formed by SRP are distinctive from their abiogenic counterparts in terms of morphology, crystal size, structural defects, dissolution behavior and presence of the wurtzite form of ZnS .

In addition to the key roles played by microorganisms in both the formation of sulphides and their weathering and breakdown, some organisms have evolved so as to synthesize sulphides for use in a particular biological function. One example is a deep sea snail (gastropod) found around ocean floor hydrothermal vents where parts of this animal’s foot are covered by sulphide scales for structural support and protection against predators. The sulphides involved are pyrite and greigite. Because of its magnetic (ferromagnetic) properties, greigite is also synthesized by certain magnetotactic bacteria. Here, intracellular greigite crystals form chains which can align with the Earth’s magnetic field to enable the organism to find its optimal position in its environment. The subject of sulphides in biosystems has been reviewed by Posfai and Dunin-Borkowski (2006).

Although a great deal is now known about the compositions, crystal structures, phase relations and paragenesis of sulphide minerals, much work is still needed in areas such as the surface chemistry and surface reactivity of sulphides, their biogeochemistry and, particularly, in the study of sulphide

nanoparticles. The importance of sulphides as ore minerals and environmental materials should ensure active programs of research on sulphide mineralogy for many years to come.

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Table 1. Sulphide mineral structural groups

Disulphide group			
Pyrite structure FeS ₂ pyrite CoS ₂ catterite	Marcasite structure FeS ₂ marcasite	Arsenopyrite structure FeAsS arsenopyrite FeSbS gudmundite	Loellingite structure CoAs ₂ safflorite FeAs ₂ loellingite NiAs ₂ rammelsbergite
Galena group			
PbS galena α -MnS alabandite			
Sphalerite group			
Sphalerite structure β -ZnS sphalerite CdS hawleyite Hg(S,Se) metacinnabar	Derived by ordered substitution CuFeS ₂ chalcopyrite Cu ₂ FeSnS ₄ stannite Cu ₂ ZnSnS ₄ kesterite		Stuffed derivatives Cu ₉ Fe ₈ S ₁₆ talnakhite Cu ₉ Fe ₉ S ₁₆ mooihoekite Cu ₄ Fe ₅ S ₈ haycockite
Wurtzite group			
Wurtzite structure α -ZnS wurtzite CdS greenockite	Composite structure derivatives CuFe ₂ S ₃ cubanite AgFe ₂ S ₃ argentopyrite		Derived by ordered substitution Cu ₃ AsS ₄ enargite
Nickel arsenide group			
NiAs structure NiAs niccolite NiSb breithauptite	Distorted derivatives FeS troilite CoAs modderite		Ordered omission derivatives Fe ₇ S ₈ monoclinic pyrrhotite Fe ₉ S ₁₀ , Fe ₁₁ S ₁₂ hexagonal pyrrhotites
Thiospinel group			
Thiospinel structure Co ₃ S ₄ linnaeite FeNi ₂ S ₄ violarite CuCo ₂ S ₄ carrollite Fe ₃ S ₄ greigite			
Layer sulphides group			
Molybdenite structure MoS ₂ molybdenite WS ₂ tungstenite	Tetragonal PbO structure FeS mackinawite ~Cu ₃ FeS ₄ idaite		Covellite structure CuS covellite
Metal excess group			
Pentlandite structure (Ni,Fe) ₉ S ₈ pentlandite	Argentite structure Ag ₂ S argentite	Chalcocite structure Cu ₂ S chalcocite Ag ₂ S acanthite	Digenite structure Cu ₉ S ₅ digenite Cu ₅ FeS ₄ bornite Nickel sulfide structures NiS millerite Ni ₃ S ₂ heazlewoodite
Ring or chain structure group			
Stibnite structure Sb ₂ S ₃ stibnite	Realgar structure As ₄ S ₄ realgar	Cinnabar structure HgS cinnabar	

Table 2. The major types of sulphide ore deposits (modified after Cox and Singer, 1987; Craig and Vaughan, 1990)

