
U3A Geology
Sulphide minerals 1

Introduction

- Sulphide minerals are economically important compounds of sulphur with one or more metals, about 80 species are common
- sulphides form in reducing environments with little or no content of oxygen
- the sulphide class also includes selenides, tellurides, arsenides and antimonides
- some sulphide minerals are economically important as metal ores
- the metals that occur most commonly in sulphides are Fe, Cu, Pb, Zn, Ni and Ag though about 15 others enter sulphide structures
- nearly all base metals come from sulphide deposits

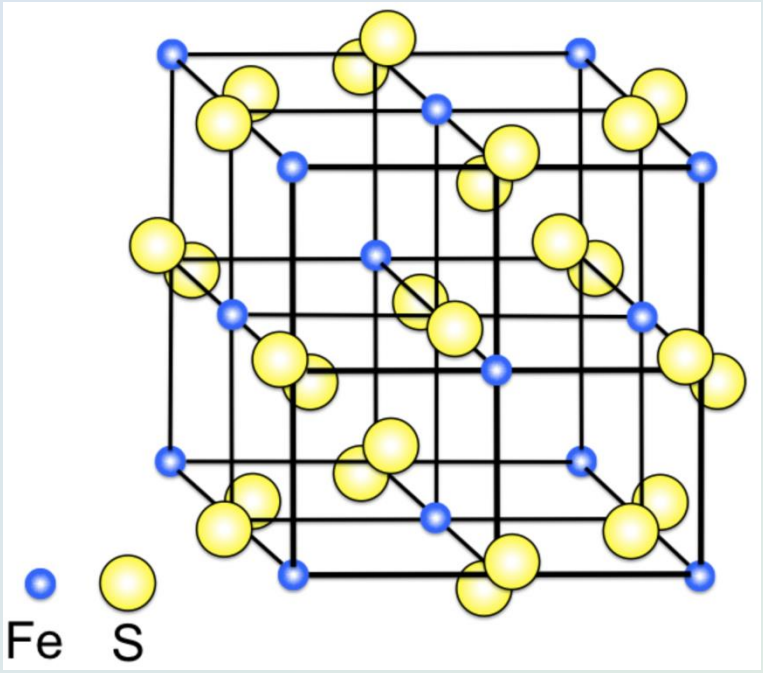
Composition of sulphide minerals

- The composition of sulphide minerals can be expressed with the general chemical formula A_mS_n, where A is a metal S is sulphur and m and n are integers
- AS, A_2S, A_3S_4 and AS_2 are stoichiometric variants

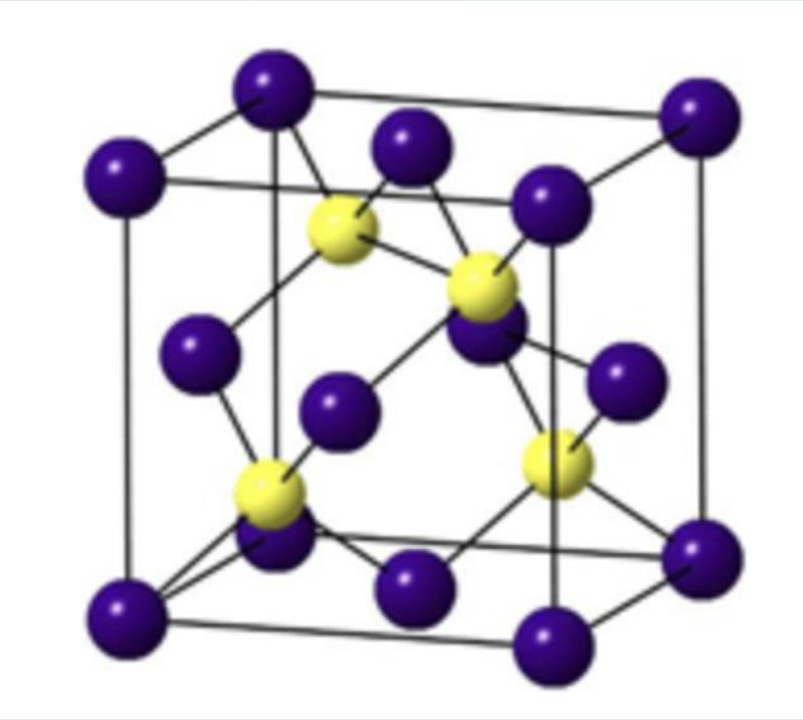
Sulphide structures

- Almost all sulphide minerals have structural arrangements that belong to 6 types, 4 of which are important
- simplest and most symmetrical of the 4 types is the sodium chloride structure where each ion occupies a position within an octahedron
- a type of packing that involves two sulphide ions in each of the octahedral positions is pyrite
- the second distinct structural type is that of sphalerite (ZnS) in which each metal ion is surrounded by 4 oppositely charged ions arranged tetrahedrally

