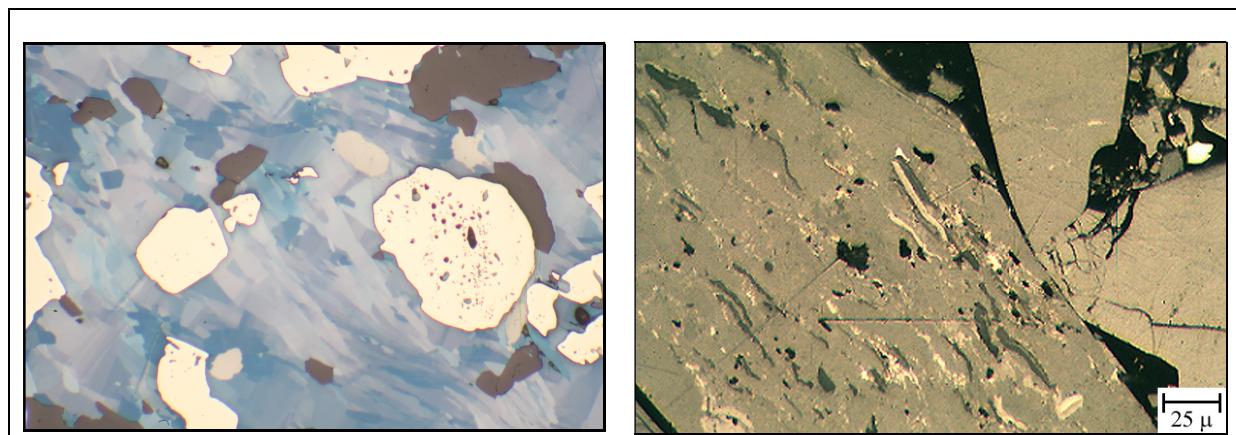


ORE MINERALOGY AND COAL PETROGRAPHY



TA3196

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Part I

Ore Mineral Associations, Petrographical Relationships

1. INTRODUCTION

Ore minerals are the valuable minerals in a rock which can be considered an ore. In general these minerals are *opaque minerals*, contrary to the rock forming minerals, which in general are *transparent* or *translucent*. Besides the ore minerals, ores also contain common rock forming minerals, which have been encountered already in the course Mineralen en Gesteenten - TA1900. Only very rarely does an ore consist completely of valuable minerals. In the course TA1900 you have learned to designate the opaque minerals as “ore”.

Ore minerals contain the valuable materials which are the reason for mining en the subsequent mineral processing. Ore minerals are often sulphides (for instance chalcopyrite (CuFeS_2), a copper ore minerals, or pentlandite, $(\text{Ni},\text{Fe})_9\text{S}_8$, a Ni-ore mineral, but also oxides. Examples of oxidic ore minerals are: hematite, Fe_2O_3 , magnetite Fe_3O_4 , pyrolusite MnO_2 , goethite, FeOOH , cassiterite, SnO_2 . Also native metals (Au, Ag) do occur. .

The genesis of ores is discussed in the lecture Economic Minerals and Rocks (TA3140), but several aspects will be repeated here in brief. This will give insight into some important minerals associations. The classification of ores from TA3140 is given again, but with reference to the specific polished sections of the relevant ores in the specimen collection.

For aspects of determination of ores, but also of mineral processing it is useful to have insight into the texture of ores. The textures tell a lot about the genesis of the ores, with often important information with respect to the determination of minerals, but textures certainly are not unimportant in the processing of ores. Inclusions, zoning, reactions rims, demixing lamellae, occurrence of crystals in small veinlets, grain size, etc. all are of important in the study of an ore.

This syllabus has the function of practical manual (see appendices), but also as a short reference work with respect to the geochemical associations, and the structure of the minerals, as well as petrographic relationships. For instance, every specimen is described in the practical manual (Appendix 2), but also in the summary of the geochemical associations. The practical manual (Appendix 2) gives the minerals occurring in a specimen, and the specimen index (part 1, section 5) indicates where a specific ore is discussed, which facilitates the study of the manner of occurrence.

2. SHORT SUMMARY OF THE GENESIS OF ORES AND THE DIFFERENT TYPES OF ORES.

In this section is discussed in brief how the different ores are formed, and which mineral associations belong to it. More extensively this is discussed in the course TA3140 – Economic Minerals and Rocks.

*Where such a type of ore occurs in the practical sample set, a more detailed description of the specific ore is given. In the margin of the text this is indicated with the word **MICROSCOPY***

You will find that the subdivision of the ores not always can be applied in a strict sense. Also, some ore types over a larger distance will grade into other ore types, or are in between two classifications. Also there are ores about which there are different theories about the genesis, and it is not uncommon that different theories place the same ore into another category. A very well-known example are the iron ores of Kiruna, Sweden, which according to one theory must be seen as volcanic exhalative ores, according to another as representatives of the class of segregation ores.

Well known characteristic minerals associations and textures can offer valuable information for the identification of the minerals in an ore. For example, galena, sphalerite and pyrite are common and often occur together, but Sn-minerals, such as cassiterite are unknown in such associations. Chalcopyrite, pyrrhotite, pentlandite, magnetite and pyrite form another well-known association, but for instance sphalerite or galena are seldom (but that is not “never”) found in this association.

Finally, the classification of ores in types and the mineral associations that are connected to them give an overview of the most important parageneses of ore minerals. The specimens in the practical collection contain typical parageneses.

One may classify the ores into the following main groups (TA3140):

2.1) MAGMATIC ORES

This is ores which are directly related to igneous rocks. Ore formation due to secondary processes, related to magmatic processes, is not part of this Category: .

2.1.1. Ores related to “Mantle Degassing”

Examples are: Diamond ores, and ores related to carbonatites. The latter are of interest for the winning of calcium, phosphate, magnetite, and Rare Earth Elements (Y, Ce, La, Nd, etc.).

There are NO examples of this class in the practical collection.

2.1.2. Segregation deposits

An example is chromite ore. Chromite (FeCr_2O_4) is formed in certain mafic or ultramafic magmas, and accumulates in the magma chamber. Such layer like accumulations of chromite are sometimes called Chromitites. Associated minerals are often olivine, plagioclase and (ortho)pyroxene. As results of later low grade weathering, olivine may be changed into serpentinite.

MICROSCOPY An example is the specimen T-11. This is a chromite ore from the Philippines. In this sample the olivine is completely altered to serpentine.

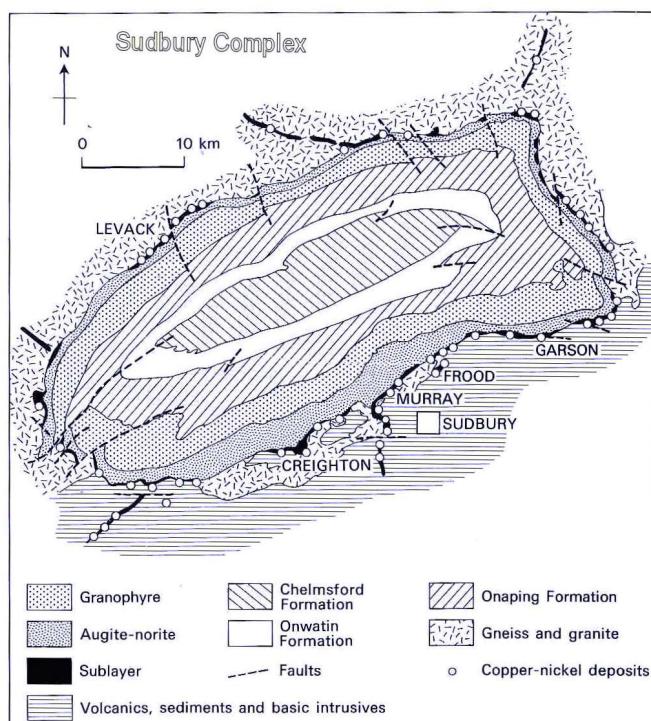
2.1.3. Deposits related to the demixing of melts

This is often the case with mafic or ultramafic silicate magmas which contain appreciable amounts of sulfur. The sulfur forms a sulphide melt, which cannot mix with silicate melt, en which separates as a result of its larger density.

Examples of such ores are:

- a) The Ni-Cu-Fe ores of Sudbury, Canada. Important minerals associations are pyrrhotite ($Fe_{1-x}S$), with pentlandite $(Ni,Fe)_9S_8$, and chalcopyrite $CuFeS_2$. Oxide may also occur in these sulfidic rocks. Spinel ($MgAl_2O_4$) and magnetite ($FeFe_2O_4$) are not uncommon.

MICROSCOPY Specimen T-4 is a typical massive sulfidic ore from Sudbury, with pyrrhotite, pentlandite, chalcopyrite and magnetite.



The Sudbury Complex, Ontario Canada.

MICROSCOPY Specimen T-8 (from the Frood-Stobie mine) shows chalcopyrite, intergrown with the (in general rather rare) mineral cubanite ($CuFe_2S_3$). In T-8 sometimes accessory Bi-Te minerals can be found.



The Frood-Stobie Mine, Sudbury Area.

- b) The Platinum Group Elements (PGE: Pt, Ru, Rh, Ir, Os, Pd). Well-known deposits are the Bushveld Complex (S-Africa), Stillwater Complex (Montana, U.S.A.). Important minerals are for instance braggite ($\text{Pt},\text{Pd},\text{Ni}\text{S}$), laurite (RuS_2) and sperrylite (PtAs_2).

There are NO examples of this class in the training collection.

2.1.4. Granitic Magmas and Pegmatites.

Granitic melts contain H_2O , because they have their origin in the Earth's Crusts. Part of the water is stored in for instance biotite (as OH-groups). Remaining water stays in the melt. At a temperature low enough during the cooling of the magma, the water-rich fluid separates. Metals accumulate in these fluids. In some cases the last silicates crystallize in a very watery fluid. Because diffusion is very rapid in such hot watery fluids, very large crystals can form. A granitic rock with large crystals is called a pegmatite. Many pegmatites crystallize in fracture zones in and around granitic rocks. Pegmatites thus look like veins. The fluid is in this last phase enriched in metals or other economically valuable elements (for instance Be, or Li, or B). There may be crystallization of minerals of economic value (e.g. beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$).

There are NO examples of this class in the training collection.

Many metals cannot be incorporated into silicates and form, after separation of the fluid phase, "their own" minerals (for instance cassiterite, SnO_2). Deposits of the separated fluids form the class of the hydrothermal ores.

2.2. HYDROTHERMAL ORES

This is a very important class of ores. The ores are formed by hot aqueous solutions. The origin of the solutions may be diverse: magmatic, metamorphous, diagenetic, meteoric, seawater. The metals in these solutions are generally transported as chemical complexes. Cl, but also F are very important in this. The representatives of this group are:

2.2.1. Magmatic Type

a) Greisen Tin Deposits (related to granite)

In a late stage of the evolution of granite, a fluid separation takes place. The segregated late magmatic hydrothermal solution will react with the country rocks of the granite, but also with crystallized granite itself. By these metasomatic changes a rock called *Greisen* is formed. Also veins and stockworks may be associated with this. Mineralizations of Sn (cassiterite – SnO_2), but also veins with mineralizations of W (wolframite – $(\text{Fe},\text{Mn})\text{WO}_4$) are often found in Greisens and associated veins. Examples are the many Sn-deposits in Cornwall, England, and N-Portugal. At Panasqeira, N-Portugal (where tungsten is the main product), cassiterite is found in greisens and in associated veins with quartz.

MICROSCOPY *An example of an ore from Panasqeira can be found in specimen T-5 from the practical collection. This is a complicated ore with many subsequent phases of mineralization. The general model is: the first mineral in the veins was cassiterite, followed by quartz, muscovite and very rare wolframite. After this, there was a sulphide rich phase, which led to the crystallization of pyrite, pyrrhotite, Fe-rich sphalerite and chalcopyrite. In a later phase, carbonate with secondary pyrite and marcasite was deposited, in which the pyrrhotite was altered. Not all pyrrhotite was altered, so it is still a prominent mineral in the polished sections. Pyrite can also be found as "melnicovite-pyrite" or "gel-pyrite", a cryptocrystalline or amorphous form of pyrite, which is deposited in concentric layers.*

In T-18 you will find an ore from Indonesia, which fits in this setting. No clear veins can be recognized.

b) Ag-Ni-Co-Bi arsenide ores

A special paragraph must be added for a peculiar, but with respect to ore minerals spectacular association: *Ag-Ni-Co-Bi arsenide ores*. Silver is often found as a native metal in these ores.

MICROSCOPY *Specimen T-6 is a sample of the ores from the Cobalt region, near Sudbury, Canada, which are considered to be typical. T-6 contains no native silver and Bi, but for the rest is a beautiful example of these ores. Minerals are among others: skutterudite ($(\text{Co},\text{Ni},\text{Fe})\text{As}_{3-\text{x}}$), nickeline (NiAs), cobaltite ($\text{Co},\text{Fe}\text{AsS}$) and loellingite/rammelsbergite¹. It can be observed that skutterudite and nickeline crystallized early, followed by cobaltite and loellingite/rammelsbergite.*

The Ag-Ni-Co arsenide ores occur during the whole history of the Earth, and

¹ Loellingite (FeAs_2) is also spelled **Jöllingite**. Rammelsbergite is NiAs_2

they are found in a whole range of rocks. They occur in veins, and closely related diabase veins are found (as in the Cobalt region). The ore bodies in the veins often show growth phenomena, and sometimes “colloform textures” (later we will learn more about this). The mineralogy is determined, besides the common ore minerals pyrite, chalcopyrite, arsenopyrite and galena, by minerals such as native silver (Ag), bismuth (Bi), nickeline and skutterudite. The paragenetical sequence of these ores is often very complicated. With respect to the origin, there are two theories: one implies a genetic relationship with the often associated diabase veins, but a more widely accepted theory lays the origin of the ore forming solutions with felsic magmatism. In the Cobalt region such an igneous rock is not exposed. Mining in the Cobalt region has stopped in the 1960's.

2.2.2. Magmatic/Groundwater

a) Skarn Tungsten Deposits

In contact with limestone, a reaction zone between granite and country rocks will form. Decomposition of calcite forms CO₂, and possible W in the hydrothermal solution can be deposited as scheelite (CaWO₄). Later meteoric water may cause retrograde reactions in the rock.

There are NO examples of this class in the training collection.

b) Porphyry Copper and molybdenum Deposits

These ores are related to granitic intrusions which have penetrated high in the Earth's Crust. They are found on the continental side of subduction zones. Aqueous solutions segregate in a late stage of the crystallization of the granitic magma. The fluids are enriched in some main and trace elements. By segregations of the aqueous solutions the melting point of the granite is raised, and enhanced crystallization takes place. The segregated fluids accumulate in the apex of the intrusion. They cause brecciation of the country rock and escape. These fluids cause metasomatism of the surrounding rocks in particular of the elements K, Cu, and Mo, dissolved in the solutions, are deposited as chalcopyrite, (CuFeS₂), chalcocite (Cu₂S), and molybdenite (MoS₂).

Crystallization of the minerals causes again pressure increase, with a second round of brecciation of the country rocks. In this way a new cycle of vein formation with ore minerals is formed. A so-called ***stockwork*** is formed. When the intrusion cools, percolating groundwater comes into contact with the intrusion, and a hydrothermal alteration zone is formed, which overlaps the previous. Also Cu-sulphides are again mobilized and newly distributed. This class deals with low grade ores of very large proportions. Famous examples are Climax Colorado (Mo), and Chuquicamata Chili (Co, Mo).

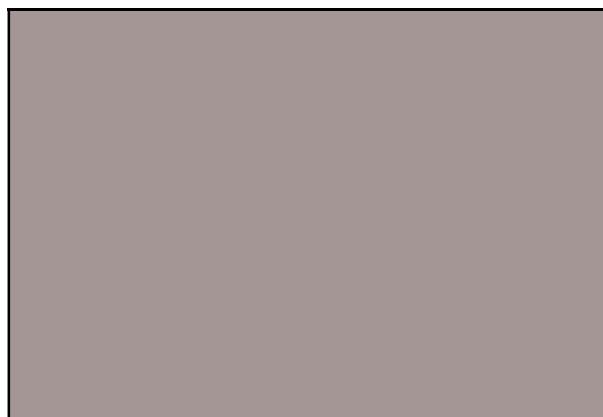
There are NO examples of this class in the training collection.

d) Mesothermal deposits

These deposits are found in the country rocks around a granitic intrusion. Aqueous solutions flow through fractures, cracks, or the bedding of sedimentary country rocks. The solutions may be magmatic, meteoric, or a mixture of both. The further away from the granite, the lower the temperature. Close to the granite minerals which crystallize at a relatively high temperature are found (cassiterite). Further away Cu-minerals like chalcopyrite and bornite (Cu_5FeS_4), are formed. Also covellite (CuS) may be found, which forms together with pyrite from alteration of chalcopyrite. In the lowest temperature zone sphalerite (ZnS) and galena (PbS) are deposited. Also Ag-minerals may crystallize. Veins may vary in diameter from centimeters to meters, and often can be followed over large distances. The veins are very rich in ore.

An important example of such a Cu-ore is found at Butte, Montana, USA.

MICROSCOPY *In the training collection you find in T-1 a specimen from such a mesothermal Pb-Zn from Casapalca, Peru. Minerals in the ore are galena, sphalerite, pyrite, and tennantite ($Cu_3(As,Sb)S_{3.25}$ (or $Cu_{12}(As,Sb)_4S_{13}$))*



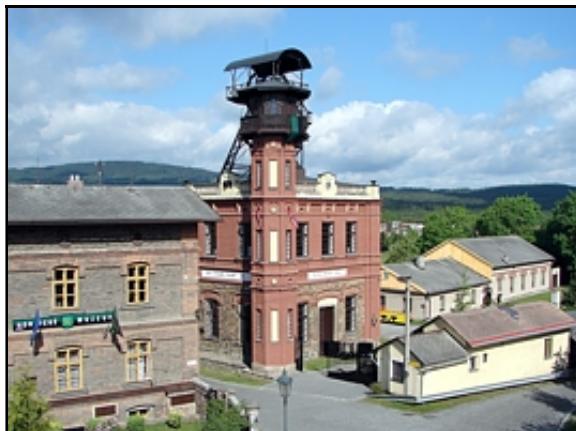
Casapalca Peru

MICROSCOPY *In the training collection you find in T-3 a Cu-ore from Bor, Serbia. The copper ores from Bor are found in a hydrothermally altered andesite. The volcanic rocks are associated with intrusive rocks varying from diorite gabbro to granodiorite. Apparently associated to the intrusives in hydrothermally altered andesite one may find massive Cu-ore as lenses, and stockwork deposits. The massive ores (typical minerals: pyrite, bornite, enargite/luzonite, chalcopyrite, chalcocite, covellite) are considered to be hydrothermal replacement ores. Porphyry copper ore is also found at Bor, in an underground mine which displays lower lying ores under the massive ores (mined in an open pit mine).*



Bor, Serbia

MICROSCOPY *The deposits of Příbram, Czechia, are mesothermal to epithermal Pb-Zn-Ag vein ores. The ores, related to the felsic magmatism of the so-called Bohemian Pluton, are of a Hercynian age. The ores have a complicated mineralogy, and are thought to have formed in multiple phases. Ore minerals are predominantly galena and sphalerite. The further away one moves from the granodiorite (exposed in a mine close to Příbram, at the deepest levels), the more one finds Ag-sulfosalts (proustite, pyrargyrite), arsenopyrite, and complex Pb-sulfosalts (e.g. jamesonite). Galena is often silver bearing. These ores are demonstrated in T-9A and T9-B. In T-9B the reaction of original galena to jamesonite is sometimes beautifully demonstrated.*



Příbram Mining Museum.

c) Epithermal deposits

These deposits occur several km's above granitic intrusions, or in the vicinity of volcanic activity. The hydrothermal solutions can be partly magmatic, but in general the fluids are of meteoric origin. The magma body is important as a heat source. Maximum temperatures are in the order of magnitude of 300°C. The gold in solution can be of magmatic origin, or it was dissolved from volcanic and sedimentary rocks. The gold is present in solution as a bisulphide or arsenic complex.