Type	Major Ore Minerals*	Metals Extracted	Examples
<u>Ores related to mafic and ultramafic intrusions</u>			
Sulphide nickel deposits	po, pn, py, cpy, viol	Ni, Cu, Co, PGM	Sudbury, Ontario Canada
Merensky reef platinum	po, pn, cpy	Ni, Cu, PGM	Merensky Reef, RSA
<u>Ores related to felsic intrusive rocks</u>			
Tin and tungsten skarns	py, cass, sph, cpy, wf	Sn, W	Pine Creek, CA, USA
Zinc-lead skarns	py, sph, gn	Zn, Pb	Ban Ban, Australia
Copper skarns	py, cpy	Cu, Au	Carr Fork, Utah, USA
Porphyry copper/ molybdenum	py, cpy, bn, mbd	Cu, Mo, Au	Bingham Canyon, Utah; USA Climax, CO, USA
Polymetallic veins	py, cpy, gn, sph, ttd	Cu, Pb, Zn, Ag	Camsell River, NWT, Canada
<u>Ores related to marine mafic extrusive rocks</u>			
Cyprus-type massive sulphides	py, cpy	Cu	Cyprus
Besshi-type massive sulphides	py, cpy, sph, gn	Cu, Pb, Zn	Japan
<u>Ores related to subaerial felsic to mafic extrusive rocks</u>			
Creede-type epithermal veins	py, sph, gn, cpy, ttd asp	Cu, Pb, Zn, Ag, Au	Creede, CO, USA
Almaden-type mercury	py, cinn	Hg	Almaden, Spain
<u>Ores related to marine felsic to mafic extrusive rocks</u>			
Kuroko-type	py, cpy, gn, sph, ttd, asp	Cu, Pb, Zn, Ag, Au	Japan
<u>Ores in clastic sedimentary rocks</u>			
Quartz pebble U-gold	py, uran, gold	Au, U	Witwatersrand, RSA
Sandstone-hosted lead-zinc	py, sph, gn	Pb, Zn, Cd	Laisvall, Sweden
Sedimentary exhalative lead-zinc	py, sph, gn, cpy asp, ttd, po	Cu, Pb, Zn, Au, Ag	Sullivan, BC, Canada Tynagh, Eire
<u>Ores in carbonate rocks</u>			
Mississippi Valley type	py, gn, sph	Zn, Pb, Cd, Ga, Ge	Missouri, USA

*Abbreviations used are as follows: po-pyrrhotite, pn-pentlandite, py-pyrite, cpy-chalcopyrite, viol-violarite, cass-cassiterite, sph-sphalerite, wf-wolframite, gn-galena, bn-bornite, mbd-molybdenite, ttd-tetrahedrite, asp-arsenopyrite, cinn-cinnabar, uran-uraninite.