Sulphide structures



pyrite

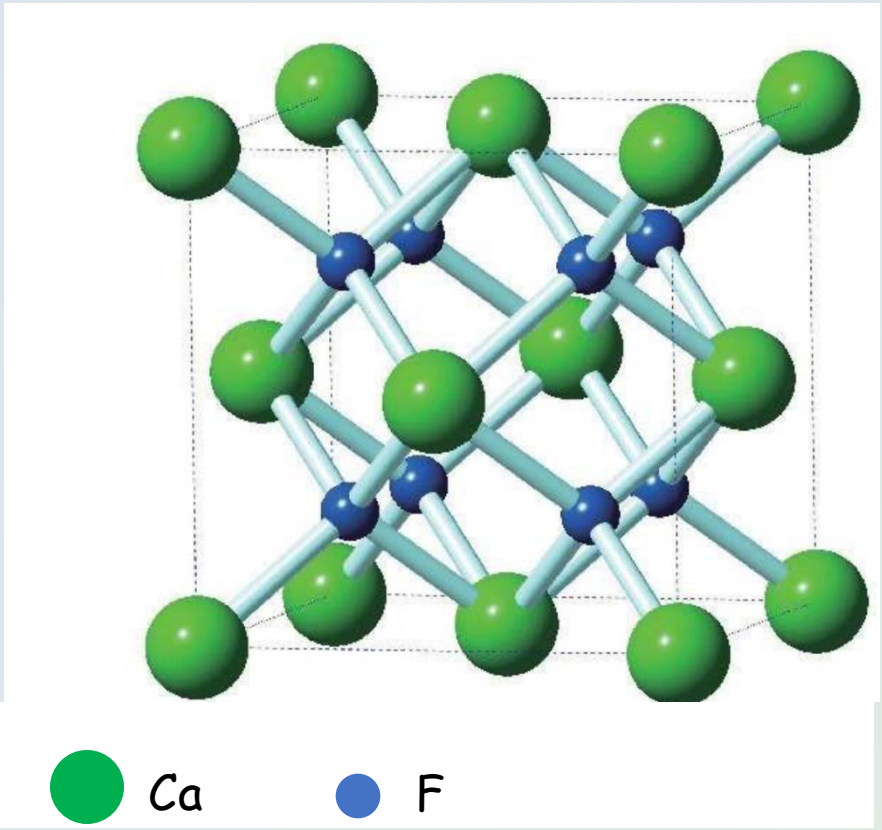


sphalerite

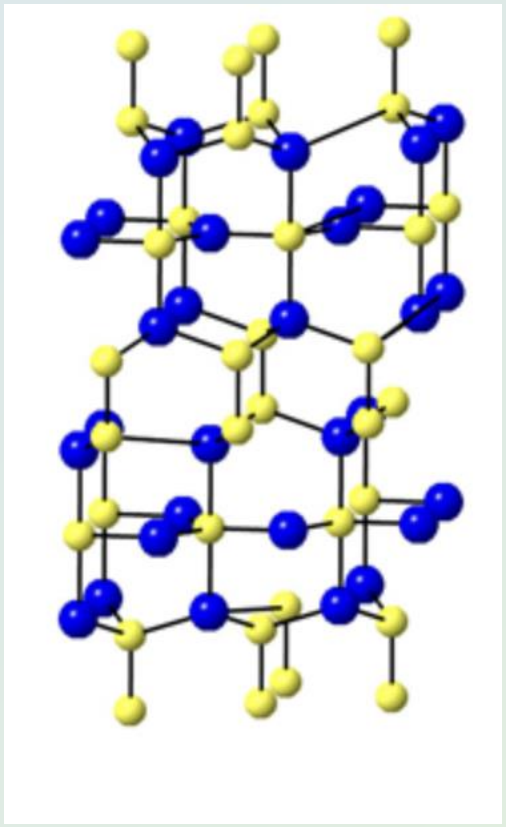
Sulphide structures

- The third distinctive structure is that of fluorite in which each metal cation is surrounded by 8 anions, each anion in return is surrounded by 4 metal cations
- in the reverse of this structure, the metal cation is surrounded by 4 anions and each anion surrounded by 8 cations (antifluorite structure) e.g. hessite (Ag_2S)
- in virtually all of the sulphides bonding is covalent, but many have metallic properties
- several sulphides including molybdenite (MoS_2) and covellite (CuS) have a layer structure

Sulphide structures



Fluorite (CaF_2)