There may be several causes for the deposition of native gold. Besides gold, often arsenic or antimony bearing minerals occur. Like for instance orpiment (As_2S_3), realgar (AsS), stibnite (=antimonite) (Sb_2S_3). If there is a lot of tellurium (Te), even gold tellurides or silver tellurides may be found, (for instance calaverite, AuTe_2). If there is a lot of pyrite and arsenic, the gold may also occur in solid solution in arsenopyrite or arsenic containing pyrite. This gold can only be demonstrated by chemical analysis (so-called “***invisible gold***”)

MICROSCOPY *In specimen T-2, you find an example of native gold, deposited in veins with galena, sphalerite, pyrite, and chalcopyrite. The ore is from Sumatra, Indonesia. Sumatra was already known in ancient times for its gold deposits. Evidence are the Sanskrit names of Swarnadvīpa ("Island of Gold") and Swarnabhūmi ("Land of Gold"), due to the gold deposits of the island's highland. Even today gold is mined on Sumatra.*



The modern Way Linggo mine on Sumatra (2010)

MICROSCOPY *Specimen T-13 shows an Au-Bi-ore from Tennant Creek, Australia. According to the most current theories this ore of Proterozoic age should be placed also in an epithermal setting. Volcanic activity, related to the intrusion of the Tennant Creek granite, and concurrent with folding of the sediments and ironstones in which the veins are found, was the heat source. The hydrothermal solutions, which caused the mineralizations, may be related to granitic intrusives or volcanic activity, or they may have their origin in the dewatering of Proterozoic sediments. The possibly acid solutions leached perhaps the metals and sulfur from the sediments, and transported them to the axial zones of anticlines, which served as channels. Contact of the hydrothermal solutions with more alkali pore fluid from overlying carbonate bearing iron-rich shales resulted in the precipitation of first magnetite, and later sulphides (pyrite, chalcopyrite). Bi-sulfosalts (e.g. bismuthinite) and gold (with a high Se-content), followed as last minerals. Sometimes colloform textures are visible (but not very clearly), which indicates local crystallization from a gel stages. Overall temperatures were low.*



Mine shaft Museum, Tennant Creek



Tennant Creek, Location

2.2.3. Metamorphic Type

Important representatives of this group of ores are the gold bearing vein-deposits of Archaic age. During metamorphism lower parts of volcano-sedimentary complexes were dewatered. The resulting solutions leached metals from the volcano-sedimentary complex. The solutions percolated through shear zones and rose, but did not reach the surface. The solutions came no further than regions with greenschist facies metamorphosis. Gold was present as a bisulphide complex. By reaction with iron containing country rocks, the bisulphide complexes broke down and gold and pyrite precipitated. Gold was precipitated at temperatures around 300 en 400°C. Such deposits are found in Archaean Greenstone belts: Golden Mile, Australia, and Porcupine, Ontario, Canada.

There are NO examples of this class in the training collection.

2.2.4. Seawater Type

1) Volcanogenic Massive Sulphide Deposits are formed on the seafloor, where as a result of the heat of submarine volcanism hydrothermal convective systems arise. The solutions originate mainly from seawater, and therefore contain chlorine. Temperatures can be as high

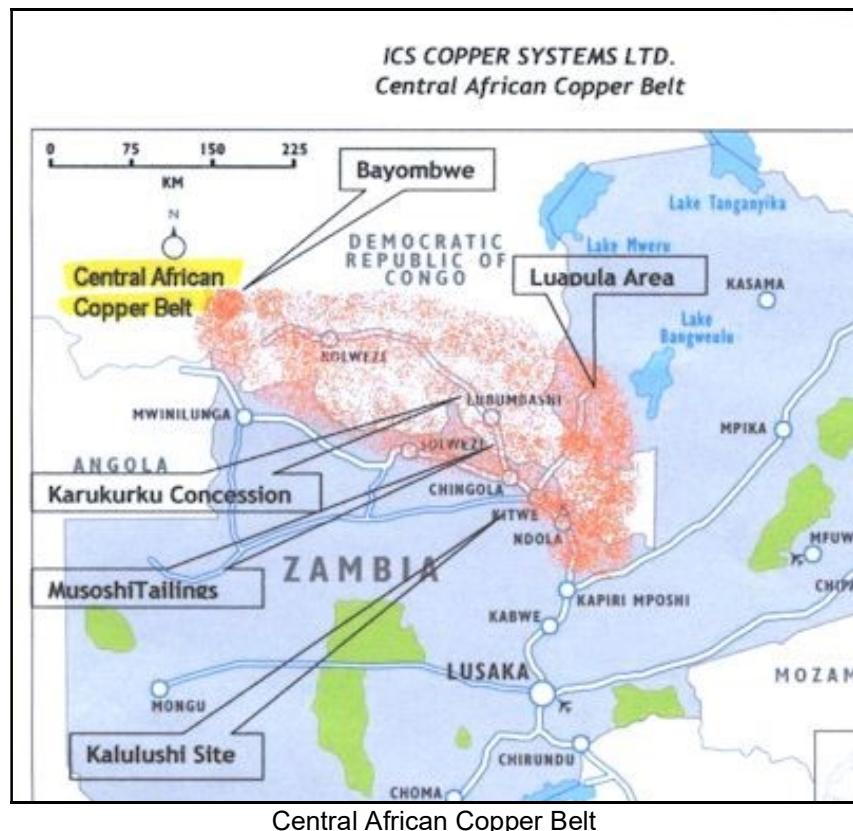
as 350°C. The solutions are mainly enriched in Cu, Fe and Zn. Solutions reach the surface (seafloor) via fractures in the seafloor. By rapid cooling sulphides like chalcopyrite (CuFeS_2), pyrite (FeS_2) and sphalerite (ZnS) are deposited.

There are NO examples of this class in the training collection.

2) ***Stratiform deposits*** occur in sedimentary basins associated with rifting. The hydrothermal solutions are formed from the dewatering of basin sediments, or can originate from rift related magmatism. The heat of the magmatic activity is the source for hydrothermal flow. Metals are leached from the sediments through which these fluids percolate. Metals are transported as chloride complexes. Brines from shallow convection are often enriched in copper (and cobalt). Because of deposition in specific clastic sediments or marine clays, clearly stratiform deposits are formed. Ore minerals are chalcopyrite, bornite (Cu_5FeS_4), carrolite (CuCo_2S_4), but also tennantite, chalcocite.

Examples of such deposits are found in the ***Central African Copperbelt***.

MICROSCOPY A sample of such an ore is found in specimen T-7 from the training collection. Here you find bornite and chalcopyrite, together with tennantite, sphalerite, and renierite ($(\text{Cu},\text{Ge})_3\text{FeS}_4$). The matrix contains quartz silicates and sometimes graphite. Carrollite can be found in just a few specimens.



Central African Copper Belt



Zambian Copper Mining in the 1970's

3) With **Sedimentary Exhalative (SEDEX)** ores, the origin of the hydrothermal solutions is seawater which intruded basin sediments. With depth, chloride concentration and temperature increase. Convection cells are being formed, , and metals are leached from the basin sediments. When these solutions reach the sea flow, they flow out, and can gather in depressions in the seafloor. Here sphalerite and galena are deposited. Mount Isa, Australia, is an example of this class of ore deposits.

There are NO examples of this class in the training collection.

4) Another class in this group of ores is the ores of the so-called **Mississippi Valley Type**. Formation water leaches metals form sediments during dewatering, as a result of increased pressure, when the sediments reach larger depths. The metal bearing solution migrates as a result of heat of nearby magmatic intrusions. In sediments which are formed in shallow water, by reduction of gypsum and anhydrite in evaporites H₂S may be released, which leads to the precipitation of lead and zinc as galena (PbS) and sphalerite (ZnS). The deposits are stratiform. They are named after deposits in the valley of the Mississippi.

There are NO examples of this class in the training collection.

2.3. URANIUM ORES

Such ores occur where 6-valent uranium is reduced of a 4-valent state. In a natural environment this occurs by pyrite, organic material or graphite. Uranium precipitates as uraninite. ***There are NO examples of this class in the training collection.*** (Not allowed, because of radiation safety measures).

2.4. AUTOCHTONOUS ORES

This is about ores which are formed by selective precipitation in specific sedimentary or weathering conditions. The processes take place under atmospheric temperatures and pressures. Separation of the metals takes place as a result of differing solubilities

in aqueous environments. These solubilities are caused by eH and pH conditions.

2.4.1. Seawater Deposits

a) Iron Ore Deposits

Well-known are deposits from shallow seas from the Proterozoic, called "Banded Iron Formation" (BIF). Specific for seawater deposits is the so-called Oxide Facies of the BIF. Precipitation took place over large areas along continental margins along shifting shorelines. This oxide facies consists of a variation of Fe-oxide (magnetite, hematite) layers and chert. In the deposits seasonal variations are present. Iron and silica were supplied by nearby landmasses. Iron and silica were also supplied by exhalation of seawater which was forced through basin sediments as a result of convection processes. Iron was leached from the sediments. Later supergene enrichment was possible by oxidation of magnetite to hematite. Remobilization of iron could take place flowed by precipitation as goethite. Later the deposits reached again a certain depth.

MICROSCOPY *A microscope sample of Precambrian iron ore, originally deposited in seawater can be found in specimen T-19. The iron ore of T-19 is a high grade detrinitic iron ore. The original ore was eroded, and re-deposited. This ore, from the Jack Hills in Australia comes from a region that belongs to the oldest parts of the Earth's Crust. Age determinations on zircons from rocks in the Jack Hills gave an age of 4½ billion year (!) They are the tough remnants of ancient rocks that have long since disappeared.*



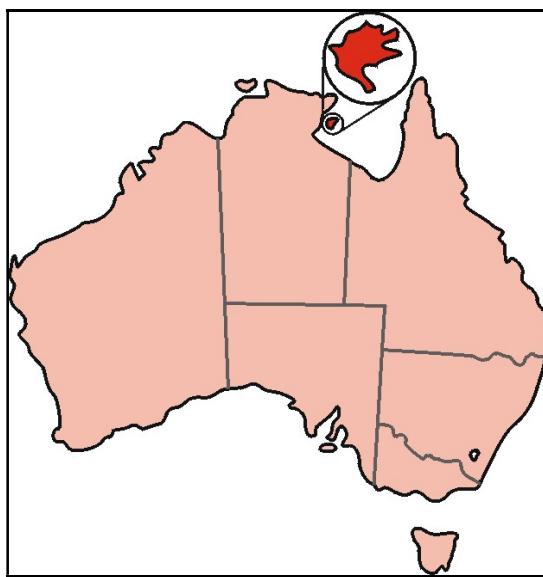
Jack Hills, Location



Jack Hills mine , W-Australia

b) Manganese ore deposits

This concerns shallow deposits in marine sediments and estuary sediments. They are deposited during periods of marine transgression at high sea levels. Mn often originates from Precambrian rocks with low Mn-contents. This Mn is liberated by weathering processes, and transported to the sea. This happened also for Fe. Certain chemical conditions (low eH) lead to different behavior for Mn (soluble) and Fe(insoluble). Fe and Mn were separated. Seawater in partially closed basins can be stratified, leading to parts with relatively high eH, and parts with relatively low eH. These waters mix not or almost not. (Cf. the Black Sea). Where these waters reach the shoreline, manganese deposits form, with Mn predominantly in the form of pyrolusite (MnO_2). When these ores reach higher eH-conditions, pyrolusite is insoluble. This gives rise to Mn-deposits with primarily pyrolusite. Examples Nikopol, Ukraine, Groote Eylandt, N-Australia.



Groote Eylandt, Australia.



Manganese mine, GEMCO, Groote Eylandt, Australia.

MICROSCOPY An example can be found in T-12, where an oölitic Mn-ore from India is shown. Mn is mainly present as pyrolusite, but also as psilomelane². You will also find later formed goethite, precipitated under higher eH conditions.



Pyrolusite

MICROSCOPY Also, you find in T-12 an example of a piece of material of a manganese nodule. Manganese nodules are well known from the Pacific Ocean, where they have been often found during dredging. As there is few land surface that can serve as a source for manganese, the metal must be almost entirely originated from volcanic activity. The manganese is generally present in the form of Mn-oxides or Mn-hydroxides. The size of the nodules is 1- 30 cm, with an average of 3cm. In size, they are generally comparable to potatoes.



Manganese nodule and potatoes.

Manganese nodules, contain, in contrast to the ores discussed above, appreciable amounts of iron.

² Discredited Mineral, 1982. Now a general term for hard, black Mn-oxides. Romanechite, $(\text{Ba},\text{H}_2\text{O})(\text{Mn}^{4+},\text{Mn}^{3+})\text{O}_{10}$, is one of the most common species.

2.4.2 Evaporites

Evaporites are precipitates of salts which under normal conditions are soluble in sea water or lake water. The most common form is rock salt or NaCl.

Evaporites form there where

- A water mass is not completely open to the sea
- The climate is such that natural evaporation exceeds rainfall.

In marine environments deposits are formed of for instance rock salt (NaCl), sylvite (KCl), gypsum/anhydrite, calcium carbonate etc. In continental environments one may find minerals like borax ($\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$) and colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$).

There are NO examples of this class in the training collection.

2.4.3. Supergene Deposits

a) Bauxites

Bauxites are the residues of weathering of aluminum rich volcanic or intrusive rocks. Conditions for bauxite formation are:

- 1) Warm tropical climate
- 2) Alternating dry and wet season
- 3) Softly undulating relief
- 4) Good downward drainage

Decaying vegetation supplies the percolating groundwater of organic acids. Feldspars are decomposed and altered into clay minerals. Residual clay gradually is altered into amorphous aluminum hydroxides, generally gibbsite. During the dry season the metastable amorphous gibbsite recrystallizes into stable crystalline gibbsite.

There are NO examples of this class in the training collection.

b) Lateritic Ni-ores

This concerns weathering products of Ni-bearing olivine. Olivine is easily hydrolyzed by hydrothermal or meteoric waters. An early weathering product is serpentine. Parent rocks are peridotites and related ultramafic rocks. Olivine from ultramafic rocks contains generally some nickel. Soluble Fe and Mg are transported by rainwater. Iron soon precipitates as goethite (FeOOH) or limonite ($\text{FeOOH} \cdot n\text{H}_2\text{O}$). Some Ni^{2+} adsorbs onto goethite, but the most of the Ni reacts with serpentine, forming garnierite³ ($\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$).

³ Garnierite (formerly $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$) is a discredited mineral. It is now a generic name for



c) *Gossan*

The weathered leached oxidic residues of (often, but not always) sulfidic ore deposits are called gossans. Gossan is usually a hard ferricrete horizon. Also they can be weathering products of oxidic iron ores. ***Gossans themselves are NOT considered ore, but are important indicators for ore deeper under the surface.***

MICROSCOPY In the training collection, you can find in T-10 an example of a gossan from Zambia, in which the original minerals (magnetite, hematite) but also the weathering products (goethite & limonite) are visible. Goethite and limonite cannot readily be distinguished under the microscope.

2.5. ALLOCHTONOUS ORES

Due to erosion, the land surface is slowly worn down. During transport mineral particles undergo sorting, and often also a size reduction. The sorting is a result of the working of gravity. When the mineral is less resistant against mechanical weathering, the grain size will also slowly decrease. Zones of weakness, such as cleavage planes may be very important in size reduction. Minerals without cleavage and great hardness often are not much reduced in size during the transport process. During sorting, density and grain shape are important.

Sorting may lead to formation of economically interesting mineral deposits. The minerals almost always share the following properties: high density, no or almost no cleavage, and chemical stability under weathering conditions. Minerals with these properties are oxides, ore oxidic minerals (e.g., phosphates), native metals and some silicates.

green nickel ore, which has formed as a result of lateritic weathering of ultramafic rocks.

Examples are for instance ilmenite, zircon, chromite, diamond, and rutile. Also quartz is sometimes concentrated in this way. The deposits are formed as a result of the action of sea currents or of rivers. Such deposits are called alluvial deposits or placer deposits.

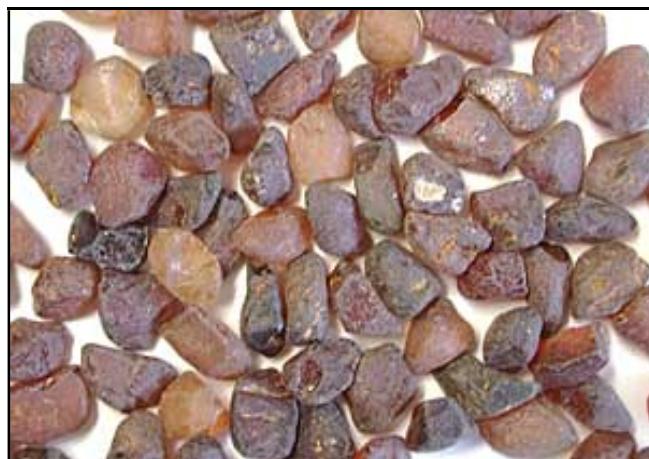
2.6. INDUSTRIAL MINERALS.

The definition of industrial minerals (and industrial rocks): mineral resources which are used because of their chemical or physical properties, and not to extract metals from them. In this Category: we find for instance clay, limestone, dolomite, ilmenite, rutile, and zircon.

Ilmenite and zircon occur usually in igneous rocks but are in general only available in economically interesting amounts in placers or in beach sands. Quartz, a common rock forming mineral, may in a barrier beach become thus concentrated, that the deposit is fit for economic winning of quartz for the production of silicon or of sand for glass manufacture.



Quartz-sand quarry of Sigrano, Heerlen, The Netherlands.



Zircon grains.

Below you will find a list of minerals that are found in placers and minerals that are

considered industrial minerals.

Some placer minerals.

Mineral	Formula	Application	Occurrence
Ilmenite	FeTiO_3	TiO_2 (white pigment), also for production of Ti.	As segregation in basic igneous rocks, or as accessory mineral. Winning in general from fossil beach sands.
Zircon	ZrSiO_4	Used as such, but also ore mineral for the extraction of Zr. Also a semiprecious stone.	Accessory mineral in granite. Mined from placers.
Rutile	TiO_2	Used as such (white pigment, Ultraviolet absorber). Also ore mineral for the winning of Ti.	Accessory mineral in felsic rocks. Mined from placers and fossil beach sands.
Monazite	(LREE,Th)(PO ₄)	winning of REE, sometimes Th.	Accessory mineral in felsic rocks., or in relation to carbonatites. Mined from placers and fossil beach sands
Xenotime	(Y, REE, U)PO ₄ REE = Sm, Gd, Eu, Er, Dy	winning of Y, REE.	Accessory mineral in felsic rocks. Mined from placers and fossil beach sands.

MICROSCOPY Several placer minerals can be studied in specimen T-14.

Some industrial minerals

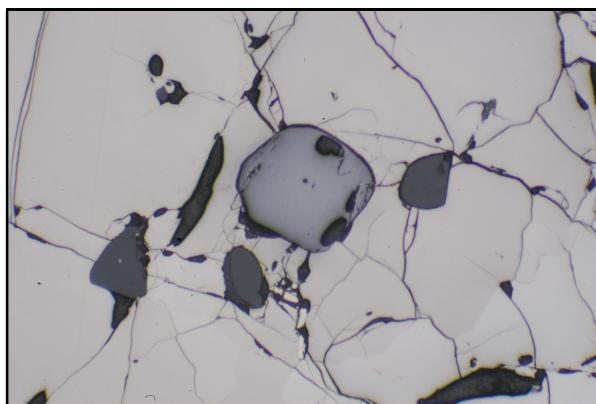
Mineral	Formula	Application	Occurrence
Quartz	SiO_2	Glass production, production van Si.	Mined from placers and fossil beach sands.
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	Glass manufacture, Chemical industry.	Dolomitic limestone, dolostone.
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{Cl},\text{F})$	Production of phosphorus or phosphorus-compounds.	Sediments (Phosphorites).
Quartz	SiO_2	Glass manufacture, Si-metal, Sicarbide	Placers, and/or fossil beach sands

The above mentioned industrial minerals, are better studied with a transmitted light polarization microscope, as they are not opaque.

3. TEXTURES IN ORES AND ORE MINERALS

The study of minerals and rocks requires more than just the identification of the minerals present. Also the interpretation of the textures, which are the special relationships between mineral grains, is important. The interpretation of textures is not only one of the most important aspects of the study of ores and rocks, but also one of the most difficult. The textures in rocks give a lot of information about the nature of processes, such as initial ore formation, but also re-equilibration after deposition or metamorphosis, deformation, annealing, or weathering as a result of meteoric influences.

However, the extent to which minerals retain their original composition and texture varies to a great deal. The nature of the mineral, temperature, and reaction kinetics are of course important parameters. It appears from research that oxides, bisulphides, sphalerite and arsenides are the most refractory with respect to re-equilibration. At the other end of the scale we find minerals like argentite (Ag_2S) and sulfosalts⁴. Pyrrhotite (Fe_{1-x}S) and the Cu-Fe-sulphides (chalcopyrite CuFeS_2 , and bornite Cu_5FeS_4) are approximately halfway this scale. However, crystals formed from a melt, may with changing melt composition during cooling become partly resorbed. This can be observed in the training collection in T-4 in somewhat rounded crystals of primary magnetite.



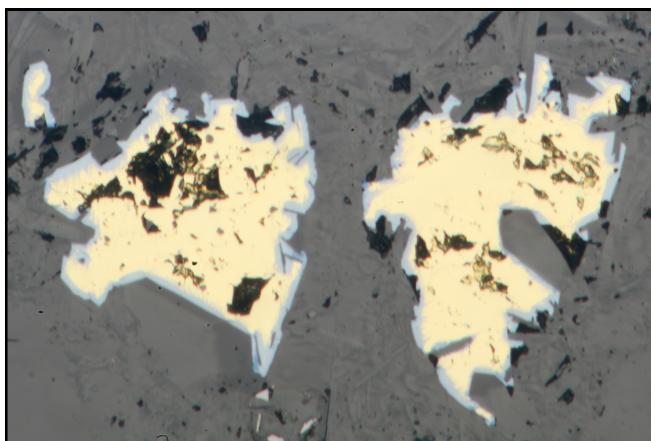
Rounded crystal of magnetite as a result of resorption. Specimen T-4.