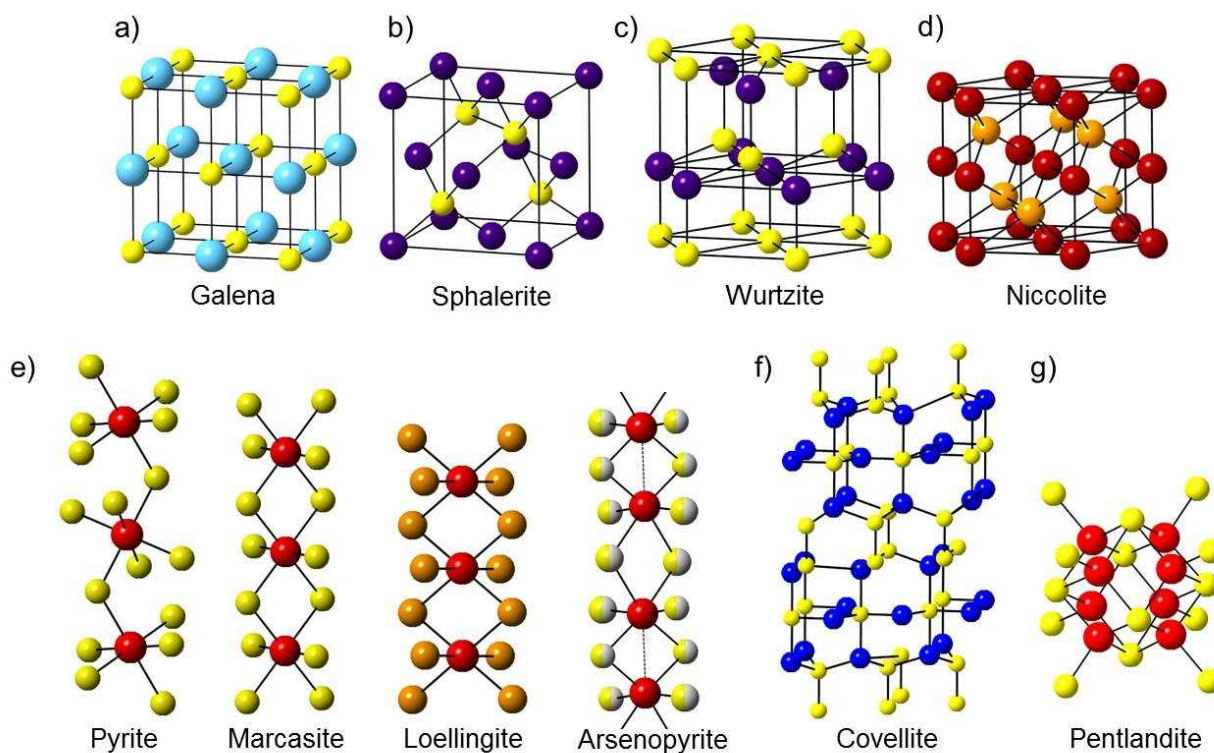


Figure 1 Crystal structures of the major sulphides: (a) galena (PbS), (b) sphalerite (ZnS), (c) wurtzite (ZnS); (d) niccolite (NiAs); (e) linkage of metal–sulphur octahedra along the *c*-axis direction in pyrite (FeS₂), marcasite (FeS₂), loellingite (FeAs₂) and arsenopyrite (FeAsS); (f) covellite (CuS) and (g) cube cluster of tetrahedrally coordinated metals in the pentlandite ((Ni,Fe)₉S₈) structure. (Adapted from Craig and Vaughan 1990). Atom colours: light blue – Pb; purple – Zn; yellow – S; red – Fe; orange – As; dark red – Ni; dark blue – Cu; in arsenopyrite, yellow/grey spheres are either S or As.