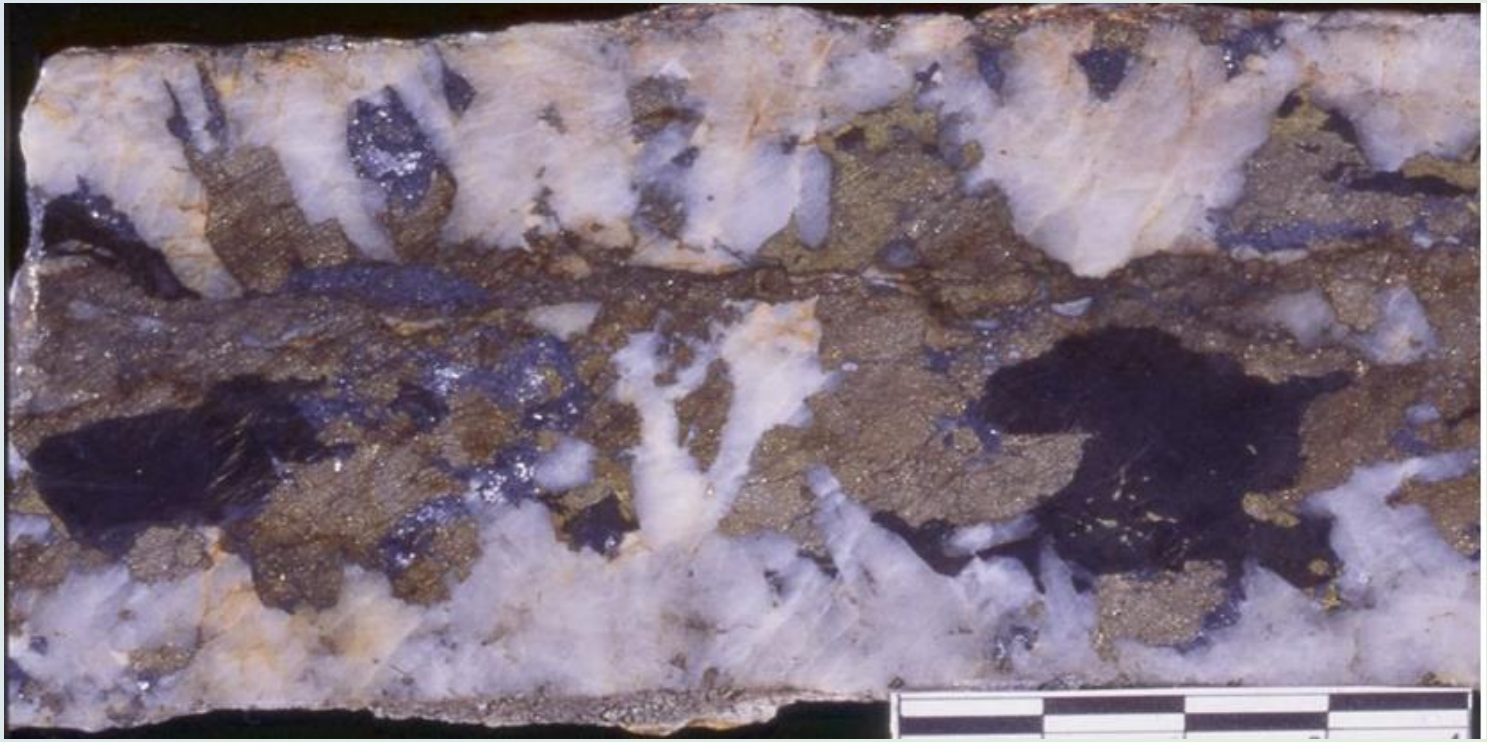


Covellite (CuS)

Sulphide occurences

- Sulphide minerals occur in all rock types sed., igneous, metamorphic
- these minerals tend to occur in isolated concentrations that compose mineral bodies e.g. veins, fracture filling, or comprise replacement of pre-existing rocks
- sulphide mineral deposits originate in two principal processes, both of which have reducing conditions:
  (1) Separation from an immiscible sulphide melt during crystallisation of basic magmas
  (2) deposition from aqueous brines at temperatures in the range 300-600°C at relatively high pressure
- sulphide minerals from first process include mainly pyrrhotite, pyrite, pentlandite and chalcopyrite

Sulphide vein



Sulphide vein containing pyrrhotite and galena, Kidston, Qld

Sulphide ores

- Sulphide minerals are the source of various precious metals e.g. Au, Ag and Pt
- also ore minerals of most metals used by industry e.g. Sb, Bi, Cu, Pb, Ni and Zn
- other industrial important elements such as Cd and Se occur in trace amounts in numerous common sulphides → recovered in refining process

Chemistry of sulphides

- Although most sulphide minerals are simple binary or ternary compounds, natural sulphides contain impurities ranging from trace (ppm) to minor (<5wt%)
- such impurities include toxic elements such as arsenic, cadmium and mercury
- more extensive substitutions associated with solid solution are also found in sulphides e.g. complete solid solution between pyrite (FeS_2) and vaesite (NiS_2) → bravoite [$(Fe,Ni)S_2$]
- certain sulphides also exhibit non-stoichiometry e.g. pyrrhotite is commonly given the general formula $Fe_{1-x}S$ where $0< x <0.125$

Paragenesis of sulphides

- Pyrite is the most abundant sulphide in most ore deposits
- notable exceptions are ores found in association with intrusive ultramafic and mafic rocks
- in Ni deposits the dominant sulphide mineral is pyrrhotite associated with pentlandite and chalcopyrite → formed from crystallization from immiscible melt
- immiscible melt separated from main silicate melt following injection into country rock → in Bushveld complex, main minerals are pyrrhotite, pentlandite, chalcopyrite

Paragenesis of sulphides

- Pyrite is the dominant sulphide in porphyry Cu deposits although chalcopyrite is the important ore mineral along with bornite
- in related porphyry Mo deposits it is molybdenite that dominates
- sulphides in such deposits occur as veinlets and disseminated grains in host intrusions
- pyrite along with sphalerite, galena or chalcopyrite occur in large masses in skarn deposits
- pyrite is also a major phase in many hydrothermal vein deposits including volcanic massive sulphide deposits where it is intergrown with galena, sphalerite and chalcopyrite