Textures, mineralogy and composition of minerals or solid solutions mirror often several stadia in the history of the ore or rock. For instance, in a polymetallic ore pyrite, pyrrhotite, sulfosalts and native metals may occur. The morphology and inclusion patterns of the refractory pyrite may reflect initial HT-conditions, whereas the coexisting pyrrhotite has equilibrated at medium temperatures during a cooling phase. Sulfosalts may have equilibrated until the lowest temperatures. Finally, weathering processes may have superimposed textures on top of these. An example of a very complicated texture, which shows different stages of formation, is shown in specimen T-5.

⁴ A **sulfosalt** is a compound containing sulfur (S) **and** As, and/or Sb, or Bi. Examples are *orpiment*, As_2S_3 , *realgar*, AsS , *bismuthinite*, Bi_2S_3 , *tennantite*, $\text{Cu}_{12}\text{As}_4\text{S}_{13}$, *tetrahedrite*, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, *enargite* (Cu_3AsS_4), *luzonite* (dimorph of enargite).

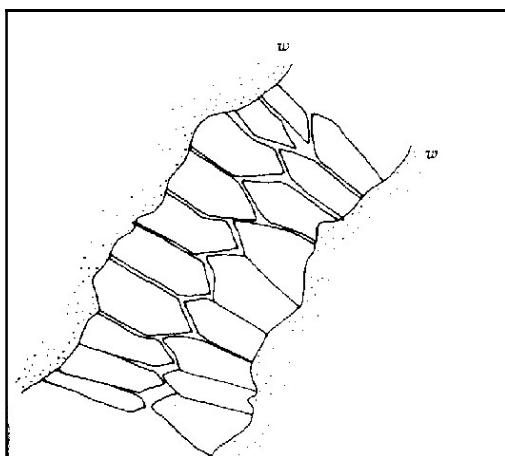
Also T-9b shows sometimes beautiful examples of reactions textures. Here the original mineral, galena, has reacted (sometimes not completely) to jamesonite. Original features of galena are often visible.

Interpretation and recognition of textures may also provide information with respect to the recognition of certain minerals. Chalcopyrite (CuFeS_2) often is altered to covellite (CuS) or digenite (Cu_9S_5). The blue covellite and digenite in minuscule grains may be difficult to identify, if one is restricted to measurement of reflection. Knowledge of the alteration reactions offers the possibility for identification with only minimal optical inspection (anisotropy, interference colors with crossed polars). Digenite is isotropic, and covellite is extremely anisotropic and has vibrant interference colors (red/orange). The difference is easily seen. Another example is pentlandite ($(\text{Ni},\text{Fe})_9\text{S}_8$), which often alters to violarite $(\text{Ni}, \text{Fe})_3\text{S}_4$. It is advisable to look in pentlandite crystals, which show some sign of alteration, for violarite.

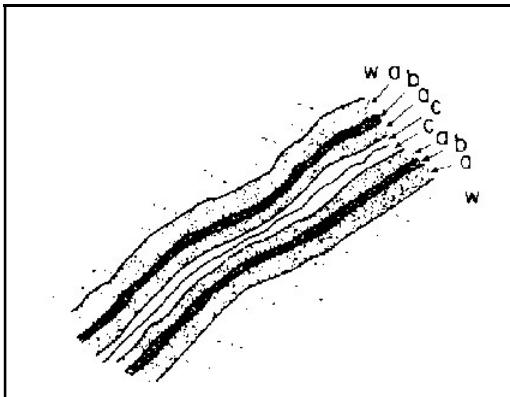


Blue (isotropic) digenite replacing chalcopyrite (yellow) at the rims, Los Bronces Mine, Chile.
Width of field 0.37 mm.

The figure below shows the growth of crystals from the walls of the crack into the fluid, leading to euhedral crystals. Crystallization as a result of changing fluid composition may lead to rhythmic banding.



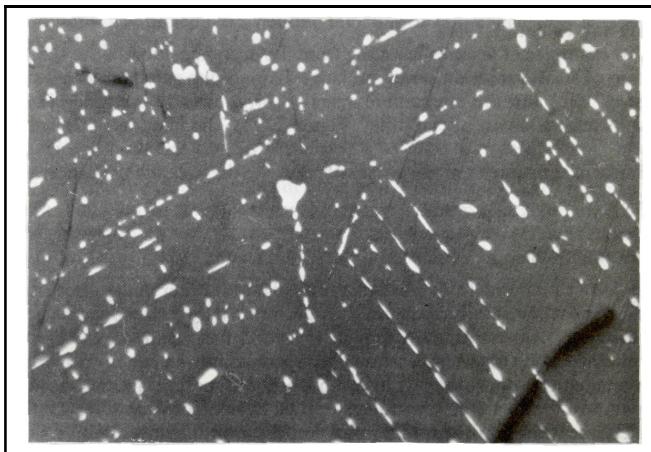
Crystals grow from the wall of a fissure into the fluid. After Craig and Vaughan (1994).



Rhythmic banding in a vein. After Craig and Vaughan (1994).

In the training collection specimen T-12 shows growth of crystals of lithiophorite from the rims of cavities into the once open voids, which are now filled with resin.

Sometimes textures may be misleading. A well-known example is the occurrence of oriented blebs of chalcopyrite. This seems to indicate demixing of chalcopyrite from sphalerite., but research indicated that the possibility of HT-solid solution of chalcopyrite in sphalerite is rather limited. Possibly the texture is the result of epitaxial growth of chalcopyrite nuclei on sphalerite surfaces, or it may be a replacement texture. .

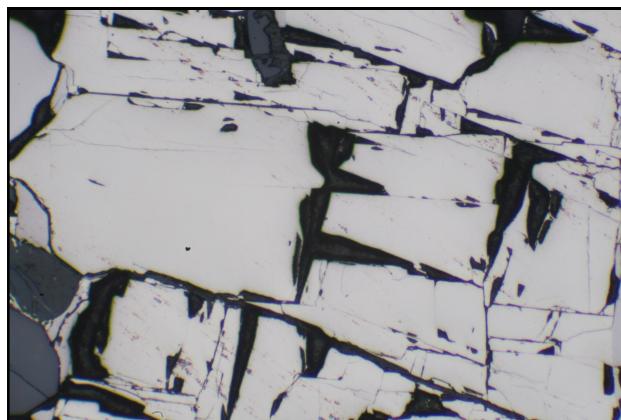


Oriented blebs of chalcopyrite in sphalerite. The oriented blebs are NOT the result of exolution. (After Craig and Vaughan, 1994).

Although demixing is well known from metallurgical systems, it is a rather rare phenomenon in mineralogy. An example of demixing is the occurrence of magnetite lamellae in ilmenite. This is however more complicated than it seems, as it appeared from research that the amount of magnetite-ilmenite solid solution at high temperatures is rather limited. But is not ilmenite that is the original phase, but ulvöspinel. On cooling the ulvöspinel may exsolve magnetite, while the ulvöspinel itself later oxidizes to ilmenite.

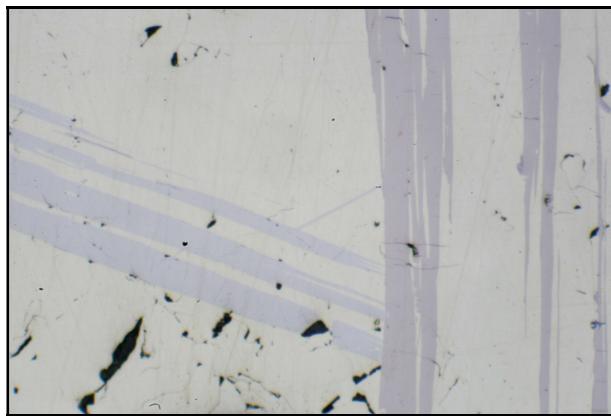
Most minerals have approximately the same thermal expansion coefficient, but this is not always the case. Pentlandite is an exception. On cooling pentlandite shrinks more than pyrrhotite and pyrite, with which it usually occurs together. Pentlandite upon cooling acquires opening fractures along its cleavage planes, leading to a somewhat

crumbling appearance. See for instance the specimens T-4 and T-8 in the training collection.



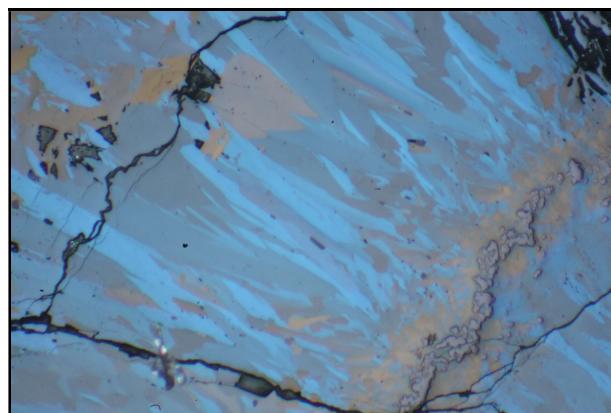
Opened cleavage planes of pentlandite. Specimen T-4

Some minerals may exhibit twinning. Twinning may be enhanced in such minerals by deformation. In the training collection this is apparent in specimen T-8, where ubiquitous twinning of cubanite may be observed.



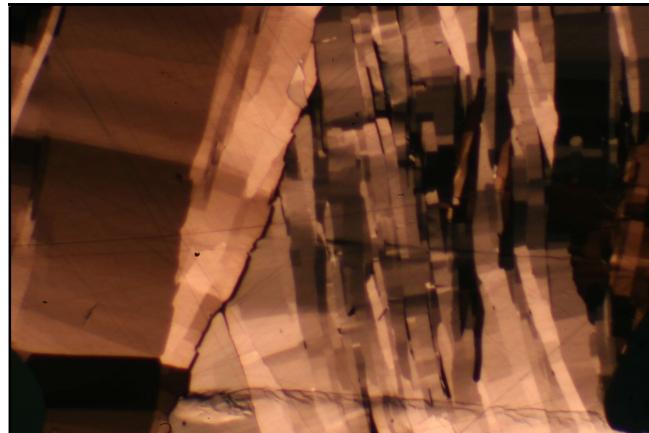
Deformation twinning lamellae in cubanite. Specimen T-8.

A clear example of deformation twinning is given in the image below, which shows deformation twinning lamellae in löllingite (Training collection T-6). The lamellae in deformation twinning are often irregular, but this is not necessarily the case.



Deformation twinning in löllingite. Specimen T-6.

Deformation of minerals may lead to **undulose extinction** (**undulatory extinction**).. This can clearly be observed in the covellite crystals of specimen T-3.



Undulose extinction in covellite. The alternating, zonal change of the interference colors is due to deformation. Specimen T-3.

4. REFERENCE

Craig, J.W. and Vaughan, D.J. (1994) *Ore Microscopy and Ore Petrography*. 2nd edition, John Wiley and Sons, New York. 434 pp.

5. OVERVIEW OF THE ORES OF THE TRAINING COLLECTION

T-1	Mesothermal Pb-Zn vein ore. Casapalca, Peru.	page 11
T-2	Epithermal Au-ore, Sumatra, Indonesia.	page 13
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T-6	Hydrothermal Ni-Co-As vein ore Cobalt, Canada.	page 9, 10
T-7	Stratiform Cu-Co-(Ge) ore, Congo.	page 15, 16
T-8	Magmatic Cu-Ni ore, Sudbury, Canada.	page 8
T-9A/B	Hydrothermal Ag-Pb-Zn ore, Pribram Czechia.	page 12
T-10	Supergene Fe-ore, Zambia.	page 22
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T-15	Industrial material: Cu-Ni matte, INCO, Sudbury, Canada.	page 67
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T-18	Hydrothermal Sn-ore, greisen association, Indonesia.	page 9
T-19	Iron ore, Jack Hills, W-Australia.	page 17

6. THE CHEMICAL FORMULAS OF SOME COMMON OPAQUE MINERALS

The formula given below is an ideal formula.

Mineral	Chemical formula	Remarks
Anatase	TiO ₂	Polymorph of rutile
Arsenopyrite	FeAsS	Most common arsenic-containing mineral.
Bornite	Cu ₅ FeS ₄	
Cassiterite	SnO ₂	
Chalcopyrite	CuFeS ₂	Name means “copper-pyrite”.
Chalcocite	Cu ₂ S	
Chromite	FeCr ₂ O ₄	Member of the spinel group.
Covellite	CuS	
Digenite	Cu ₉ S ₅	
Galena	PbS	Name originates from Latin.
Goethite	FeOOH	
Hematite	Fe ₂ O ₃	
Ilmenite	FeTiO ₃	
Loellingite	FeAs ₂	Name also spelled as löllingite
Magnetite	Fe ₃ O ₄	Member of the spinel group. Formula also written as FeFe ₂ O ₄ . Most well-known magnetic mineral.
Marcasite	FeS ₂	Polymorph of pyrite.
Molybdenite	MoS ₂	Only molybdenum ore mineral.
Nickeline	NiAs	In the past known as niccolite.
Pentlandite	(Fe, Ni) ₉ S ₈	
Pyrite	FeS ₂	Dimorph of marcasite.
Pyrrhotite	Fe _{1-x} S	May exhibit magnetic properties, depending on the exact composition.
Pyrolusite	MnO ₂	
Rammelsbergite	(Co, Ni, Fe)As ₂	
Rutile	TiO ₂	Polymorph of anatase.
Scheelite	CaWO ₄	
Sphalerite	ZnS	Polymorph of wurtzite.
Tennantite	Cu ₁₂ As ₄ S ₁₃	Complete solid solution with tetrahedrite.
Tetrahedrite	Cu ₁₂ Sb ₄ S ₁₃	Complete solid solution with tennantite.
Ulvöspinel	Fe ₂ TiO ₄	Member of the spinel group
Wurtzite	ZnS	Polymorph of sphalerite.
Wuestite	Fe _{1-x} O	Name also spelled as wüstite.

Part II

Ore Microscopy

1. INTRODUCTION

To determine the composition of an ore or raw material, a simple chemical analysis is not enough. To make a scheme for the technological processing of an ore, one must study the material using different approaches. One of them is microscopical study. Many ores and intermediate products consist of opaque phases, which make transmitted light microscopy impossible.

In the study of ores, a number of questions can be answered by microscopic study.

- 1) Which phases are present ?
- 2) How much valuable material is present and in which phases is it present ?
- 3) What is the grain size, and what is the shape of the grains ?
- 4) How is the intergrowth of coexisting phases ?
- 5) What are the shape, size and distribution of pores (if present) ?
- 6) What is the spatial distribution of important phases, with respect to later liberation ?
- 7) In case of liberation: are the desired particles liberated or not in a specific milling step?

Usually, in combination with microscopy also micro-analysis (electron microprobe) and quantitative image analysis is used. With electron microprobe of very small grains a qualitative or quantitative chemical analysis can be made. With quantitative image analysis microtextures can be analyzed.

2. MICROSCOPICAL DESCRIPTION OF OPAQUE MINERALS

In this chapter we will pay attention to a series of parameters, which can be determined with the polarization microscope. Also an overview is given which optical properties are important for the determination of opaque minerals. An elaborate treatise of the optics of reflected light microscopy is beyond the scope of this manual. In Appendix 6 a short overview is given. One can subdivide the microscopically determinable features in 2 groups, based on whether the analyzer is used or not used.

Observations with parallel polars

- *Color and reflection pleochroism*
- *Reflection and bireflection*
- *Morphology of crystals, cleavage, zoning, texture.*
- *Polishing hardness.*

Observations with crossed polars

- *(An)isotropy*
- *Internal reflections.*

2.1. Observations with parallel polars

2.1.1. Color and reflection pleochroism

The explanation why a mineral has a color under the reflection microscope is related to reflection. The intensity of reflected light from a polished surface not necessarily is the same for every wavelength. When white light is used, some wavelengths may be more strongly reflected than others. This may result in a noticeable color. Sometimes the color is very strong. The colors of ore minerals in general are weak to very weak.

The human eye functions better with respect to the registration of contrast (comparative situations) then with respect to absolute color values. This results in the phenomenon that the color perception of a mineral may be influenced by the surrounding minerals. Perception of color is, however, strongly depending on the person, and there may be differences between the color as perceived by different people. Also the description of the color may be expressed different by different people (for instance yellowish white, beige, vivid white, brownish white, etc. may all be a description of the same shade of white). Color sensation is also dependent on the illumination used. Illumination and light optics also change with microscopes (make, alignment, etc.).

However, a large number of colors may be identified by many people unambiguously, so color may be used as a selection criterion.

Examples of strongly colored ore minerals: chalcopyrite (greenish yellow), covellite (bluish colors) nickeline (pinkish orange), bornite (orange, brown or pink), renierite (orange), digenite (light blue).

Examples of weakly colored ore minerals: chalcocite (bluish grey), sphalerite (grey), pyrite (yellowish white), magnetite (brownish grey, grey, brown).

For anisotropic minerals the reflection of light of a specific wave length may be depending on the orientation of the crystal. Color differences may be observed depending on the orientation: **reflection pleochroïsm**. Reflection pleochroïsm occurs always together with bireflection. Where in the following pleochroïsm is mentioned, always reflection pleochroism is meant.

Some examples of pleochroïtic minerals are: covellite, molybdenite, pyrrhotite, cubanite, proustite.

2.1.2. Reflection

The intensity of the *reflection (R)* may be measured with a photo-electric cell and a millivolt meter. The intensity of the reflection may vary with the orientation of the mineral grain. This change of reflection with orientation may be used for identification. The maximum difference in reflection that can be measured on a mineral is called the *bireflection (ΔR)*. **Minerals with a noticeable bireflection are**

anisotropic. By the way, the bireflection not necessarily results in a noticeable pleochroïsm: the color difference may be too faint to be observable.

$$\Delta R = R_{\max} - R_{\min}$$

2.1.3. Crystal Morphology, Cleavage, Zoning, Texture.

When crystals can grow without or with minimum restrictions, specific morphologies develop. The shape of the crystal depends on the crystal structure. In many cases the form is characteristic for a mineral. Examples are the cubic crystals of pyrite and galena. Such well-formed crystals are called *euhedral* (or *idiomorphic*). Crystals that do not show a typical morphology are called *anhedral*.

For the crystal shape, the following division is used: *isometric crystals*, *elongated crystals*, *bladed crystals*.

Examples: **pyrite** (isometric, "cubes"); **arsenopyrite** (elongated), **jamesonite** (elongated, needles, fibers); **covellite** (bladed).

Because in a polished section only a 2-dimensional image is visible, it is not always possible to identify the shape. This may even be impossible.

A special case is dendritic crystals: they are formed under extreme non-equilibrium conditions, often during rapid cooling.



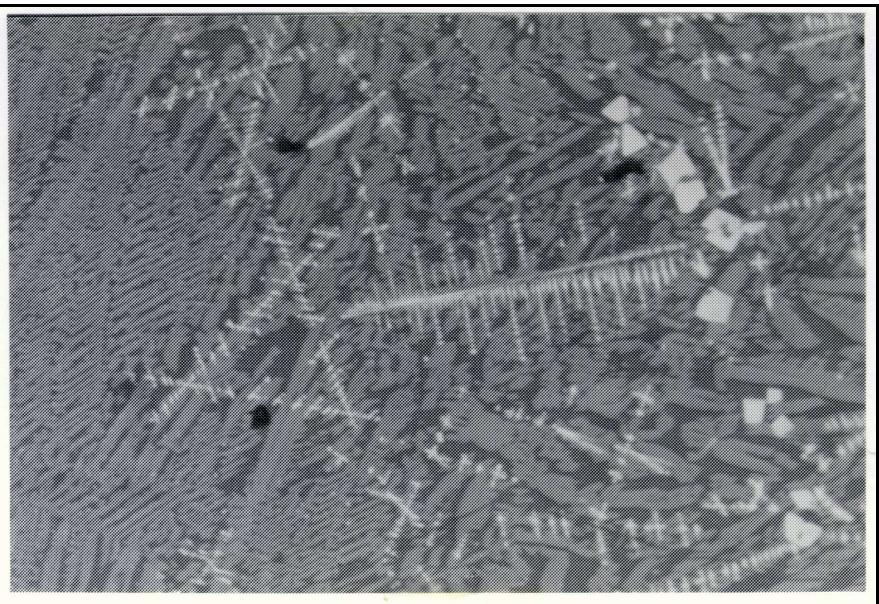
Isometric crystals of pyrite.



Bladed (tabular) crystals of covellite.



Elongated crystals of jamesonite.



A microscopical image of dendritic crystals in a polished section.



Dendritic crystals (of ice) in 3D.

Cleavage is also caused by the crystal structure and thus may serve for determination.
Example: galena, millerite.



Galena. Its three perpendicular cleavage directions are clearly visible.

Zoning: zoning may be chemical (compositional gradient) or physical (zones with inclusions). Zoning is seldom determinative, but may be of use. Zoning is often very important with respect to the formation of rocks. The occurrence of large amounts of inclusions is of course also relevant for ore processing.