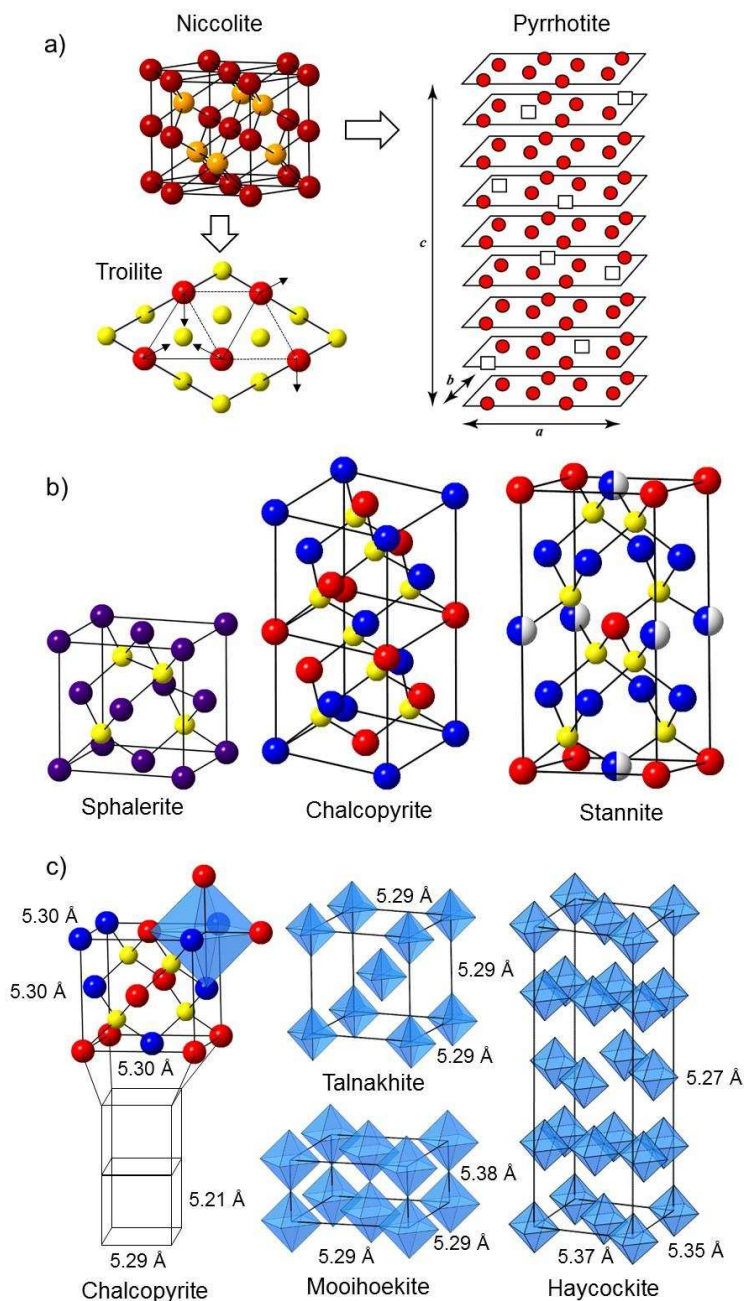


Figure 2. Parent and derivative crystal structures in the sulphide minerals: (a) the structure of niccolite (NiAs), parent of derivatives troilite (FeS) and monoclinic pyrrhotite (Fe₇S₈). Also shown are atoms in the basal plane of troilite with arrows indicating atom movements when distortion occurs; the ordered omission of iron atoms in monoclinic pyrrhotite is also shown, with vacancies represented by squares (only the iron-atom layers are shown); (b) the sphalerite (ZnS), chalcopyrite (CuFeS₂) and stannite (Cu₂FeSnS₄) structures; and (c) the sphalerite and chalcopyrite unit cells with an octahedral site outlined which is empty in chalcopyrite, but within which are located the additional metal atoms in the ‘stuffed derivatives’ talnakhite (Cu₉Fe₈S₁₆), mooihoekite (Cu₉Fe₉S₁₆), and haycockite (Cu₄Fe₅S₈). The ordered arrangement of additional metals in these octahedral sites, and the dimensions in terms of the parent sphalerite cell are also shown (Adapted from Craig and Vaughan, 1990). Atom colours: purple – Zn; yellow – S; red – Fe; orange – As; dark red – Ni; dark blue – Cu; blue/grey – Sn.