Paragenesis of sulphides

- In Besshi-type Cu deposits pyrite, chalcopyrite, sphalerite and galena are found in predominantly sedimentary sequences
- disseminated to massive stratiform sulphide ores are often conformable in sedimentary grading into volcanic deposits
- pyrite dominates the sulphide mineralogy in deposits such as those of the Zambia Cu-belt that has a range of Cu sulphides (chalcopyrite, bornite, chalcocite, covellite)
- in ores associated with sedimentary rocks, galena and sphalerite are the major phases in Mississippi Valley deposits

Sulphide minerals

- Several hundred sulphides are known but only five are sufficiently abundant accessory minerals to have been categorised as rock forming. These five are:

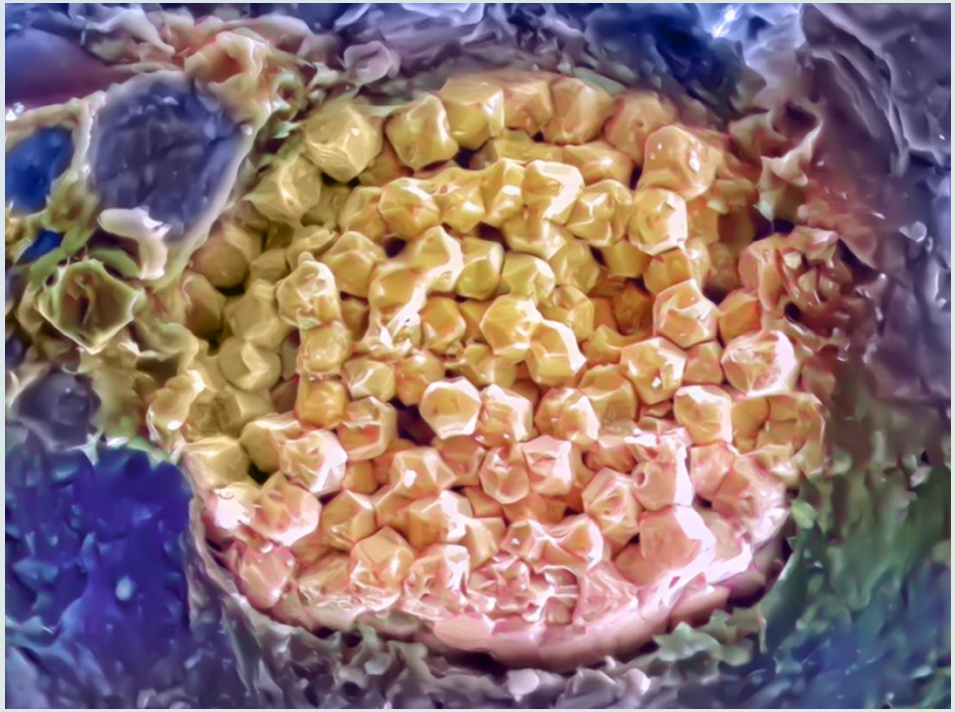
pyrite	(FeS_2)
pyrrhotite	($Fe_{1-x}S$)
galena	(PbS)
sphalerite	(ZnS)
chalcopyrite	($CuFeS_2$)

- most sulphide minerals are opaque with distinctive colours

Pyrite (FeS_2)

- Naturally occurring bisulphide, most common sulphide mineral
- usually found with other sulphides or oxides in quartz veins, igneous rocks, sedimentary rocks and metamorphic rocks
- used in 16th and 17th centuries as source of ignition in early firearms
- usually forms cuboid crystals, sometimes forming in close association to form raspberry shaped framboids
- occurs as primary mineral in sediments and as secondary mineral deposited during diagenesis
- pyrite and marcasite commonly replace fossils in black shales and other sedimentary rocks under reducing conditions

Pyrite crystalline forms



Framboidal pyrite

Pyritohedron

Pyritised Ammonite fossil

Pyrite – physical properties

Colour: pale brass-yellow

Habit: massive, cubic, pyritohedral crystals

Streak: black

Lustre: metallic

Cleavage: indistinct

Hardness: 6 – 6.5

S.G.: 5.02

pyrite

Pyrrhotite ($Fe_{1-x}S$)

- Pyrrhotite → unusual Fe sulphide → non-stoichiometric variant of FeS (troilite)
- weakly magnetic, magnetism increases as Fe increases
- associated with other sulphide minerals e.g. pentlandite, pyrite, chalcopyrite
- occurs in mafic igneous rocks and as segregations in layered intrusions (e.g. Sudbury intrusion), skarns, exogreisens
- if pyrrhotite containing rocks are crushed and used as an aggregate in concrete, it causes concrete to crumble

Pyrrhotite – physical properties

Colour: brownish bronze

Habit: hexagonal prisms, massive

Streak: black

Lustre: metallic

Cleavage: none

Hardness: 4

S.G.: 4.58 – 4.65

Magnetic

pyrrhotite

Marcasite (FeS_2)