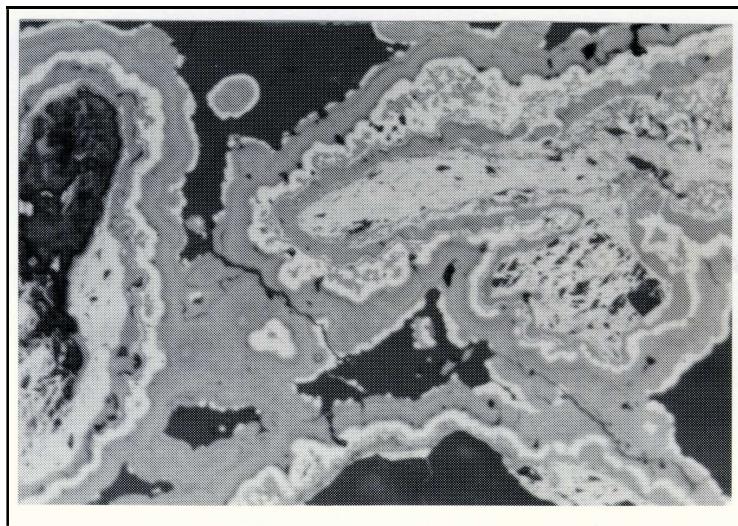


Zoning in sphalerite, due to difference in Fe-content.

When mentioning texture, this is about issues as intergrowths, grain size, shape of grains, grain size distribution, lineation in the rock. Most ores are have no porosity.. Intergrowths and grain size (distributions) are important for mineral processing. For identification this is in general not of importance.

Colloform Texture: there are minerals that occur in a specific texture. An example is a so-called colloform texture. Minerals in a colloform texture often are precipitated from colloidal solutions. The appearance of the aggregates is often more or less spherical or ***botryoïdal*** (which means: like a bunch of grapes). In these cases one should be aware of the possibility of dealing with cryptocrystalline aggregates.

Cryptocrystalline is a rock texture made up of such minute crystals that its crystalline nature is only vaguely revealed even microscopically in thin section by transmitted polarized light. Crystal sizes are thus submicroscopic. In general, the minerals in such textures can only be determined by other techniques (x-ray diffraction, electron probe micro-analysis, scanning electron microscopy). Cryptocrystalline textures may give the suggestion to consist of optically isotropic minerals, but this may not at all be the case (although it is possible).



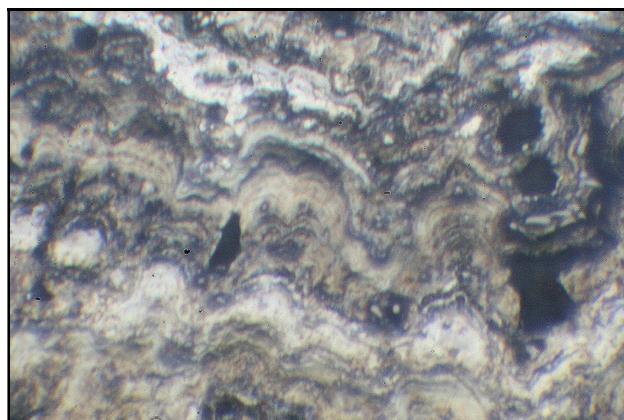
Colloform texture, microscopic image.



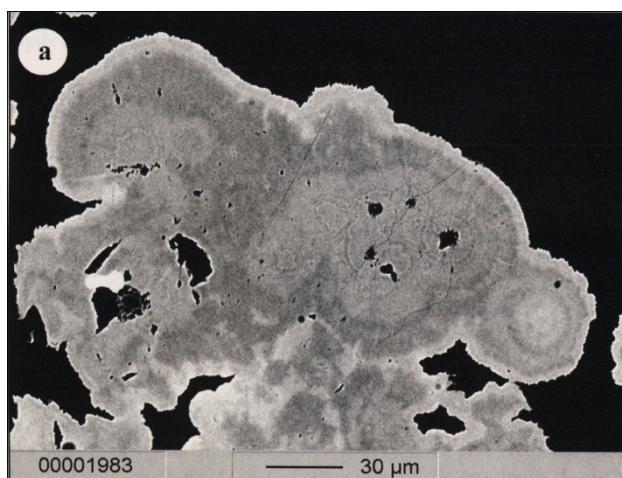
Minerals with a colloform habitus appear macroscopically ***botryoïdal***
(= like a bunch of grapes).



Colloform texture in a polished hand specimen.



Colloform texture (micron scale) in a manganese nodule. Light microscopy.



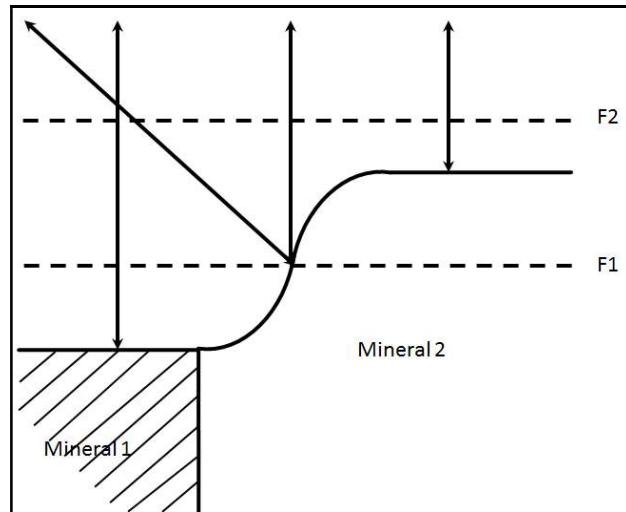
Colloform texture in arsenian pyrite. SEM-image.

2.1.4. Polishing Hardness

Due to differing hardness of minerals, during polishing a relief is formed. In microscopy, light is scattered on the flanks of the harder grain. This leads to the appearance of a white line, similar to the Becke⁵-line, but different in origin. This

⁵ After Friedrich Johann Karl Becke, Austrian mineralogist (1855 - 1931)

light line, called the **Kalb⁶-line**, can best be observed with a closed aperture diaphragm. This line is not visible if the interface is in focus, but becomes visible if the microscope is focused above the hardest grain (F2). The white line moves to the **softer** one of the two grains if the table of microscope is **lowered** (= increasing the free working distance). The Kalb-line is sometimes called the pseudo-Becke line.



The scattering of light on the flank of the hardest grain causes the Kalb-line to appear. This line is NOT visible if the microscope is focused on plane F1. Focusing on F2, or near F2 makes the line appear.

2.2. Observations with crossed polars.

2.2.1. Anisotropy

When minerals are studied with crossed polars, anisotropic minerals will show interference colors. So far this is comparable to the situation in transmitted light microscopy. However, the optics of ore mineralogy is far more complicated. The light being reflected back from the mineral surface is **not linearly polarized**, but **elliptically polarized**. It is beyond the scope of this text to explain all the optical phenomena in detail. (However, see Craig and Vaughan, 1994, Ch. 4, for a clear explanation).

Anisotropy occurs for crystals with non-cubical symmetry. Just like in the optical mineralogy of transparent minerals, they can be subdivided in uni-axial and bi-axial minerals. This subdivision is, however, never used, because in many cases, uni-axial and bi-axial minerals cannot be clearly distinguished. Also konoskopic observations using a Bertrand lens (interference figures, in Dutch called “assenbeelden”) are not applied. If konoskopical observations are to be meaningful, a light path **through** the crystal must exist. This is not the case for opaque minerals.

Thus: Konoscopic procedures are useless in ore microscopy. See also Appendix 6. This also means that we cannot distinguish uni-axial and bi-axial crystals in a simple way. Also the determination of the optical sign is almost impossible. As a result the determination of ore minerals is a lot more complicated, and also less accurate than

⁶ After Georg Kalb, German mineralogist, early 20th century.

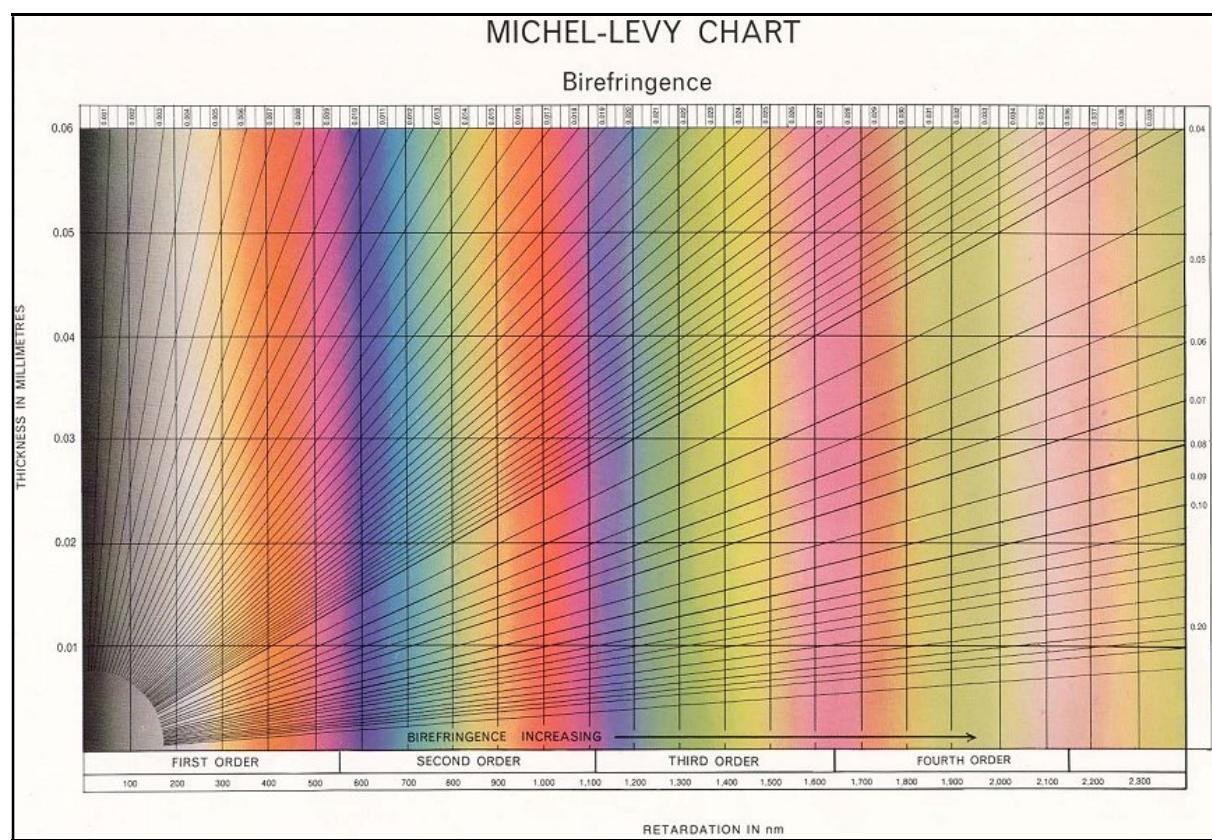
the determination of transparent minerals. A reflection microscope for polarized light (“ore microscope”) only has a Bertrand Lens if the microscope can also be used intransmission mode.

Anisotropy in reflection is caused by:

- 1) Difference in phase
- 2) Difference in amplitude.
- 3) A combination of both.

It appears that interference colors are often more clearly observed when the polarizers are not perfectly crossed (at 90° angle), but turned from that position for 4 or 5°. This is mainly the case for weakly anisotropic minerals, and therefore also for the determination of the anisotropy class

Unlike the birefringence in transmitted light microscopy, it is not necessary to quantify the anisotropy precisely. This is also quite difficult, as interference colors in reflection are **NOT** simply related to each other, as is the case in transmitted light polarization microscopy (*Michel-Levy Chart*, with colors in the 1ste, 2e, 3e order etc.).



The Michel-Levy color chart for birefringence. In ore microscopy this chart is **NOT** applicable.

Because in the case of reflection, in general a clearly visible **dispersion** occurs, the interference colors usually are (in terms of the transmitted light polarization microscopy) “anomalous”: they do **NOT** appear in the Michel-Levy color chart. Arsenopyrite (FeAsS) is a rare exception: it shows blue/green/yellow second order

interference colors.

In general a more or less arbitrary subdivision is made in:

- "Extremely anisotropic" (EA)
- "Strongly anisotropic" (SA)
- "Distinctly anisotropic" (DA)
- "Weakly anisotropic" (WA)

Of course, **bireflection**, if measurable, is also a measure for the anisotropy, but the measurement of bireflection is in general not accurate enough to quantify the subdivision given above. When measured in monochromatic light, such quantification indeed often *can* be made. Nevertheless, bireflection of uncorrected lamplight is an important piece of data. The microscope should be used at a **medium or low magnification**, and the **blue filter** should be **switched off**.

For practical use, the subdivision given above can be characterized as follows:

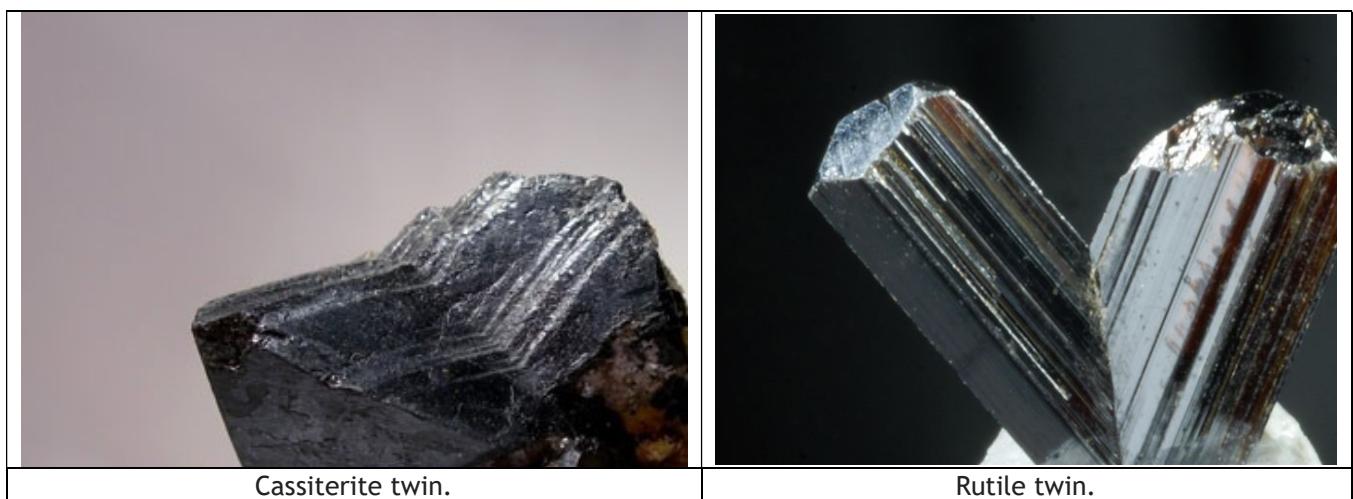
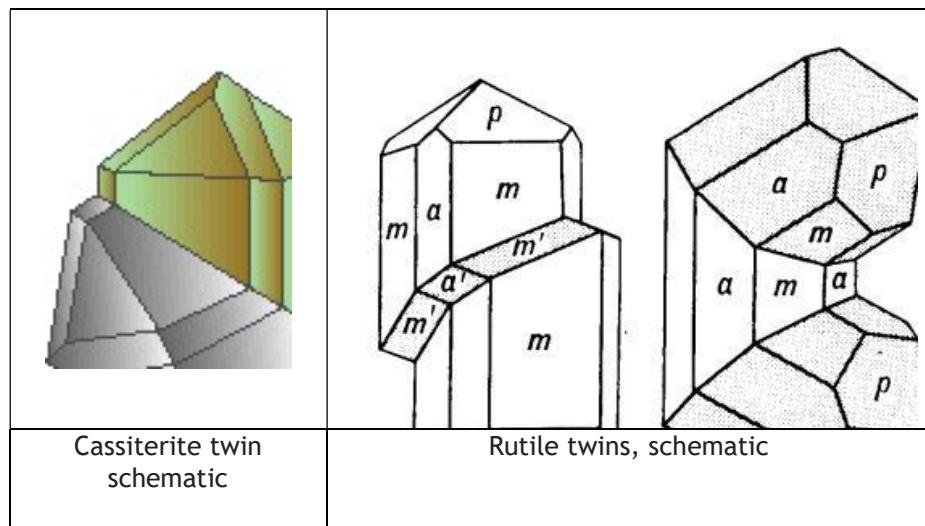
- **Extremely anisotropic (EA):** interference colors are very strong. They are visible at perfectly crossed polars (90°) crossed polars, and at low light intensity (transformer approximately at position 4).
Examples: covellite, lithiophorite, mackinawite.
- **Strongly anisotropic (SA):** the interference colors are vibrant and clear. Perfectly crossed polars (90°), and maximum light intensity.
Examples: marcasite, pyrrhotite, rammelsbergite, nickeline (niccolite).
- **Distinctly anisotropic (DA):** Greyish and whitish interference colors, sometimes still vibrant. Well visible at 90° crossed polars, and maximum light intensity, and better when the polars are 2° out of the 90° -position. This is approximately half the distance between two scale marks on the analyzer of the DM-LP-microscopes.
Examples: cassiterite, hematite.
- **Weakly anisotropic (WA):** Interference colors are grey, brown, and bluish. Very difficult, or even not at all visible at maximum light intensity with perfectly crossed polars (90°). Much better visible when the polarizer is 5° out of the 90° position. On the DM-LP microscopes this is 1 mark on the scale of the analyzer
Examples: chalcocite, bornite.

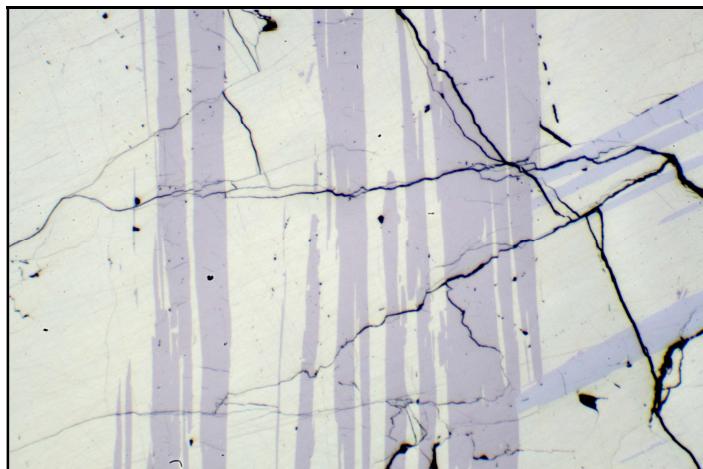
Isotropic minerals (minerals with a cubic symmetry) have **no** interference colors.
Examples: pyrite, skutterudite, sphalerite, tennantite.

It is advisable to study more than one grain when determining the anisotropy. The observed anisotropy may be strongly dependent on the direction in the crystal. Compare this with finding the birefringence in studying transparent minerals: one should look in that case for “the highest interference color”, in order to determine the

correct value for the birefringence. In studying ore minerals also the maximum effect should be looked for. When there is doubt about the anisotropy class, one may indicate that the anisotropy is in between two classes, e.g. I-WA, Isotropic - Weakly Anisotropic, or SA – EA, Strongly Anisotropic - Extremely Anisotropic.

Twinning is with anisotropic minerals best visible with crossed polars. By the way, cubic minerals can also exhibit twinning (for instance of pyrite twinning is well known). Twinning can appear in many forms. For ore microscopy the type of twinning is important: singular or multiple twinning (lamellar, cyclic). Examples are for instance *chalcopyrite* ($CuFeS_2$) and *cubanite* ($CuFe_2S_3$), both lamellar; *rutile* (TiO_2) and *cassiterite* (SnO_2), both singular. *Stannite* (Cu_2FeSnS_4) may even show raster-like twins, like microcline. Of *arsenopyrite* ($FeAsS$), besides *twins* also *triplets* are known.

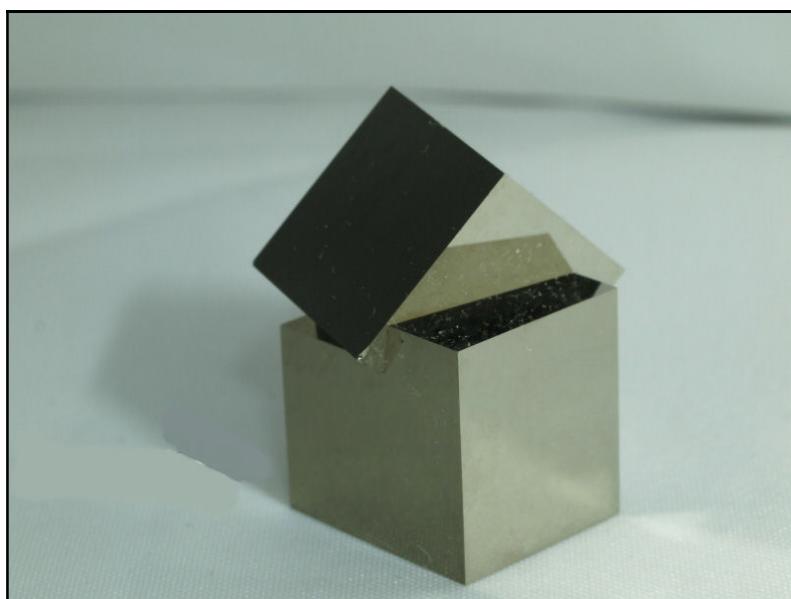




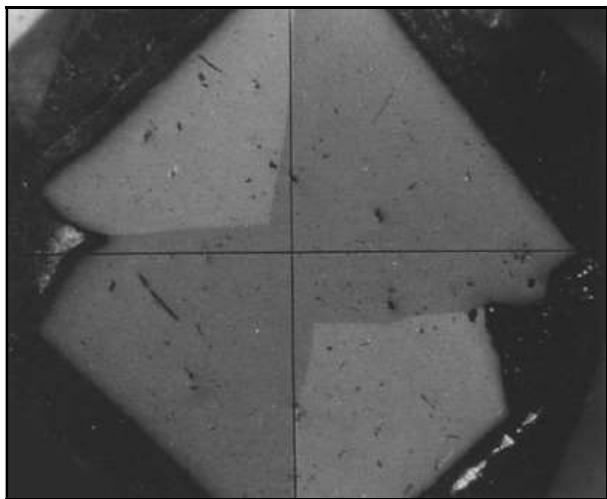
Lamellar deformation twins in cubanite (CuFe₂S₃)



Pyrite twins

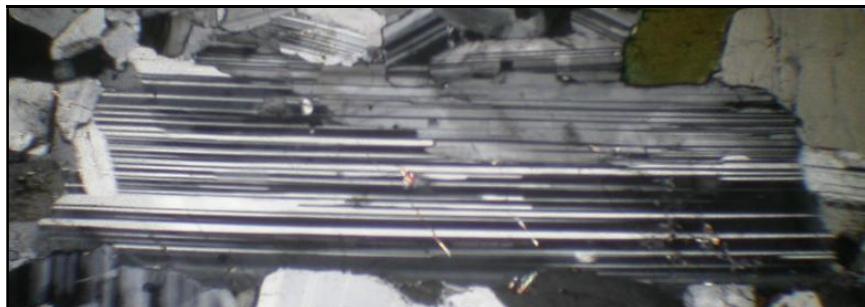


Pyrite twins



Pyrite twin in a polished section (a so-called “iron cross”).