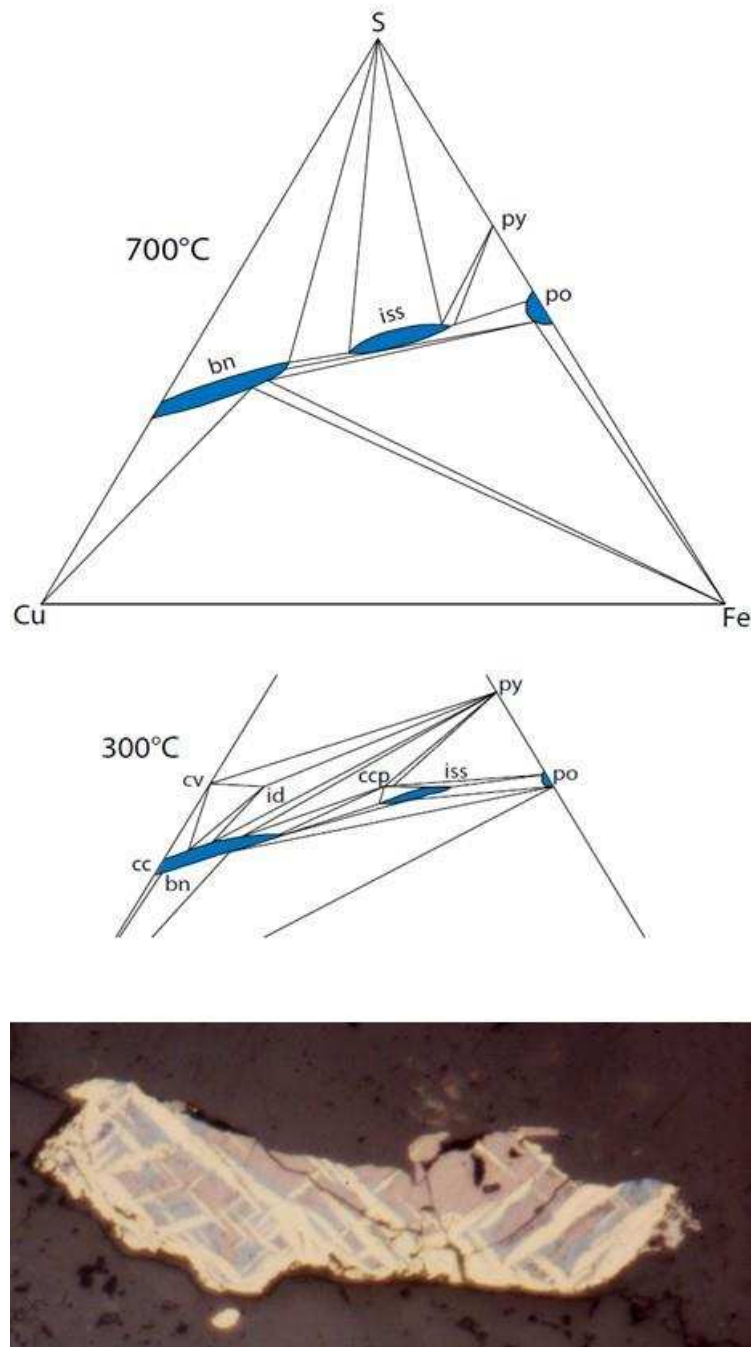


Figure 3. Phase relations in the Cu-Fe-S system at 700°C and 300°C. Apart from the pure Cu, Fe, and S end-members, at 700°C, pyrite (py) is a stable phase and pyrrhotite (po) has a small area of solid solution coloured blue. There are two large fields of solid solution (also coloured blue), one centred around bornite (bn) and the other the so-called intermediate solid solution (iss) which centres around chalcopyrite and related minerals. On cooling to 300°C all three solid solution fields decrease in area. New phases now stable are covellite (cv), chalcocite (cc) and idaite (id). Chalcopyrite (ccp) exsolves from the iss as it shrinks on cooling. Also shown is a reflected light microscopy image (Width of Field = 900µm) showing crystallographically oriented chalcopyrite laths (yellow) now hosted by bornite (brown). The blue-grey areas are chalcocite alteration of the bornite. The sulphides are in a silicate mineral host and the sample is typical of a porphyry copper deposit (see Table 2).