- Marcasite → polymorph of pyrite
- physically and crystallographically distinct from pyrite, marcasite has tetrahedral structure, pyrite cubic
- less dense and more brittle than pyrite
- can form as primary or secondary minerals under low temperature, highly acidic conditions
- occurs in sedimentary rocks (shales, limestone, low-grade coal) and in low temperature hydrothermal veins
- as a secondary mineral it forms chemical alteration of a primary mineral such as pyrrhotite or chalcopyrite

Marcasite – physical properties

Colour: pale bronze-yellow to almost white

Habit: tabular, reniform, massive

Streak: black

Lustre: metallic

Cleavage: one distinct

Hardness: 6 – 6.5

S.G.: 4.89

marcasite

Cu sulphide minerals

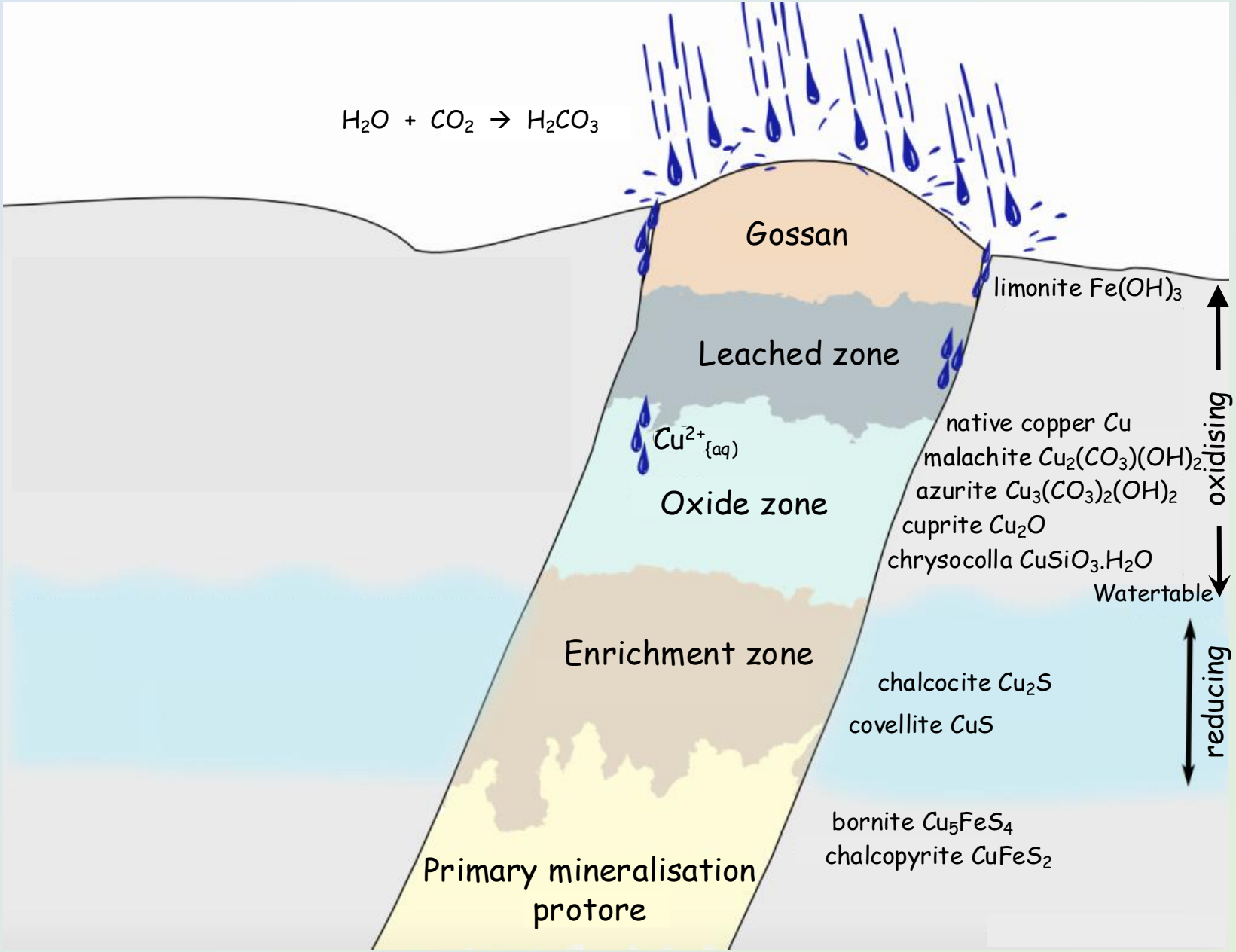
- Cu sulphide ore is the major source for metallic Cu
- Cu sulphide ores occur in a variety of deposits, magmatic, veins and lodes, contact metasomatic deposits (skarns)
- sulphides of Cu that occur at shallow depth in Cu lodes are converted by oxidation and other chemical actions to the native metal, oxides and carbonates

Cu sulphide ore minerals

- The major Cu sulphide ores comprise chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), chalcocite (Cu_2S) and covellite (CuS)
- chalcocite has the highest Cu content of the Cu sulphide ores
- chalcopyrite is by far the most abundant Cu sulphide ore mineral but has a lower Cu content than the other ore minerals