N.B.: Also the transparent minerals may be *anisotropic* (WA, DA, SA, EA), and **also** may *show twinning* under an ore microscope (e.g. feldspars, like plagioclase).



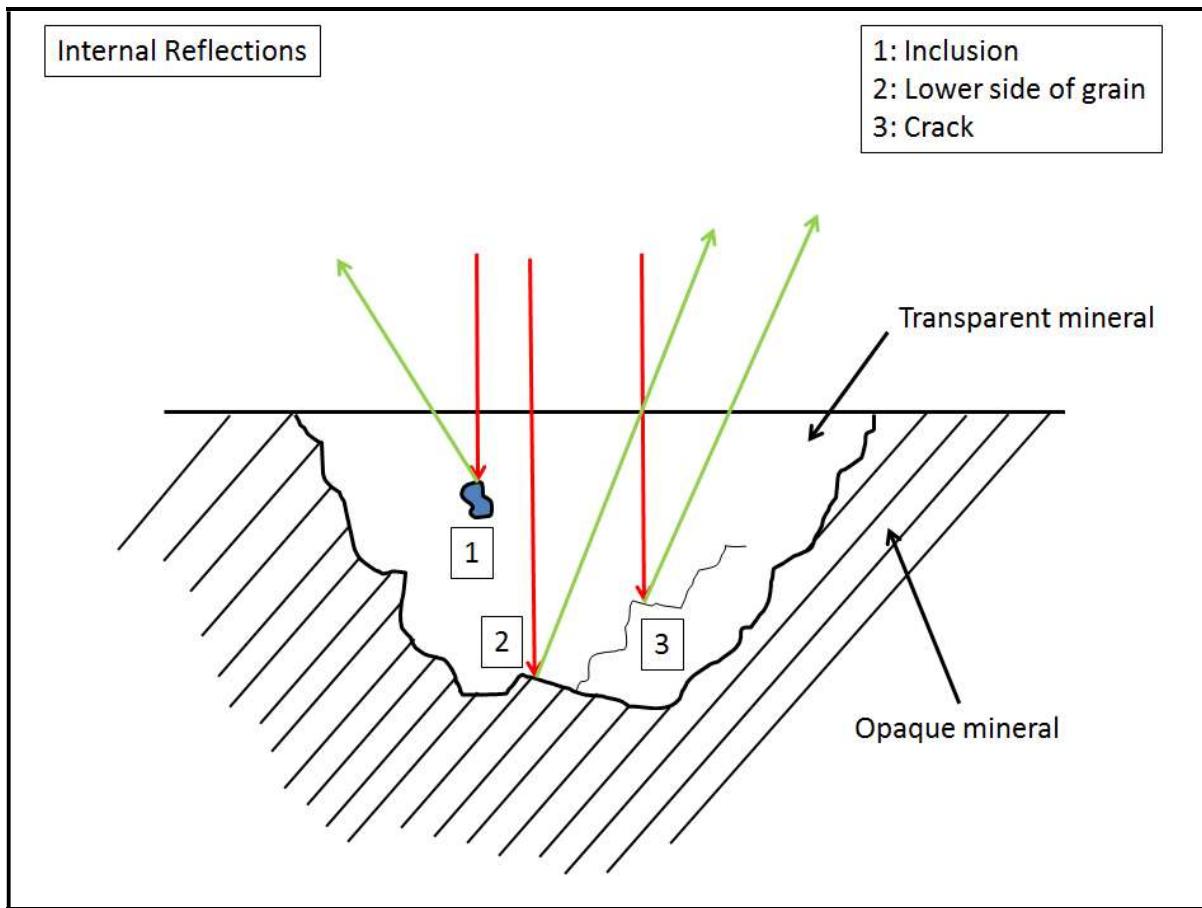
Lamellar twinning in plagioclase (a silicate). The mineral is strongly anisotropic. Although this is a picture from a thin section, it may also be visible in a polished section.

2.2.2. Internal Reflections

Internal reflections are formed under the surface of the specimen in transparent minerals at defects (cracks, cleavage planes, inclusions), or at the boundary of the crystal at depth. Not always the whole spectrum of light is reflected, and the mineral is (somewhat) transparent for certain wavelengths (often long wavelengths, e.g. red and yellowish colors. This light can then be reflected at defects or the boundary of the crystal, to emerge again from the surface.

In this way the specific colors of the internal reflections of certain ore minerals may be explained. It seems as if the mineral is lighted up from below. At rotating the table of the microscope, the internal reflections may remain the same, change or disappear. Internal reflections of course are normal for transparent minerals in the specimen (in

general silicates). Because they transmit a large part of the visible spectrum, their internal reflections in general are multicolored, but this does not have to be that way. For opaque minerals with a reflection > 40%, internal reflections are extremely rare.

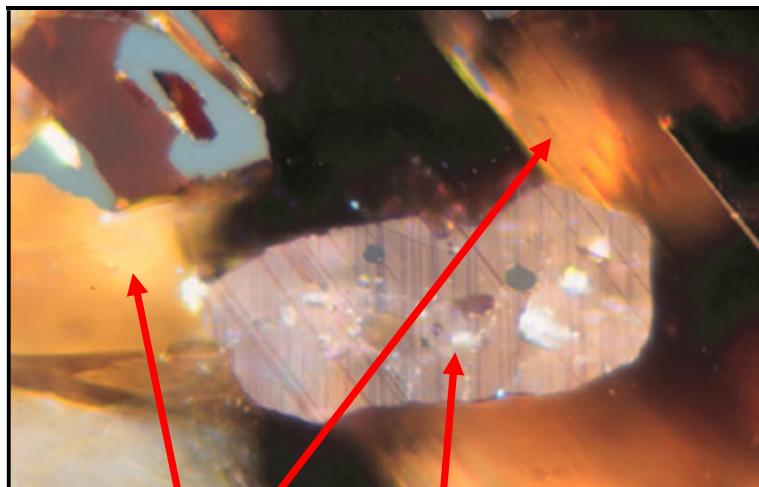


Internal Reflections (schematic)

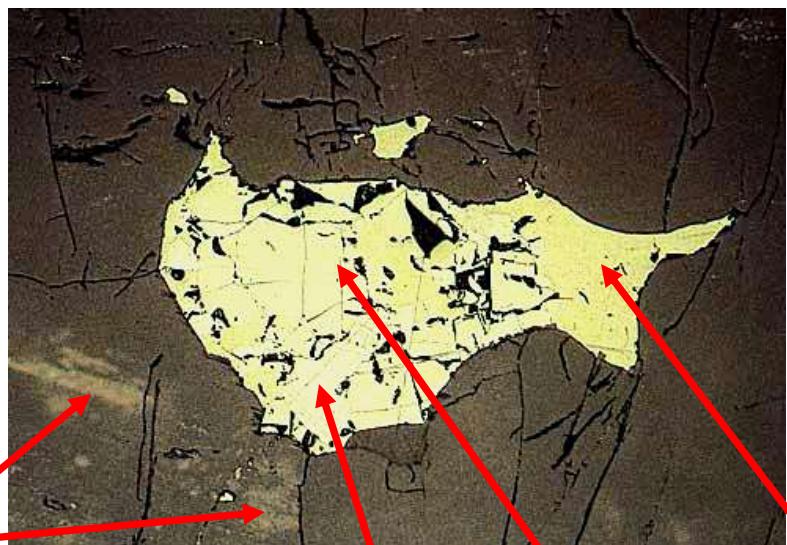
To make internal reflections visible, usually one must apply a low or medium magnification (10x, 20x). The blue filter must be switched off, and the analyzer should be switched on. The latter blocks the rays reflected from the surface to a great extent. Sometimes the internal reflections are that strong, that they can be seen with the analyzer off.

Examples of minerals with internal reflections:

- | | |
|---------------------------|---|
| - white, milky, cloudy | carbonates, quartz |
| - yellow, yellowish brown | cassiterite, sphalerite |
| - orange | goethite, zinkite |
| - red | cuprite, hematite, pyrargyrite, proustite |
| - brown | cassiterite, sphalerite, chromite |
| - reddish brown | rutile |
| - many colored | silicates |



Internal reflections and grain at the surface



Internal reflections in gangue. The ore grain consists of pentlandite (left), chalcopyrite (right) and pyrite (bottom).

3. SHORT DESCRIPTION OF THE POLISHED SECTIONS IN THE TRAINING COLLECTION (T-COLLECTION).

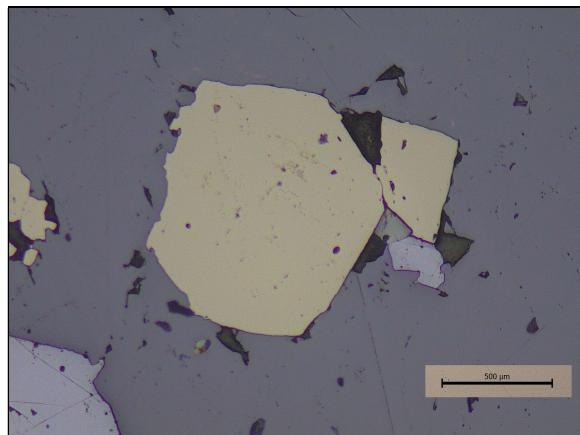
The descriptions given here are very short, and are intended to give an overview of the minerals present, so that they may be easier traced. Example images of minerals in these polished sections are given.

Abbreviations: *I* = Isotropic, *WA* = Weakly Anisotropic, *DA* = Distinctly Anisotropic, *SA* = Strong Anisotropic, *EA* = Extremely Anisotropic, *R* = Reflectance

Polished section T-1

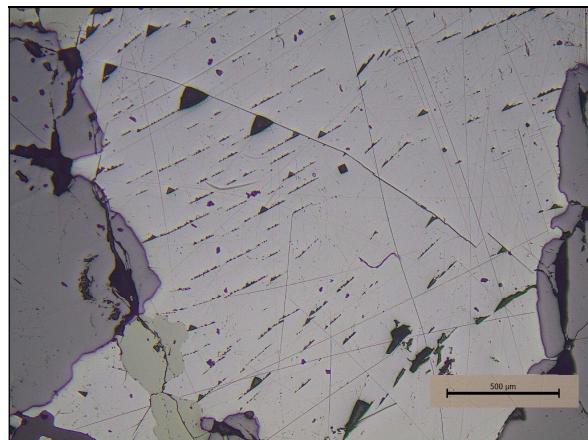
Pb-Zn ore, Casapalca, Peru

Pyrite - Chemical composition: FeS₂.
Light yellow,
Optical Category: I - WA.

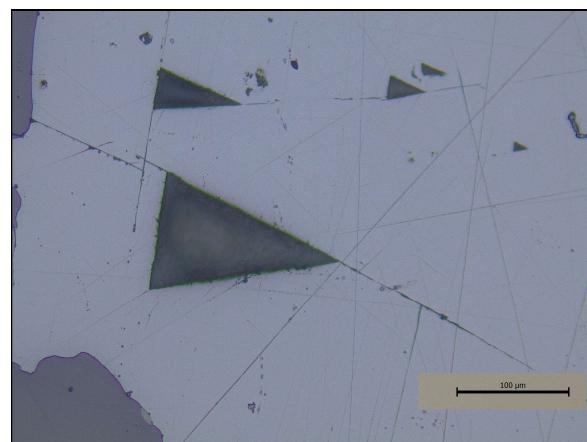


More or less euhedral pyrite (center). Euhedral crystals are those that are well-formed with sharp, easily recognized faces. The opposite is *anhedral*.

Galena - Chemical composition: PbS.
Whitish grey,
Optical Category: I, with triangular pits.
Mark the three cleavage directions of galena.
Triangular pits are formed by crosscutting of the three cleavage directions of galena in the plane of the thin section. During polishing, triangular sections of this rather soft mineral are torn out.



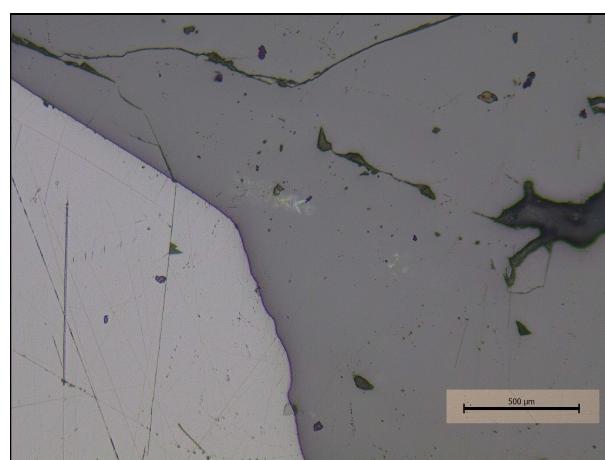
Galena with clearly visible cleavage.



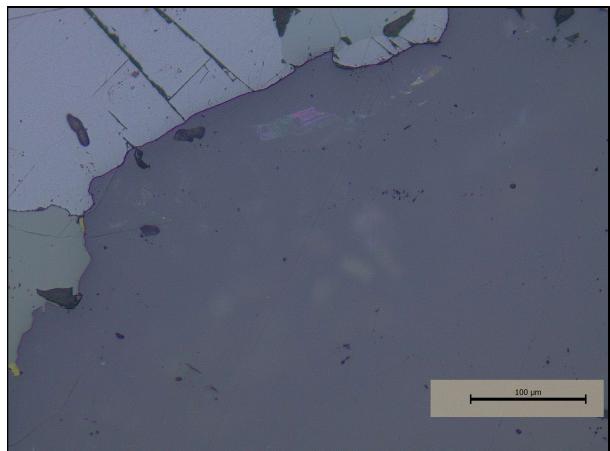
Clear triangular pits in galena. The three cleavage directions are clearly visible, as well as scratches.

Sphalerite

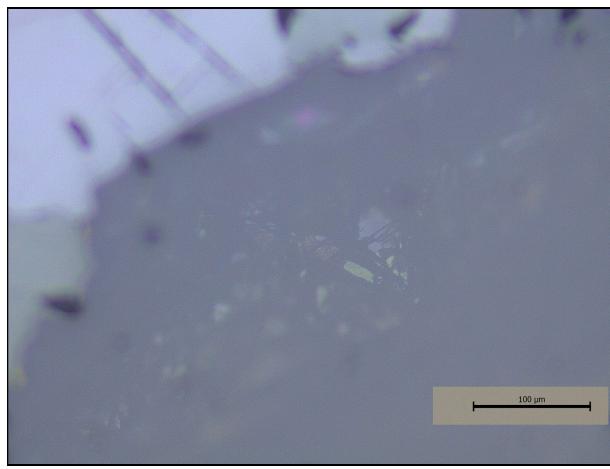
- Chemical composition: ZnS.
- Grey,
- Optical Category: I



Sphalerite (grey, right) and galena (white, left). In the center region internal reflections are visible. These are much more clearly visible with crossed polars, but it is very hard to catch that on photograph.



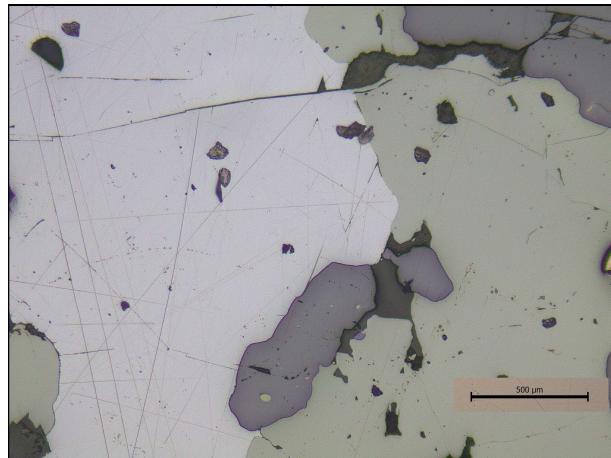
Sphalerite (grey) with **internal reflections**. As internal reflections occur **below** the surface, it is possible to focus on the planes where these reflections occur.



Sphalerite (grey) with **internal reflections**. As internal reflections occur **below** the surface, it is possible to focus on the planes where these reflections occur. **This has been done here** in the center of the image. Surface features are now out of focus.

Tennantite

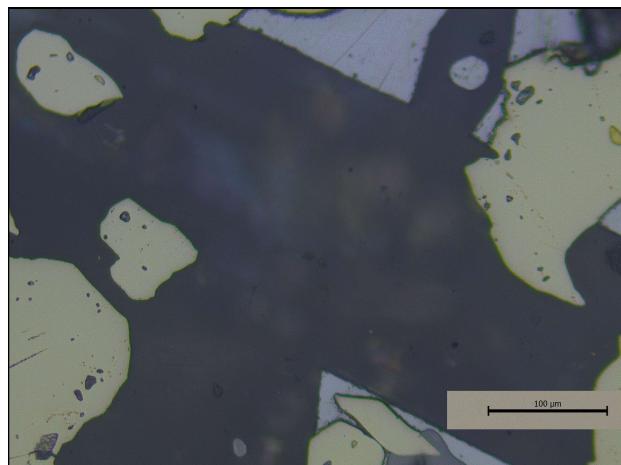
- Chemical composition: $(\text{Cu},\text{Fe})_{12}\text{As}_4\text{S}_{13}$.
- Greenish.
- Optical Category: I.
- Tennantite is an example of a **sulphosalt**.



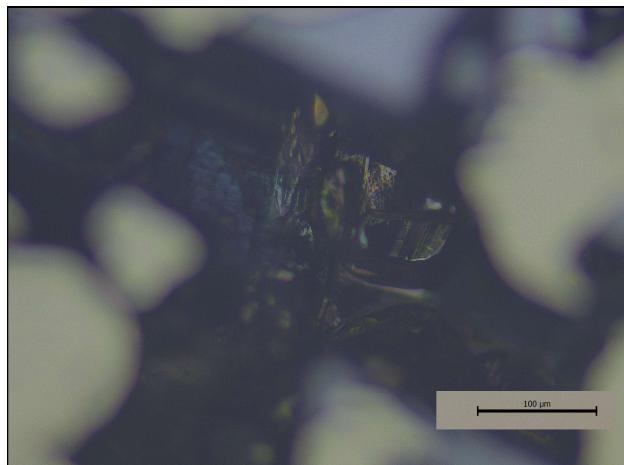
Tennantite (greenish, right) with galena (white, left), and sphalerite (grey, middle, and upper right).

Gangue

- Chemical composition: variable (silicates, carbonates, oxides).
- Dark grey, dark brown. Usual abundant internal reflections of all possible colors. Internal reflections especially well visible with crossed polars. Exact identification with reflection microscopy is impossible.



Gangue (dark brown) with **internal reflections**. As internal reflections occur **below** the surface, it is possible to focus on the planes where these reflections occur.



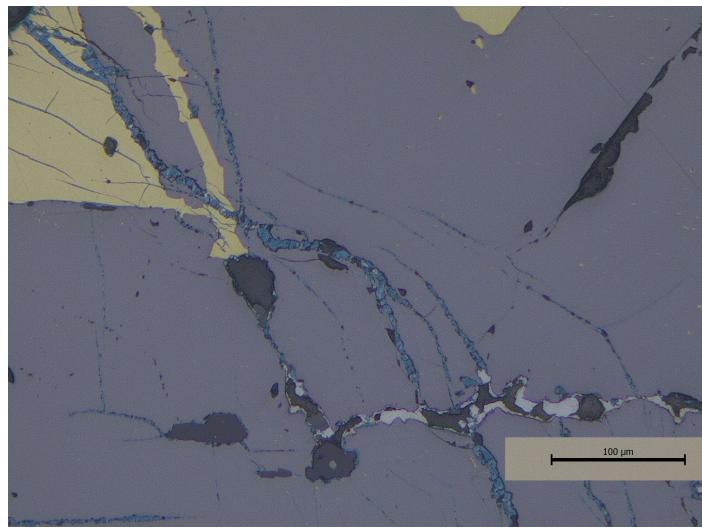
Gangue (dark brown) with **internal reflections**. As internal reflections occur **below** the surface, it is possible to focus on the planes where these reflections occur. **This has been done here** in the center of the image. Surface features are now out of focus.