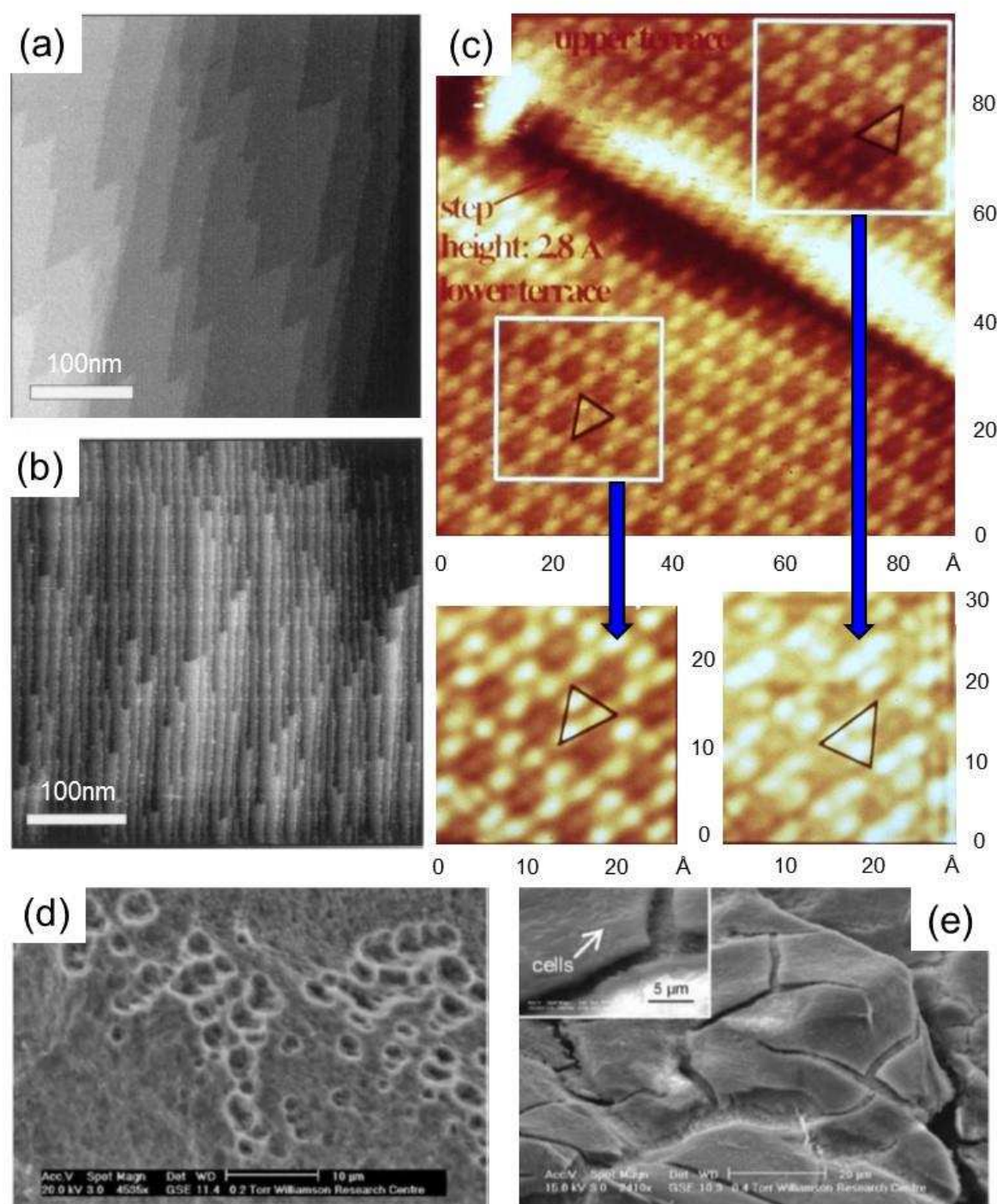


Figure 4. Images of sulphide surface structures, showing (a) STM observation of large stepped (100) pyrite (FeS_2) terraces in the $\langle 10 \rangle$ direction, (b) which were commonly present at a high step density (after Rosso et al. 1999); (c) STM images of monoclinic pyrrhotite (Fe_7S_8), showing $\sim 2.9 \text{ \AA}$ step height and triangles of groups of three S atoms in alternate directions of orientation on neighbouring layers across the 2.9 \AA step (after Becker et al. 1997); (d) bacterial leach pits on the surface of arsenopyrite (FeAsS) reacted in the presence of *L. ferrooxidans*, which were found below a layer of (e) extracellular polymeric substance, hypothesised to act as a dual direct and indirect oxidation mechanism for enhanced arsenic release (after Corkhill et al. 2008).