Ore mineral	Cu content
chalcocite	79.9%
covellite	66.5%
bornite	63.3%
chalcopyrite	34.6%

Supergene enrichment (after Asmus 2013)



Chalcopyrite ($CuFeS_2$)

- Chalcopyrite → most common Cu ore mineral
- crystallises in tetragonal crystal system
- often confused with pyrite and gold → all have yellowish colour, metallic lustre
- they can be distinguished by their hardness and streak
- chalcopyrite is softer than pyrite but harder than gold
- chalcopyrite has a black streak as has pyrite, gold has a gold coloured streak

Environments of formation of chalcopyrite

Chalcopyrite is present in a variety of ore-bearing environments

(1) Volcanogenic massive sulphide deposits e.g. Rosebery, Mt Lyell

(2) Sedimentary exhalative deposits e.g. Mt Isa

(3) Porphyry Cu deposits e.g. Chile

(4) Komatiitic Ni ore deposits e.g. Kambalda, WA

(5) Ultramafic lavas

Chalcopyrite is present in the supergiant Olympic Dam Cu-Au-U deposit in South Australia → main ore mineral

Chalcopyrite – physical properties

Colour:	brass yellow
Habit:	massive
Streak:	greenish-black
Lustre:	metallic
Cleavage:	indistinct
Hardness:	3.5 - 4
S.G.:	4.1 – 4.3

chalcopyrite

Bornite (Cu_5FeS_4)

- Bornite also known as peacock ore (iridescent tarnish when exposed to air)
- widely occurring, important Cu mineral
- usually found associated with other sulphides (chalcopyrite, chalcocite, pyrite and pyrrhotite) in hypogene deposits
  e.g. porphyry Cu systems
- less frequently found as supergene mineral in upper enriched zones of Cu veins
- not as important an ore of Cu as chalcopyrite and chalcocite

Bornite – physical properties

Colour: copper red, pink, purple

Habit: massive

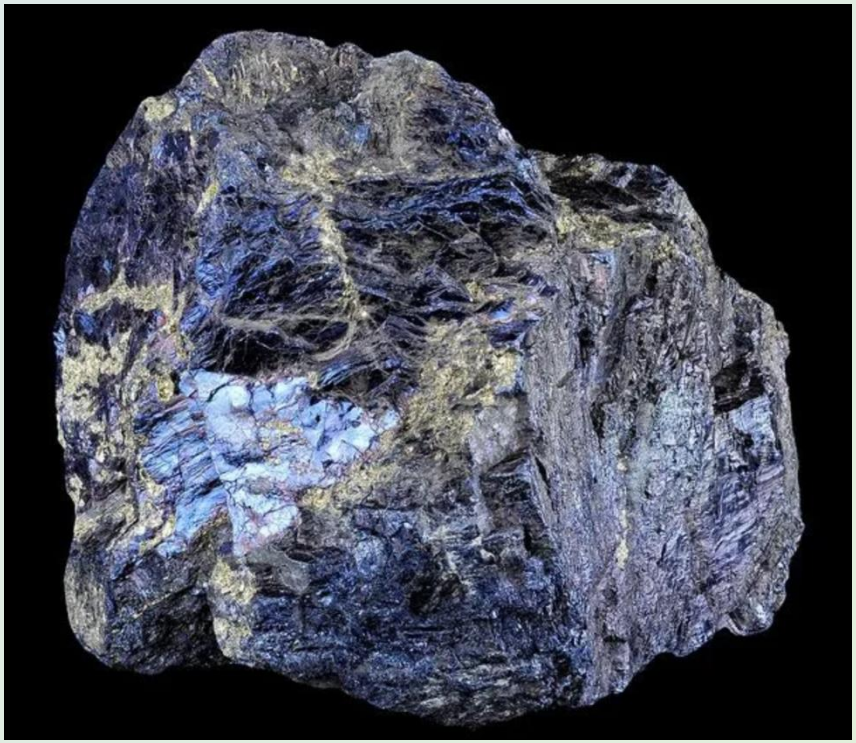
Streak: black

Lustre: metallic if fresh, iridescent tarnish

Cleavage: poor

Hardness: 3 – 3.25

S.G.: 5.06 – 5.08



bornite

Covellite (CuS)

- Covellite is a rare secondary Cu sulphide mineral that forms in the oxidation and supergene zones of Cu sulphide deposits
- it is associated with other Cu minerals, principally chalcocite, chalcopyrite, bornite and enargite (Cu_3AsS_4)
- it is derived from those minerals by alteration
- covellite has a platy habit
- covellite is mainly used for display in mineral collections, jewellery and lapidary