Polished section T-2

Au-ore Sumatra, Indonesia

An example of the way to describe a the minerals in a polished section.

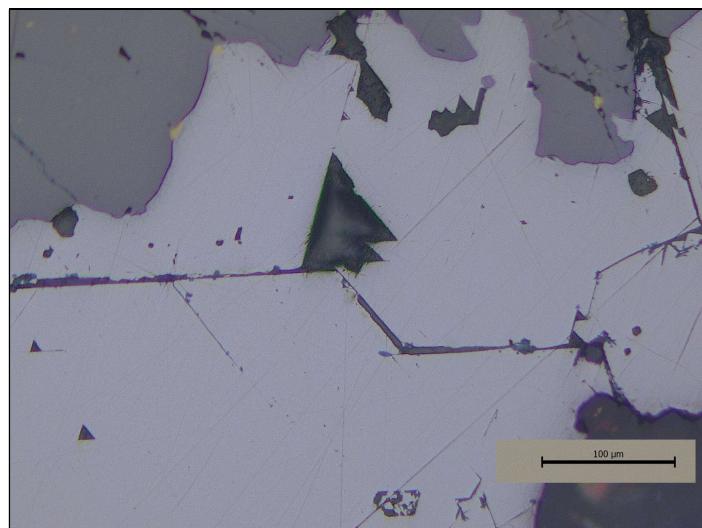
Sphalerite Chemical Composition: ZnS
Color: grey; pleochroism by bireflection: no
Reflection: 17 %
Optical Category: : I
Internal Reflections: brown
Polishing Hardness: Sphalerite > Galena
VHN: 128 - 276
Other Properties:
Twins: no
Cleavage: no
Typical crystal morphology: no
Typical texture: no



Sphalerite (grey) with chalcopyrite (yellow) and covellite (blue). Scale bar is 100 μm .

Galena

Chemical Composition: PbS
Color: white; pleochroism as a result of bireflection: no
Reflection: 42 %
Optical Category: : I
Internal Reflections: no
Polishing Hardness: Galena < Chalcopyrite
VHN: 56 - 116
Other Properties:
Twins: no
Cleavage: yes, three directions.
Typical crystal morphology: no
Typical texture: no



Galena, with sphalerite (upper part of image). Galena shows triangular pits and three cleavage directions.

Chalcopyrite

Chemical Composition: CuFeS₂
Color: yellow; pleochroism by bireflection: no

Reflection: 44 - 46 %

Optical Category: : WA - DA Interference colors (recognizable if the analyzer is turned (more than) 5 degrees): yellowish, Bluish

Internal Reflections: no

Polishing Hardness: Chalcopyrite > Gold

VHN: 174 - 219

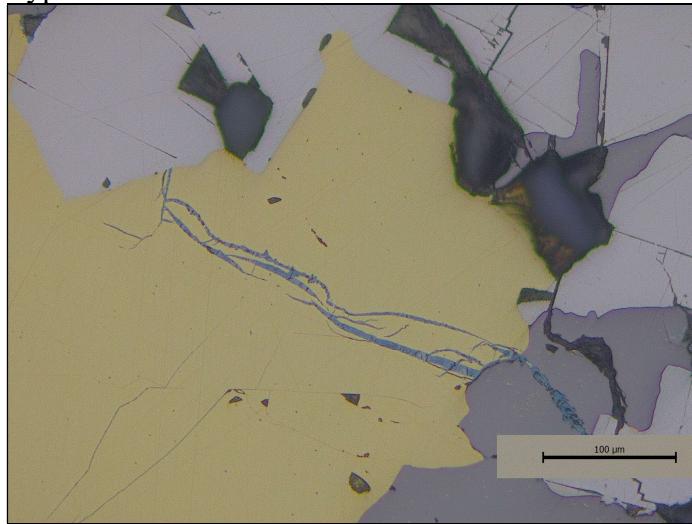
Other Properties:

Twins: lamellar, may sometimes be observed

Cleavage: no

Typical crystal morphology: no

Typical texture: no



Chalcopyrite (yellow) with galena (whitish, top) and sphalerite (greyish, lower right), and covellite (blue, in veins).

Pyrite

Chemical Composition: FeS₂

Color: pale yellow; pleochroism by bireflection: no

Reflection: 53.5%

Optical Category: I

Internal Reflections: no

Polishing Hardness: hardest mineral present

VHN: > 1000

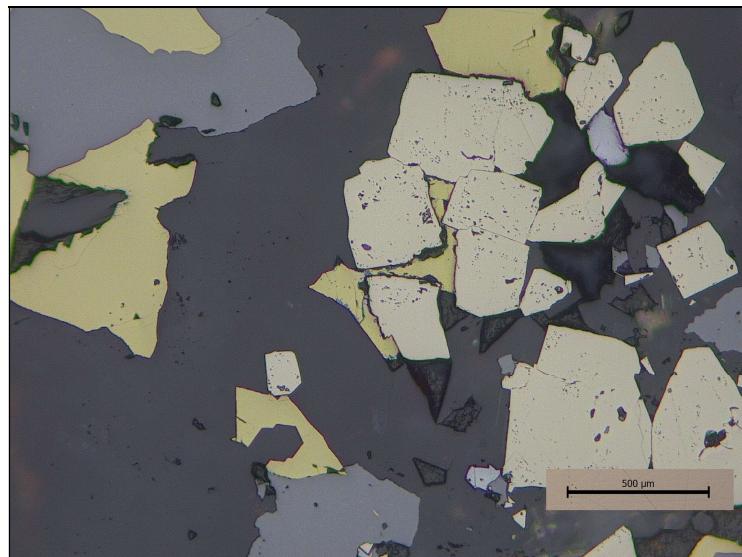
Other Properties:

Twins: no

Cleavage: no

Typical crystal morphology: yes, isometric

Typical texture: no



Pyrite (whitish-yellowish, cubes, rectangles), with chalcopyrite (yellow), sphalerite (gray) and gangue (dark brown).

Gold

Chemical Composition: Au, with Ag.

N.B.: Native gold often contains appreciable amounts of Ag (silver).

Electrum is a natural gold-silver alloy with more than 45–55% % of Au. The gold grains in this specimen contain some 10 -15 % of silver.

Color: light yellow;

Pleochroism by bireflection: no

Reflection: > 60 %

Optical Category: : I - WA

Internal Reflections: no

Polishing Hardness: < Chalcopyrite

VHN: < 100

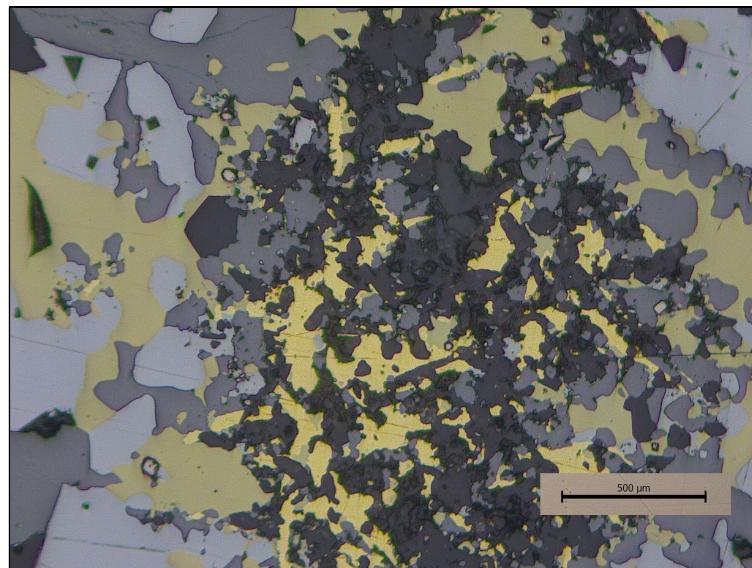
Other Properties:

Twins: no

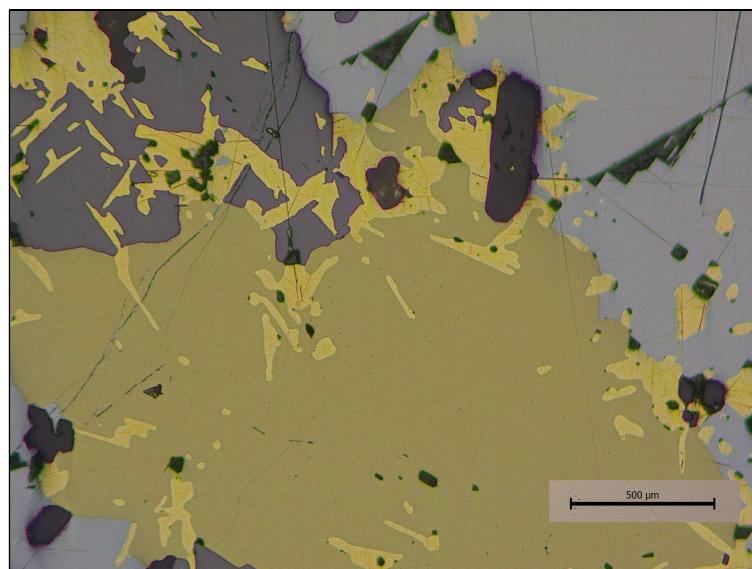
Cleavage: no

Typical crystal morphology: no

Typical texture: no



Gold (bright yellow) with chalcopyrite (greenish yellow), sphalerite (grey), galena (whitish), and gangue (dark grey).



Gold (bright yellow) with chalcopyrite (greenish yellow), sphalerite (grey), galena (whitish), and gangue (dark grey).

Remark: Gold is an accessory mineral !!

(Gold ores may contain as low as ±10 gram/ton gold to be economic.
So there are never much gold grains in a piece of gold ore).

Covellite

Chemical Composition: CuS

Color: greyish blue – blue ; pleochroism by bireflection: yes.

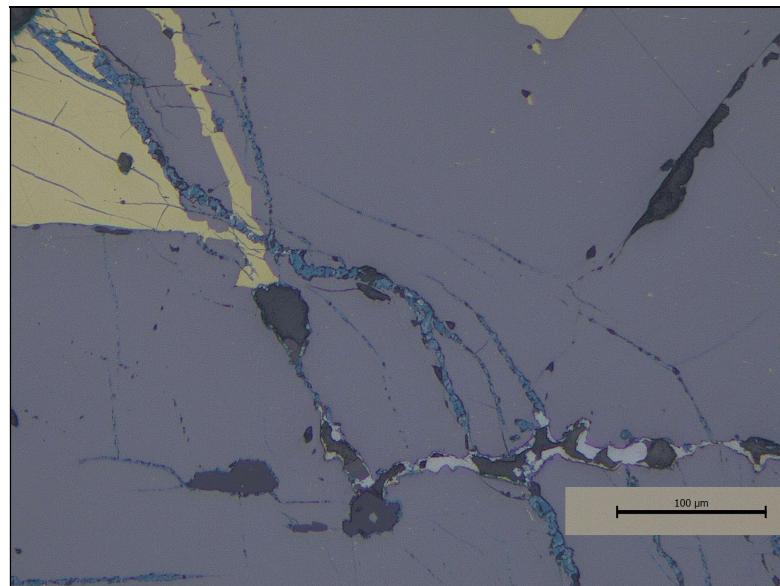
Reflection: 7 - 23 % (difficult, sometimes not even measurable)

Optical Category: : SA - EA; observed interference Colors: orange, orange-brown

Internal Reflections: no

Polishing Hardness: < Chalcopyrite

VHN: not measurable



Covellite (blue) in veins crosscutting sphalerite and chalcopyrite.

Other Properties:

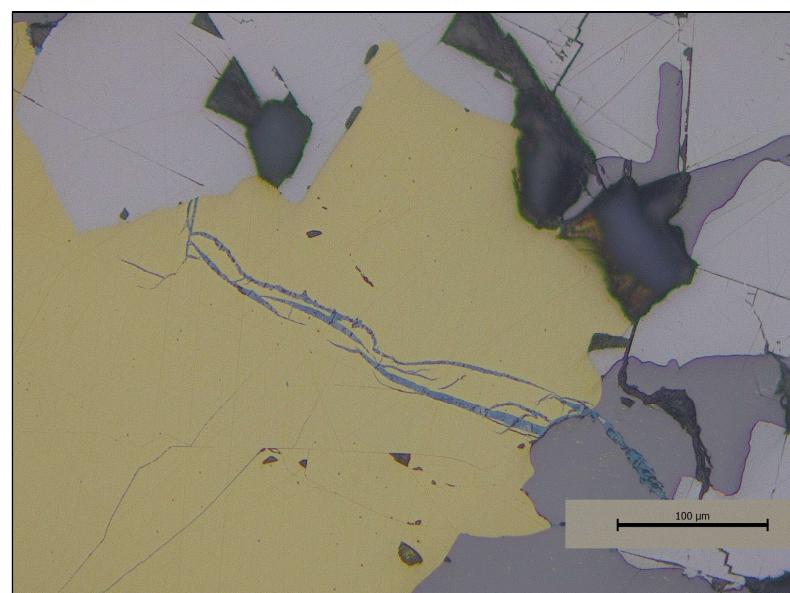
Twins: no

Cleavage: no

Typical crystal morphology: no indication

Typical texture: in veins

Remark: accessory



Covellite (blue) in veins cutting through sphalerite and chalcopyrite.

Other Minerals

Color: dark grey,

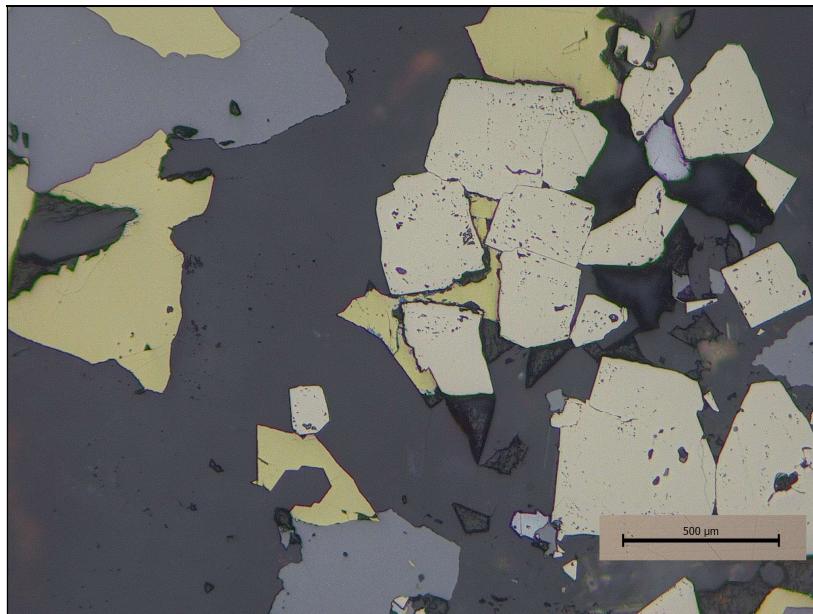
pleochroism by bireflection: possible

Reflection: < 10 %. Minerals with a reflection < 10 % are usually transparent (silicates etc.). **Covellite (R: 7 - 23 %) is an exception.**

Optical Category: diverse

Internal Reflections: many colors

Conclusion: Transparent minerals (silicates, carbonates, oxides)



Dark gangue minerals (silicates and related minerals). These minerals have a very low reflection, as they are transparent.

Polished section T-3

Cu-ore, Bor, Serbia

Main minerals:

- | | |
|------------------|---|
| Covellite | - Chemical Composition: CuS
- Blue pleochroitic. (The shape of the covellite crystals: is bladed).
- Optical Category: EA. |
| Pyrite | - Chemical Composition: FeS ₂
- Light yellow, isometric crystal with many inclusions.
Optical Category: I.
(Mark the high relief of the pyrite crystals. (Pyrite is one of the hardest minerals in the training collection, VHN > 1000)). |
| Enargite | - Chemical composition: Cu ₃ AsS ₄ .
Somewhat pinkish-grey, irregular masses.
Optical Category: SA.
Enargite is an example of a sulphosalt. |

Transparent minerals

- | | |
|---|--|
| - | Dark grey or dark brown with many internal reflections.
The silicate minerals/transparent minerals are from here on not mentioned anymore in the description. |
|---|--|

Minor minerals and accessory minerals:

Digenite	- Chemical composition: Cu ₉ S ₅ Bluish green, Optical Category: I - WA, Often inclusions in enargite.
Chalcocite	- Chemical composition: Cu ₂ S, White grey, Optical Category: I - WA, In general rims and segregations in digenite.
Bornite	- Chemical composition: Cu ₅ FeS ₄ Violet or orange, Optical Category: I- WA, Inclusions in enargite of digenite, little present
Chalcopyrite	- Chemical composition: CuFeS ₂ Yellow, inclusions in bornite/enargite, very little present

Polished section T-4

Cu-Ni ore, Sudbury, Canada

Main minerals:

Pyrrhotite	- Chemical composition: Fe _{1-x} S (x= 0-0.17) Beige brown, Optical Category: SA, Bireflectant
Pentlandite	- Chemical composition (Fe,Ni) ₉ S ₈ Cream, Optical Category: I. Pentlandite occurs in two distinct forms: 1) Irregular, usually isometric grains with two sets of cleavage, which intersect in angle of approximately 90° 2) "Flames" related to fissures and cracks. The second pentlandite is younger.
Chalcopyrite	- Chemical Composition: CuFeS ₂ (Dark) yellow, Optical Category: WA - DA. Chalcopyrite may exhibit (lamellar) twinning.

Accessory Minerals:

Magnetite	- Chemical Composition: FeFe ₂ O ₄ Grey, R = 22, Optical Category: I, isometric idiomorphic crystals. Magnetite is magnetic, but if it is just a little bit present, the whole specimen may not show magnetic behavior at all.
Ilmenite	- Chemical Composition: FeTiO ₃ Pinkish grey, R = 19, Optical Category: <u>SA</u> , as elongated crystals or segregated laths or blebs in magnetite.

Polished section T-5

Sn-ore, Portugal

Main minerals:

- Pyrite** - Contains some pinkish inclusions of pyrrhotite.
- "Melnicovite"** - "Colloform Pyrite", as yellow, pockmarked aggregates with clear zoning, or sometimes so-called "birds-eye" structure.
- Pyrrhotite** - Brownish/pinkish, Optical Category: SA. This is the original mineral.
- Cassiterite** - Chemical Composition: SnO_2
Grey, hard (high positive relief),
Optical Category: DA,
Shows IR.
Shows often singular twins with a straight twinning plane.
- Sphalerite** - Optical Category: I. Grey.

Accessory minerals:

- Tennantite** - Light bluish grey,
Optical Category: I - WA.
- Chalcopyrite** - Yellow.
-

Polished section T-6

Ni-Co arsenide ore, Cobalt, Ontario, Canada

Main minerals:

Löllingite/

- Rammelsbergite** - Chemical composition of Löllingite: FeAs_2
Chemical composition of Rammelsbergite: NiAs_2 .
White,
Optical Category: SA (- EA),
Radial aggregates.
Löllingite and Rammelsbergite are optically very difficult to distinguish.

Other similar mineral in this series of arsenides:

safflorite - $(\text{Co}, \text{Fe})\text{As}_2$

N.B.: Despite similar composition and structural similarity, these minerals do *NOT* form a solid solution.

Nickeline

- Chemical Composition: NiAs. (Formerly called niccolite).
Orange,
Optical Category: SA (- EA)

Cobaltite

- Chemical composition: CoAsS
Optical Category: SA (displays in this specimen anomalous isotropic character, due to impurities).
Pinkish grey,

	Hard.
Skutterudite	-Chemical composition: $(Co,Ni)As_{3-x}$ White, Sometimes idiomorphic rectangular crystals, Optical Category: I.

For all these minerals R > 50 %.

Accessory minerals:

Chalcopyrite	- <i>Greenish-yellow</i> (!). The apparent color of a mineral grain is strongly dependent on the color of the mineral grains directly adjacent to it.
Sphalerite	- Grey

Polished section T-7

Cu-ore, Zambia

Main minerals:

Bornite	- Chemical Composition: Cu_5FeS_4 Brownish/violet/purple, Optical Category: WA, Tarnishes easily.
Chalcopyrite	- Yellow.
Tennantite	- Greenish grey.
Renierite	- Chemical Composition: $(Cu,Zn)_{11}(Ge,As)_2Fe_4S_{16}$ Orange, Optical Category: SA. Renierite is one of the very few germanium (Ge) ore minerals. In general, germanium is a byproduct of zinc ore processing.
	N.B. : Do NOT confuse Renierite with Reinerite: Zn₃(As³⁺O₃)₂
Sphalerite	- Grey.

Accessory minerals:

Digenite	- Greyish blue, together with chalcocite.
Chalcocite	- White-grey, sometimes bluish grey, Optical Category: I- WA, Rims.
Carrollite	- Chemical composition: $Cu(Co,Ni)_2S_4$ Pinkish white, veined.
Enargite	- Pinkish grey, Optical Category: DA - SA, Rare.