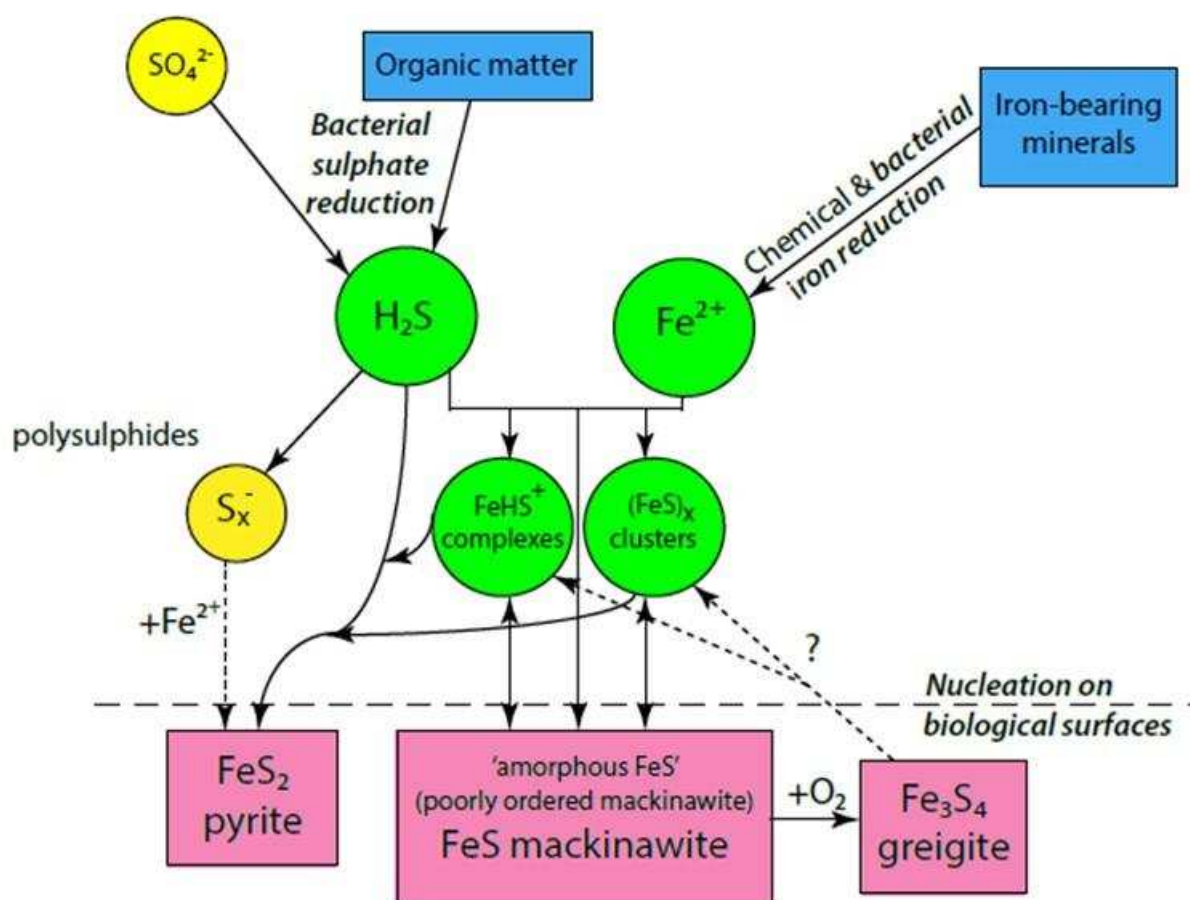


Figure 5. The pathways leading directly to the formation of pyrite or other iron sulphides (mackinawite and greigite) in the sedimentary environment (information taken from Berner, 1984; Lennie & Vaughan, 1996; Rickard & Morse, 2005).