Covellite – physical properties

Colour: indigo blue

Habit: platy crystals

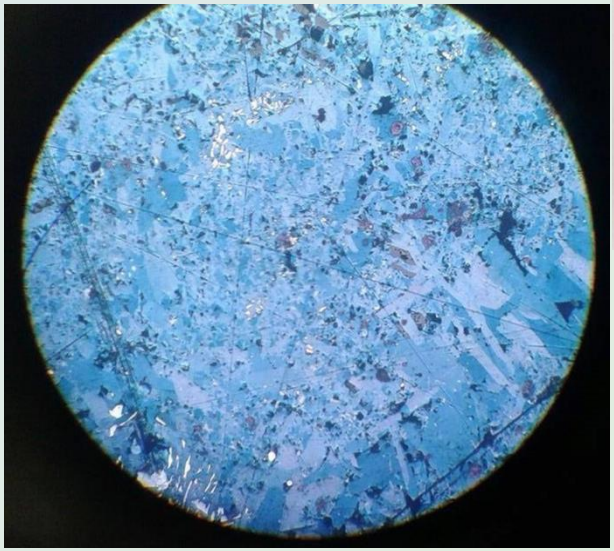
Streak: lead-grey

Lustre: sub-metallic

Cleavage: 1 good platy cleavage

Hardness: 1.5 - 2

S.G.: 4.6 – 4.8



covellite- reflected light

covellite

Chalcocite (Cu_2S)

- Chalcocite is an important Cu ore mineral
- chalcocite may occur as a primary mineral in veins with bornite, chalcopyrite, enargite (Cu_3AsS_4) and pyrite
- its principal occurrence is as a supergene mineral in enriched zones below oxidation zones of Cu sulphide deposits
- also found in sedimentary rocks
- one of the most profitable Cu ores with ~80% Cu

Chalcocite – physical properties

Colour: dark grey to black

Habit: massive

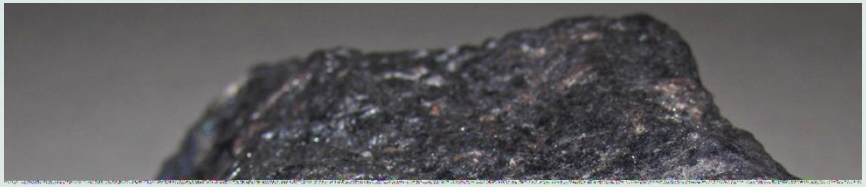
Streak: black

Lustre: metallic-dull

Cleavage: indistinct

Hardness: 2.5 - 3

S.G.: 5.5 – 5.8



chalcocite

Galena (PbS)

- Galena → most important source of Pb and important source of Ag
- commonly occurs in hydrothermal veins in association with sphalerite, chalcopyrite, cerussite, anglesite, quartz and fluorite
- also occurs in Mississippi Valley deposits along with sphalerite in cavities and brecciated zones in limestone and chert
- can contain up to 1.0% Ag that occurs as inclusions of Ag sulphide or limited Ag in galena structure
- within weathering zones, galena alters to anglesite ($PbSO_4$), cerussite ($PbCO_3$) or pyromorphite [$Pb_5(PO_4)_3Cl$]
- Australia is world's largest producer of Pb (Broken Hill, Mt Isa)

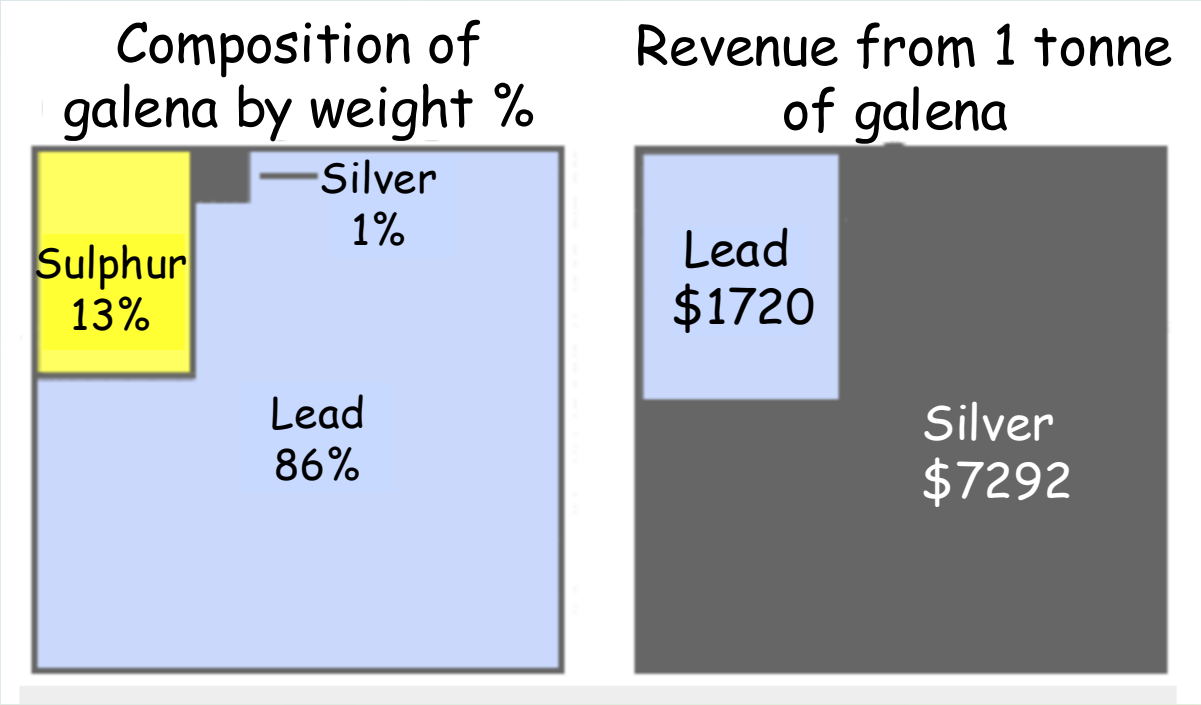
Galena - physical properties

Colour:	silver to grey
Habit:	cubic crystals
Streak:	black
Lustre:	metallic
Cleavage:	perfect cubic
Hardness:	2.5
S.G.:	7.4 – 7.6