Polished section T-8.

Cu-Ni ore, Sudbury, Canada.

Main minerals:

Chalcopyrite	- Yellow.
Cubanite	- Chemical Composition: CuFe ₂ S ₃ . This is the third mineral in the group of Cu-Fe-sulphides. Cubanite is quite common in the ores of Sudbury, but on the whole it is a quite rare mineral. Khaki, cream, Optical Category: SA.
Pyrrhotite	- Pinkish, Optical Category: SA.
Pentlandite	- Cream, Optical Category: I, With 2 sets of cleavage.
Mackinawite	- Chemical composition: (Fe,Ni)S _{0.9} Grey-pinkish, Optical Category: EA, Small lamellar segregations in chalcopyrite. In one orientation, the color is quite similar to chalcopyrite, in another direction rotated 90°, the color is much darker. N.B.: Pronunciation (phonetically): “makkienáwait”.

Accessory minerals:

Sphalerite	- Grey.
Violarite	- Chemical composition: FeNi ₂ S ₄ . Violarite is a common alteration of pentlandite. If one has identified pentlandite in a specimen, it is worthwhile to check if there is alteration to violarite.
Magnetite	- Pinkish, Optical Category: I,
	- Grey and hard,
	- Optical Category: I.
Ilmenite	- Pinkish grey, Optical Category: SA.

It is possible in these ores to find greyish-white and strongly anisotropic minerals. These are Bi-tellurides (compositions containing the element Tellurium, Te). Tellurides are not treated in this course.

Polished section T-9 Ag-Sb ore, Pribram, Czechia

There are two types of specimens, Ag-poor and Ag-rich. You must exchange the specimens to be able to study both.

T-9 A) Ag-rich

Main minerals:

Proustite/pyrargyrite	- Chemical composition: Proustite: Ag_3AsS_3 Pyrargyrite: Ag_3SbS_3 Bluish, Optical Category: SA (-EA), Abundantly present deep red IR (very typical!). R: 27 – 30 % Proustite and pyrargyrite are very difficult to distinguish optically ⁷ .
Arsenopyrite	- Chemical Composition FeAsS. This is the most common As-containing mineral in the world. White, Optical Category: SA, R > 50 %. Occurs in this specimen as somewhat diamond shaped crystals.
Sphalerite	- Grey.
Pyrite	- Light yellow

Accessory minerals:

Chalcopyrite	- Yellow.
Galena	- White.

T-9 B) Ag-poor

Main minerals:

Jamesonite	-Chemical composition: $\text{Pb}_4\text{FeSb}_6\text{S}_{14}$ Greenish: needles, fibers.
Arsenopyrite	Optical Category: DA - SA -White, Optical Category: SA, R > 50. Occurs in this specimen as rather elongated crystals.
Sphalerite	- Grey
Pyrite	- Light yellow.

⁷ The French chemist Joseph L. Proust (1754-1826) in 1804 chemically distinguished proustite from pyrargyrite. In 1832 this mineral was named in his honour.

Accessory minerals:

Galena

- White.

Galena is **altered** to *Jamesonite*, and occurs locally as **relicts**, whereas at most places galena has been completely altered to fibrous jamesonite masses.

Chalcopyrite

- Yellow, Optical Category: I - WA

Ag-rich

Tetrahedrite/freibergite- Chemical composition:

- Tetrahedrite - $(\text{Cu}, \text{Fe})_{12}\text{Sb}_4\text{S}_{13}$.

Tetrahedrite forms a solid solution with tennantite $(\text{Cu}, \text{Fe})_{12}\text{As}_4\text{S}_{13}$. Tennantite is somewhat bluish with respect to tetrahedrite).

Freibergite - $(\text{Ag}, \text{Cu}, \text{Fe})_{12}(\text{Sb}, \text{As})_4\text{S}_{13}$

Both minerals: Greenish grey, Optical Category: I.

Polished section T-10

Fe-ore (gossan) Zambia

Main minerals:

Magnetite

- Chemical composition: FeFe_2O
Pinkish brown,
Optical Category: I

Hematite

- Chemical composition: Fe_2O_3
White (Bluish),
Optical Category: SA

Goethite

- Chemical composition: FeOOH
Bluish grey,
Optical Category: DA,
yellowish, red-orange IR.

Polished section T-11

Cr-ore, Philippines

Chromite

- Chemical composition: FeCr_2O_4
Grey,
Optical Category: I,
 $R = 12 - 13$.
Brown IR, rarely visible.

Serpentine matrix with white-greenish IR.

Chromite is structurally strongly related to magnetite. Both belong to the **spinel-group** (general formula $AB_2\text{O}_4$). Spinel sensu strictu is MgAl_2O_4 , chromite is FeCr_2O_4 , and magnetite is FeFe_2O_4 , ($\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$).

Other minerals in the spinelgroup are for instance: *hercynite*, *FeAl₂O₄*, *gahnite*, *ZnAl₂O₄*, *ulvöspinel*, *TiFe₂O₄*, *jacobsite*, $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})(\text{Fe}^{3+}, \text{Mn}^{3+})_2\text{O}_4$, *trevorite*, *NiFe₂O₄*. The spinelgroup is subdivided in *normal* and *inverse spinels*. See for further

information: Part III.

Polished section T-12 Mn-ore, India/Mn-nodule, Pacific Ocean

Mn-ore, India:

Main minerals:

Pyrolusite	-	Chemical composition: MnO ₂ Optical Category: SA Yellowish white, Pleochroitic, Elongated crystals, Cleavage
Cryptomelane	-	Chemical composition: KMn ⁴⁺ ₆ Mn ²⁺ ₂ O ₁₆ Bluish grey, occurs here in a <i>cryptocrystalline aggregate</i> , as such the anisotropy is SA. However, a cryptocrystalline aggregate may <i>appear</i> to be <i>isotropic</i> , while the minerals in the aggregate, here cryptomelane, actually are <i>not!</i>
Lithiophorite	-	Chemical composition: (Al,Li)Mn ⁴⁺ O ₂ (OH) ₂ Bluish grey, pleochroitic Optical Category: EA (interference color are black or white.), Around open cavities, Relative low reflection (10 - 20 %). May be a rather common mineral in hydrothermal lithium deposits.
Goethite	-	Bluish grey, with red/orange IR. Optical Category: WA - DA

Mn-nodule, Pacific Ocean:

Mark the colloform textures! Several Mn-minerals are present in intimate intergrowths.

Optical determination of the different ore minerals is impossible!!
The resolution of the optical microscope is *too low* for this. The technique to solve this is electron microprobe (also: Electron Probe Micro Analysis or EPMA) or scanning electron microscopy with element analysis facility. The following minerals have been identified in this way: *todorokite*, *woodruffite*, *pyrolusite*, *hollandite*, *cryptomelane*, *birnessite*.

Polished section T-13

Au-Bi ore, Tennant Creek, Australia

Magnetite	-	Grey
Bismuthinite	-	Chemical composition: Bi ₂ S ₃ . White, Optical Category: EA-SA. Cleavage. Undulose extinction.
Chalcopyrite	-	Yellow.
Guanajuatite	-	Chemical composition: Bi ₂ Se ₃ . White with cleavage. This is a very rare mineral.
Hematite	-	Bluish, wormlike inclusions, and circles in magnetite.
Pyrite	-	Light yellow.

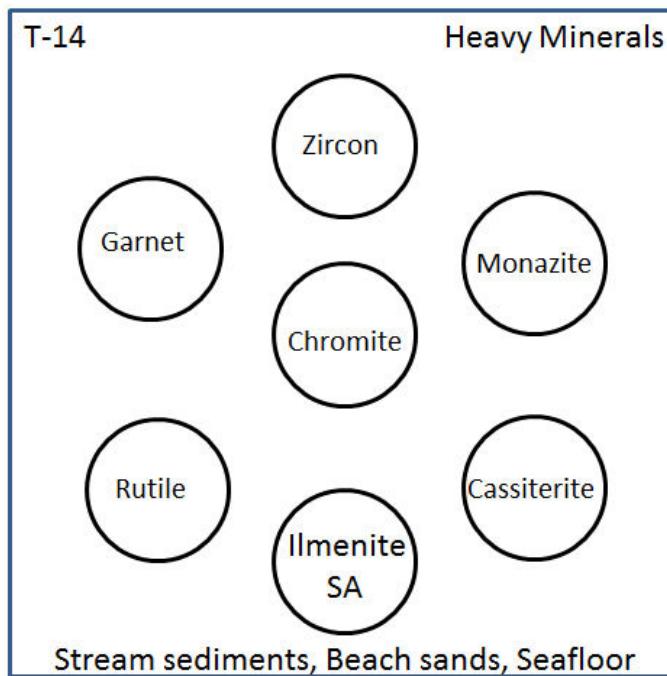
Accessory mineral:

Gold	-	Yellow, R > 70. Contains some selenium (Se). (Just a few grains present, but this was a very important mineral in the ore).
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Polished section T-14

Heavy Minerals

In this composite polished section you find seven fractions of heavy minerals.



One can determine *chromite*, *cassiterite*, *ilmenite* and *rutile* with an ore microscope. The minerals *zircon*, *monazite* and *garnet*, which are also shown for comparison, are better determined in thin section with a transmitted light polarizing microscope. However, all these minerals occur in heavy mineral sands.

Polished section T-15**Ni-Cu Matte, INCO Ltd. Sudbury, Ontario, Canada**

In this polished section you find a piece of a so-called “slow cooled matte” from the nickel ore processing according to the INCO-process. This process is one of the most important industrial processes with respect to the processing of sulfidic nickel ores. The ore for this process could have been the ore of T-4, or T-8.

Polished section T-16**Iron-ore, pellet and sinter, Tata Steel, IJmuiden**

In this composite polished section you find a pellet and a sinter, both from the industrial practice of the iron making process.

Pellet:

Main mineral: **hematite**.

Sporadic you may find: **magnetite, silicate**.

Study the texture of the pellet. Can you identify sinter-necks ?

Sinter:

Main minerals:

Hematite

Magnetite

Ca-ferrite (needle-like crystals, rather low reflection, not to be determined by ore-microscopy). Ca-ferrite is added as a slag conditioner.

Silicate (unspecified).

Polished section T-18**Sn-ore, Pamantoe, Indonesia**

Main mineral:

Cassiterite

-

Chemical composition: SnO_2

Grey,

Reflection between 10 and 14 %.

Very hard.

Clearly pleochroitic.

Optical Category: DA, but difficult to determine because of the ubiquitous brown red internal reflections.

Sometimes twinning is visible.

Zoning is sometimes beautifully visible.

Polished section T-19**Fe-Ore, Jack Hills Mine, W-Australia**

Lump ore concentrate, broken, sieved at 10 – 15 mm, from a detritic iron ore deposit in the Jack Hills, W-Australia.

Minerals:

- | | | |
|------------------|---|---|
| Hematite | - | Chemical composition: Fe ₂ O ₃
White,
Optical Category: SA,
Complex twinning.
Sometimes red IR. |
| Magnetite | - | Chemical composition: FeFe ₂ O ₄
Brown,
I,
alteration to hematite. |
| Goethite | - | Chemical composition: FeOOH
Grey,
Optical Category: WA,
Orange IR, fills spaces between grains, cement. |
-

Part III

Crystal Chemical and Crystallographic Aspects of Sulphides, Oxides and Hydroxides.

1. INTRODUCTION

In this chapter, some crystal chemical and crystallographic aspects of sulphides and oxides will be treated. The goal is to give some insight into what kind of compounds these minerals are, and how they are, or are not, related in a crystallographic and chemical way. This may be of importance in understanding their physical behaviour, important for mineral separation, and to understand more of the intergrowths, which minerals with a similar crystal structure may show. Also this chapter gives a classification of ore minerals, and so places them in a larger framework. (This is to prevent that ore minerals are to you “just a big bunch of exotic names”).

2. SULPHIDES⁸

2.1. Properties of sulphides (and arsenides)

When a sulphide is compared with “normal” rock forming minerals, it soon appears that sulphides have a number of peculiar properties, like a metallic appearance, high reflection, high density etc. Below you find a list of properties that are encountered in sulphides. Not every sulphide needs to possess all these properties.

- *high density*
- *high reflection (e.g. pyrite, chalcopyrite)*
- *electrical conductivity*
- *sometimes magnetic properties (e.g. pyrrhotite)*
- *high ductility (e.g. galena)*
- *surface reactivity*
- *"tarnishing": subject to oxidation and sometimes even physical degradation in different gradations (e.g. bornite).*

An explanation for these properties is not easy to give. It requires a thorough understanding of the chemical bond (orbitals and wave functions). It is possible to give a more qualitative explanation for the origin of the phenomena, without going to much in depth in solid state chemistry or solid state physics.

High Density

This is caused by two things.

1. The first (and most simple) is the often high atomic number of the elements in the sulphides/arsenides (Cu, Fe, Ni, Co, Pb, Bi, Sn, Sb, As etc.) with respect to the elements in silicates (O, Si, Al, Na, K, Ca, Mg, Fe, Ti, etc.)
2. Short interatomic distances in sulphides and arsenides. This is because more than one valence electron participates in the chemical bond, which makes short atomic distances possible (hybridization and overlap of orbitals).

⁸ Arsenides, selenides, tellurides and complex sulphur compounds (sulfo-antimonides, sulfo-arsenides) are usually treated together with sulphides.

High Reflection

Reflection is influenced by the surface layer of a compound. Higher reflection implies a higher absorption of light, excitation by surface atoms, and re-emittance of light (de-excitation). Reflection of sulphides can be explained by the Band Theory of Solids.

Bands in solids are described as closely spaced permitted electrical energy levels in a solid. One can define a valence band (takes part in the bonding), and a conduction band (does not take part in the bonding). In sulphides the valence band is usually formed by the $3p$ en $3s$ orbitals of sulphur, and it is usually filled with electrons. The conduction band (formed by the $4p$ en $4s$ orbitals of the transition metal) is usually empty. Valence band and conduction band are separated by an energy gap. The amount of radiation that can be absorbed depends on the amount of empty energy levels. By uptake of electromagnetic radiation, a transition can take place of electrons from the valence band to the conduction band, after which the delocalised electrons fall back to their previous state under the emittance of light. The width of the absorption band related to the amount of empty energy levels that is present. This in turn is influenced by the composition of the sulphide. Compositional differences in sulphides thus may influence the reflection behaviour.

Electrical Conductivity

Delocalized electrons in overlapping orbitals explain the great variation in electrical conductivity of sulphides.

Magnetical properties

Magnetic properties of sulphides have their origin in unpaired electrons of the metal atoms, similar to the magnetism of some spinels (magnetite). Magnetism of sulphides (e.g. pyrrhotite, Fe_{1-x}S) is, in comparison with that of spinels, extremely complex. Type of bonding and coordination of the metal ion (e.g. Fe^{2+}) in a sulphide has its effect on the net amount of magnetic moment (unpaired electron spins), and thus on the magnetic properties of the mineral. The well-known and very complex pyrrhotite group comprises magnetic and non-magnetic members. A detailed explanation of this matter is too complicated and too extensive for this course.

High ductility

Most sulphides are rather soft, and ductile. This can be explained by the covalent or metal character of the chemical bonds.

However, not all sulphides have all covalent or metal bonds. Pyrite (FeS_2) consists of a Fe^{2+} -ion and a S_2^{2-} group, which are bonded via an ionic bond. This stronger bond makes pyrite in comparison to other sulphides rather hard en brittle.

Surface reactivity and tarnishing

Tarnishing: By means of bonding of oxygen to the surface the character of the bonds of the sulphide at the surface will be disturbed, en exert influence on the reflection. By bonding with oxygen, the number of empty energy levels present is lowered, and so the reflectivity for a large bandwidth of light. Selective adsorption and re-emission of electrons becomes possible, and colored bands may develop. (This is very well visible for bornite).

Surface reactivity: sulphides show a large range in de extend of wettability, if they are treated with collectors. The collector is a heteropolar compound, with a polar, water soluble part and a hydrophobic part. The large variation in collector behaviour is due to the complexity of the metal-sulphur bonding. With effective use of the collectors and activators, specific wettabilities can be achieved, which makes mineral separation on basis of flotation possible.

2.2. Classification and structure of common sulphides and arsenides

2.2.1. Sulphides and Arsenides

Although a classification on basis of crystal structures and crystal chemical aspects is the most usual, also attention will be paid to an older, German, classification on basis of external properties. This classification is still found in popular names or terms in the mineralogy of sulphides, and therefore is useful to explain this classification in short. On the basis of the external properties, the sulphides are subdivided into the following classes:

- Glanze. Properties like galena, thus metallic lustre, lead grey colour, low hardness, perfect cleavage. Often this are sulphides of Cu, Pb, and Ag, like galena, chalcocite). Galena is in German: Bleiglanz, and in Dutch: loodglans.
- Kiese. The properties of pyrite serve as a model for the Kiese. Usually these are Ni, Fe, Co and Pt-sulphides (e.g. pyrite, cobaltite, but also arsenopyrite)
- Fahle. The Fahle are in between the Kiese and Blende. They have lower reflectivity than the Kiese, but have no cleavage, like the Blende. Well-known examples are tennantite and tetrahedrite. These minerals are also often (in a peculiar mix of English and German) termed “Fahlores”
- Blende Blende have covalent bonds and therefore have properties like translucency, low hardness, perfect cleavage. Sphalerite (zincblende) is the model for this group. Another example is covellite (copperblende).

Arsenides, tellurides and antimonides have rather metal-like properties and are outside this classification.

On basis of crystal structure, the sulphides can be subdivided into:

1. Monosulphides (MS) and derived structures.

- a. *Sphalerite (ZnS) structure* with derivatives like the chalcopyrite structure, the tennantite-tetrahedrite series, the sulphosalts luzonite⁹.
- b. *Wurtzite structure (ZnS)*, with as derived structures those of the sulphosalts enargite.
- c. *Nickeline structure (NiAs)*, with derivatives Troilite (FeS) and pyrrhotite ($Fe_{1-x}S$)
- d. *Millerite structure (NiS)*
- e. *Pentlandite structure (Ni,Fe)₉S₈*
- f. *Galena structure (PbS)* with as derivatives silversulphosalts and cinnabar (HgS).
- g. *Covellite structure (CuS)*

2. Disulphides (MS₂) and derived structures

- a. *Molybdenite structure (MoS₂)*
- b. *Pyrite structure (FeS₂)* and the cobaltite group (cobaltite, CoAsS, gersdorffite, NiAsS, and similar minerals, e.g. ullmannite, NiSbS)
- c. *Marcasite structure (FeS₂)* and arsenopyrite (FeAsS)¹⁰

3. Other stoichiometries (M_xS_y)

- a. *Chalcocite structure (Cu₂S)*
- b. *Stibnite structure (Sb₂S₃)* and related Bi, Pb- and As-Sb sulphosalts

In the descriptions of these structures, you will encounter a series of important common sulphides (chalcopyrite, galena, bornite, sphalerite, digenite). The goal is to give an overview of fundamental crystal structures encountered with sulphides, and to elucidate relationships between important sulphides.

2.2.2. Monosulphides (MS)

a) Sphalerite¹¹ structure and wurtzite structure

⁹ N.B.: a **sulphosalts** is a name for a compound of metal, sulphur and Group V elements from the periodic system, like Bi, As, Sb. Examples are jamesonite, ($4PbS.FeS.Sb_2S_3$), pyrargyrite ($3Ag_2S.Sb_2S_3$), geocroneite ($Pb_{14}(As,Sb)_6S_{23}$). Sulphides and sulphosalts are generally treated together in mineralogical handbooks.

¹⁰ **Pyrite** and **marcasite** are both FeS_2 , and are thus dimorphs. **Pyrite** is cubic, **marcasite** orthorhombic. The name **pyrite** is derived from Greek *pyrites lithos*, "stone which strikes fire," in allusion to the sparking produced when iron is struck by a lump of pyrite. **Pyr**, meaning **fire** is one of the oldest recognized words in **(proto)Indo-European**. Compare with the prefix "**pyr**" in **pyrolysis**, **pyrometallurgy** etc.. The name **marcasite** is derived from the **Arabic** or **Moorish** name for pyrites and similar material of uncertain origin.

¹¹ **Sphalerite**: from Greek *sphaleros*, meaning "misleading", as it occurs often together with galena, but does not yield lead on smelting. **Wurtzite**: after the French chemist, Charles A. Wurtze (1817-1884).

These structures are given in figure 1 and 2. In both cases it concerns closest packings (of S), in which the metal atoms occupy the halve of the tetrahedron positions. One can see these structures as two polytypes¹² which differ in the stacking of the tetrahedrons. In the case of sphalerite, it is a cubic symmetry (ccp)¹³, in the case of wurtzite it is a hexagonal symmetry (hcp). In theory, these structures can alternate, leading to planes in the structure where the symmetry of the crystal changes: so-called stacking faults.