galena

Ag in galena

- Galena can contain up to 1% Ag that occurs as inclusions of silver sulphide or as limited Ag in galena structure
- Ag is 364 times more valuable than Pb (Ag $25/oz, Pb $1/lb)
- some Pb mines produce more revenue from the Ag content of their galena than their Pb content



Sphalerite (ZnS)

- Sphalerite is the most important ore mineral of Zn
- it is among the most common sulphide minerals and is found in a number of deposit types, primarily sedimentary exhalative (SEDEX), Mississippi Valley type, volcanogenic massive sulphide deposits and skarns
- it is found in association with galena, chalcopyrite, pyrite, calcite, dolomite, quartz, rhodochrosite and fluorite
- about 50% of Zn and Pb comes from sedimentary exhalative deposits (SEDEX) that form on sea floor

Sphalerite – physical properties

Colour: brown, black, yellow, red, green

Habit: crystal aggregates

Streak: brown, colourless when pure

Lustre: resinous, admantine

Cleavage: 6 perfect

Hardness: 3.5 - 4

S.G.: 7.4 – 7.6

Sphalerite (marmatite)

Low Fe sphalerite

Sphalerite with a low Fe content is non-opaque and occurs in a range of colours

Ni sulphides

- Ni is an important metal with major uses in stainless steel (~65%), metal alloys (~20%) and plating (~9%)
- Ni is common in two principal ore types, sulphide or laterite ores
- Ni sulphide ores are typically derived from volcanic or hydrothermal processes and usually include Cu and Co and sometimes other precious metals such as Au, Pt and Pd
- the main source of mined Ni is the mineral pentlandite $(Fe,Ni)_8S_9$
- in nature, Ni sulphides commonly occur as solid solution with Fe in minerals such as pyrrhotite

Pentlandite [$(Fe,Ni)_9S_8$]

- Pentlandite is normally found as abundant granular masses in ultramafic rocks
- it is occasionally found in mantle rocks and 'black smokers'
- it is a Ni-Fe sulphide with a narrow range in Ni to Fe ratios, usually 1:1 but is skewed by pyrrhotite inclusions
- pentlandite occurs along with other sulphides e.g. bravoite [$(Ni,Fe)S_2$], chalcopyrite, pyrrhotite, cubanite and millerite (NiS)
- pentlandite is found within lower margins of layered intrusions e.g. Sudbury complex, Bushveld complex
- it is also the dominant mineral in Kambalda komatiite Ni deposits

Pentlandite – physical properties

Colour: yellowish bronze

Habit: massive to granular

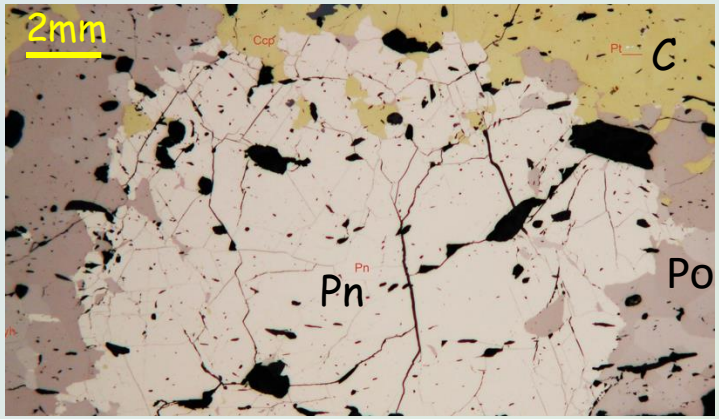
Streak: light bronze-brown

Lustre: metallic

Cleavage: absent, octahedral parting

Hardness: 3.5 - 4

S.G.: 4.6 - 5



Pentlandite in reflected light

pentlandite

Millerite (NiS)

- millerite (NiS) is an important Ni ore mineral
- it is a common metamorphic mineral replacing pentlandite within serpentine ultramafic rocks
- this occurs by removal of S from pentlandite during metamorphism or metasomatism
- millerite contains a higher percentage of Ni than the major Ni ore mineral, pentlandite
- millerite occurs in serpentinised ore bodies in WA

Millerite – physical properties

Colour: pale brass-yellow to bronze-yellow,

Habit: typically acicular

Streak: greenish black

Lustre: metallic

Cleavage: perfect

Hardness: 3 – 3.5

S.G.: 5.3 – 5.5

millerite