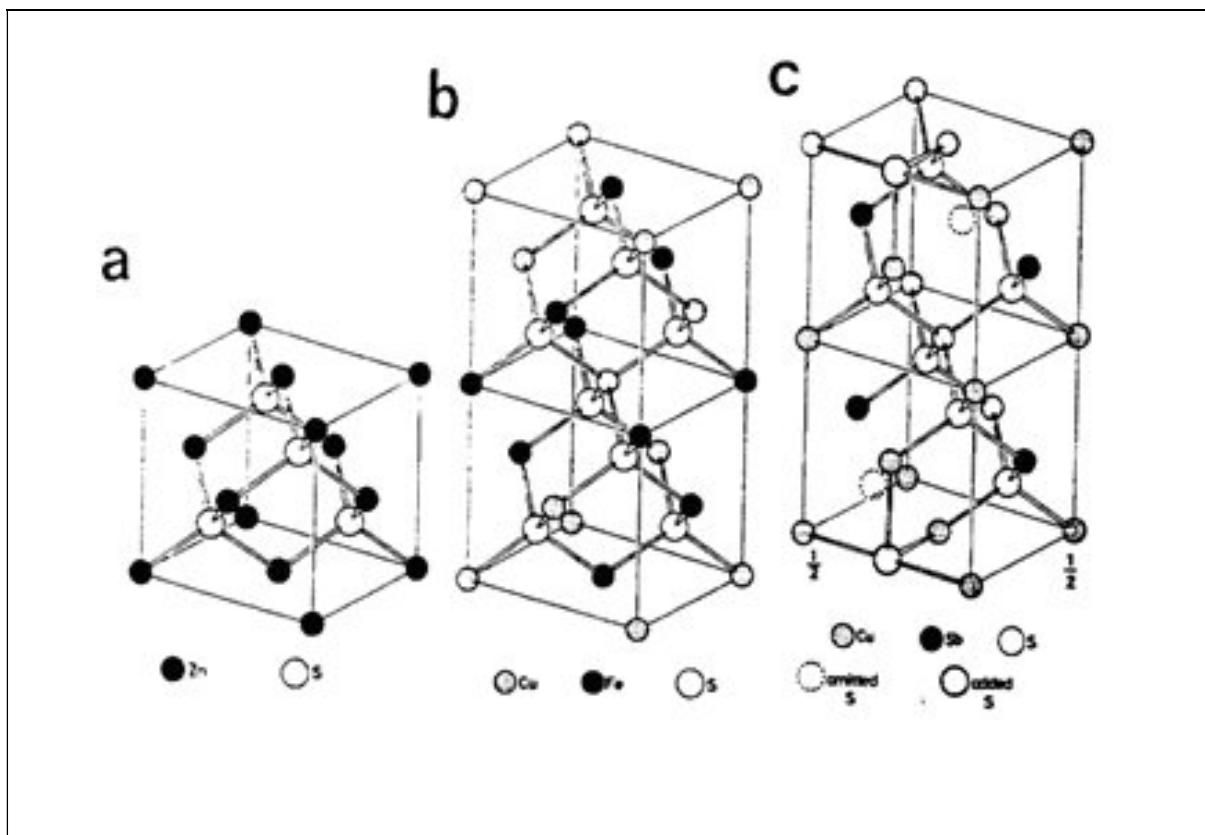


Fig. 4.1. The sphalerite structure (a) with the derivative structures of chalcopyrite (b) and tetrahedrite (c)

There are many derivatives of the sphalerite structure known. A very well known example is the structure of chalcopyrite (CuFeS_2), a tetragonal structure with an ordered distribution of Cu and Fe. Cubanite (CuFe_2S_3) is the wurtzite analogue of chalcopyrite. Stannite ($\text{Cu}_2\text{FeSnS}_4$) has a similar structure, where layers of ordered Cu and Sn alternate with layers with Cu.

Luzonite¹⁴ ($\text{Cu}_3(\text{As},\text{Sb})\text{S}_4$) is a tetragonal derivative of chalcopyrite. Enargite, a polymorph of luzonite is derived from the wurtzite structure (fig. 4.2.). Typical is a

¹² **Polytypes:** variations of the same chemical compound that are identical in 2 dimension and differ in the third. Thus, they can be viewed as layers stacked in a certain sequence.

¹³ **ccp** = cubic closest packing; **hcp** = hexagonal closest packing.

¹⁴ **Enargite** (Cu_3AsS_4) and **luzonite** (also Cu_3AsS_4) are dimorphs. Enargite is orthorhombic, luzonite is tetragonal. Names: **enargite** from the Greek enarges - "obvious." **Luzonite** from Mancayan, Luzon Island, Philippines.

tetrahedral coordination of As or Sb by S. Many sulphosalts are derived from the sphalerite structure.

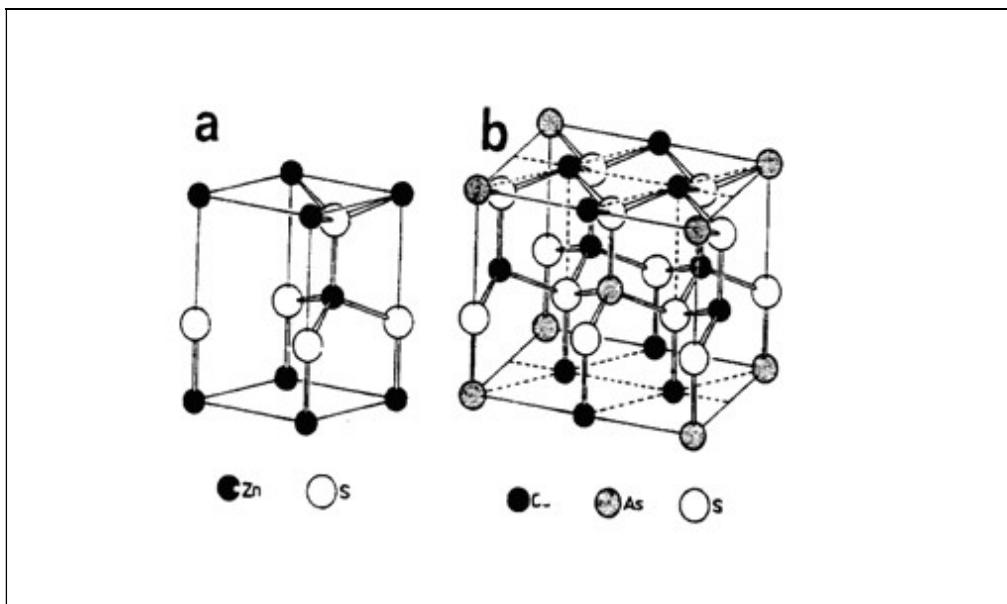
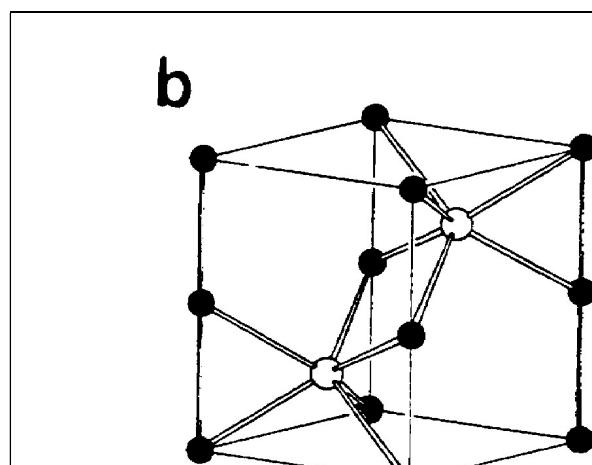


Fig. 4.2 The wurtzite structure and the derived structure of enargite.

Tennantite¹⁵ ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) and tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) are more complex derivatives of the sphalerite structure, in which the sphalerite cell is doubled. One fourth of the metal atom sites is occupied by a group V element, which forms only three bonds with sulphur. One fourth of the S-atoms is deleted, but two additional S-atoms are added. There are Cu-sites with a 4-coordination by S and Cu-sites with a 3-fold coordination by S. The tetrahedrite/tenantite series is a complete solid solution, which also can take up other elements (Hg, Ag).



*Fig 4.3. The structure of Nickeline NiAs.
Closed spheres are Ni, open spheres are As.*

¹⁵ **Tenantite:** named after the English chemist, Smithson Tennant (1761-1815).
Tetrahedrite: name is derived from its crystal form.

b) Nickeline Structure.

The nickeline¹⁶ structure is hexagonal, with the more electronegative ions arranged in a hcp. The remaining ions occupy the octahedral positions. Metal-metal bonds along the c-axis give the structure its stability. The nickeline structure is quite important and occurs a lot for sulphides of transition metals. A-stoichiometry is also frequently encountered. A complex derivative of the nickeline structure is the structure of pyrrhotite¹⁷ (Fe_{1-x}S). This is actually a whole group of structures, which are monoclinic, or orthorhombic. Pyrrhotite can take up appreciable amounts of Ni at high temperatures (a monoclinic structure), but no Ni at low temperatures (orthorhombic structure). The a-stoichiometry of pyrrhotite gives rise to unpaired electrons at the Fe-sites, leading to magnetism. The magnetism is dependant on the a-stoichiometry. Not every pyrrhotite is as magnetic, and even non-magnetic examples are known. Troilite¹⁸ (stoichiometrical FeS) is also derived from the nickeline structure, but this structure is much simpler.

c) Millerite- en NiS-structure.

The compound NiS occurs in two forms. The HT-form ($T > 379 \text{ }^{\circ}\text{C}$) has the NiAs-structure, and has also a-stoichiometry, like pyrrhotite. The LT-form (millerite¹⁹) is stoichiometric, and has a rhombohedral structure.

d) De pentlandite structure ($\text{Ni},\text{Fe})_9\text{S}_8$.

Pentlandite²⁰ has a complicated fcc-structure²¹. The unit cell contains 32 sulphur atoms in 2 different positions, which results in a ccp structure. The 36 metal atoms occur in 4 octahedral positions and 32 tetrahedral positions. Metal atoms in 4-fold coordination are clustered in groups of 8.

e) Galena²² structure and its derivatives: sulphosalts and cinnabar.

The galena structure is analogous to the NaCl-structure. With the Pb-containing sulphosalts, a distortion can occur, leading to a monoclinic symmetry. Cinnabar (HgS) has a hexagonal structure, which is also derived from the NaCl-structure by distortion.

¹⁶ **Nickeline** (synonym **nicolite**): named after its composition.

¹⁷ **Pyrrhotite:** from the Greek, phyrrotes, "redness," in allusion to the color.

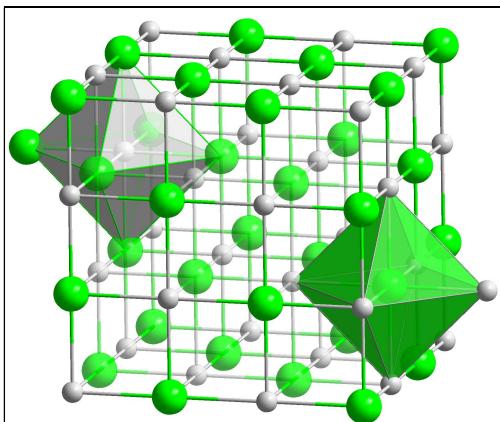
¹⁸ **Troilite:** named for Dominico Troili, who described, in 1766, a meteorite which fell in Albareto, near Modena, Italy.

¹⁹ **Millerite:** named after the English mineralogist, William Hallowes Miller (1801-1880).

²⁰ **Pentlandite:** named after the Irish natural historian, J. B. Pentland (1797-1873).

²¹ fcc= face centered cubic, ccp = cubic closest packing.

²² **Galena:** the Roman naturalist, Pliny, used the name **galena** to describe lead ore.



*Fig. 4.4a. The crystal structure of sodium chloride.
Each atom has six nearest neighbours, in octahedral geometry*

e) Covellite structure.

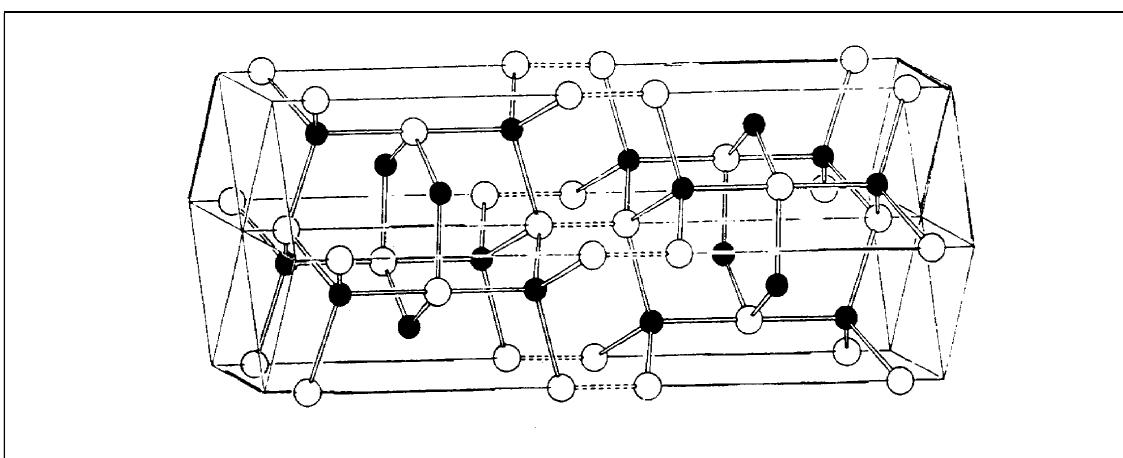


Figure 4.5. The structure of covellite. Closed spheres are Cu, open spheres are S. Dashed lines indicate the covalent bonds which keep the layers together.

The chemical formula of covellite²³, CuS does not indicate the complex structure. Figure 4.5 shows the covellite structure. Cu occurs in two ways, one in tetrahedral coordination. The tetrahedra share corners and form a layer. Two of these layers have tops. A second type of Cu-atoms occurs in the trigonal spaces between these tops and forms a CuS-layer. The resulting layer structure consists of a stacking of different layers. In the structure, two of the tetrahedral layers will meet (middle of the figure 4.5) and here the plates are connected by relatively weak covalent bonds. Covellite plates are relatively easy to separate.

Covellite is a relatively unimportant as a copper ore mineral. The more common ore minerals are CuFeS₂, chalcopyrite, Cu₅FeS₄, bornite, and Cu₂S, chalcocite. Covellite is important because this indigo blue mineral was the *first discovered natural superconductor*. Material science is now aware of several of covellites favourable properties and several researchers are intent on synthesizing covellite.

²³ **Covellite:** named after the Italian mineralogist, N. Covelli (1790-1829).

2.2.3. Disulphides

a) Molybdenite structure (MoS_2)

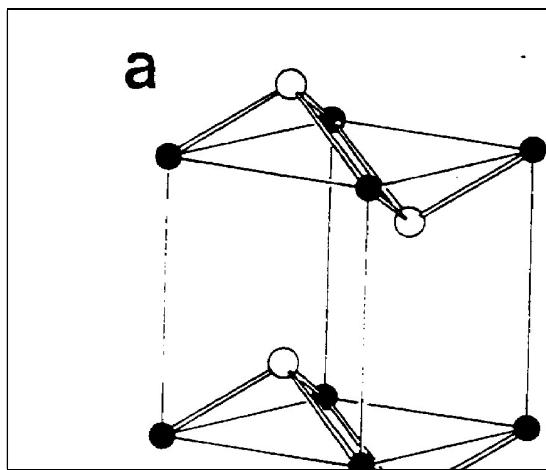


Fig. 4.6. De structuur van CdI_2 . Molybdenite also crystallizes in this structure. Closed spheres are metal atoms.

This structure is similar to that of CdI_2 . In MoS_2 Mo has a six fold coordination by S, which is more or less prismatic and not rhombohedral. These structures are comparable with that of CdI_2 (figure 4.6). A comparable structure is found in SnS_2 .

b) Pyrite structure and derivatives

Two very important structure types are the pyrite structure and the marcasite structure. The pyrite structure is given in fig. 4.7

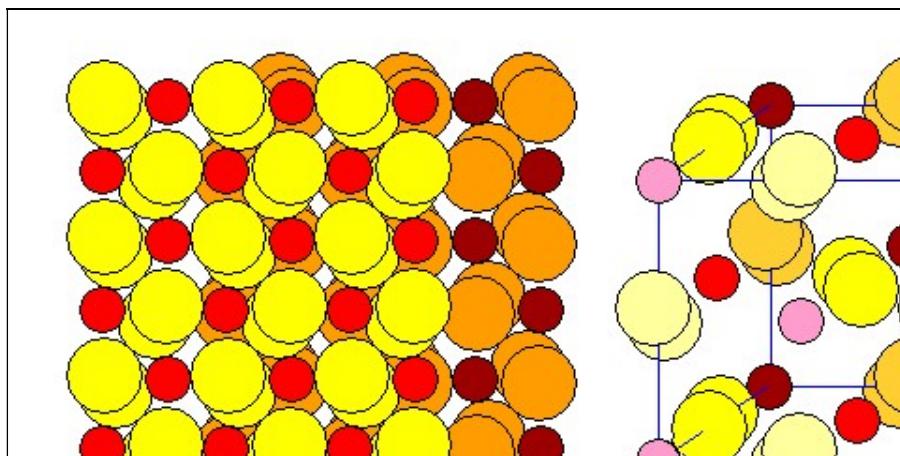


Figure 4.7. Pyrite is often described as having a modified halite structure. However, iron atoms alternate with pairs of covalently-bonded sulphur atoms. The pairs of atoms are skewed in alternate directions, so pyrite has lower symmetry than halite. In this sketch, iron atoms are red and sulphur yellow. Darker shades are used for atoms further away from the viewer.

The pyrite structure is given in figure 4.7 and 4.8. Fe-atoms are arranged according to a fcc-lattice. A covalently bonded S₂-pair takes positions similar to the Cl⁻ ion in the NaCl-structure. The unit cell contains 4 of such pairs. The Fe-atoms form an octahedron around and S₂-pair. The pyrite group is quite numerous. Members include vaesite²⁴ (NiS₂), hauerite²⁵ MnS₂, sperrylite²⁶ (PtAs₂).

Members of the cobaltite-group (cobaltite²⁷, CoAsS, gersdorffite²⁸, NiAsS, and ullmannite²⁹ NiSbS) have structures which resemble the pyrite structure very much. The group –V metals (As, Sb) replace one S of the S₂-pair. See fig. 4.9 for a comparison of the pyrite and ullmannite group.

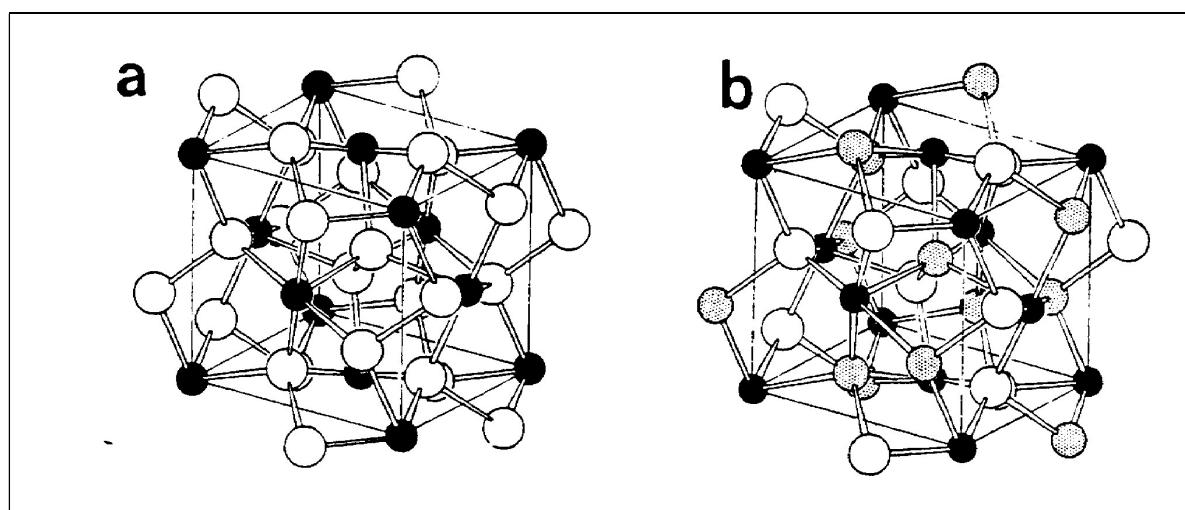


Fig. 4.8. a) The structure of pyrite. Closed spheres are Fe. b) The structure of ullmannite NiSbS. Grey spheres are Sb.

c) Marcasite structure and derivatives

Marcasite is an orthorhombic polymorph of pyrite. The structure is given in figure 4.9. Arsenopyrite³⁰ is derived in the same way from marcasite as the members of the cobaltite group are derived from pyrite. The As-ratio can vary however, from 1.22 to 0.82. The structure of arsenopyrite is triclinic, but As-rich varieties can approach a monoclinic symmetry. Loellingite³¹ (or Löllingite), FeAs₂, also crystallizes in the marcasite structure.

²⁴ **Vaesite:** named for Johannes Vaes, Belgian mineralogist for the Union Miniere du Haut Katanga.

²⁵ **Hauerite:** named after the Austrian geologists, J. R. Hauer (1778-1863) and F. R. Hauer (1822- 1899).

²⁶ **Sperrylite:** named after its discoverer, the American chemist, F. L. Sperry

²⁷ **Cobaltite:** named after mines in the Cobalt district, Ontario, Canada

²⁸ **Gersdorffite:** Named after Herr von Gersdorff, owner of Schladming Mine, Austria.

²⁹ **Ullmannite:** Named after the German chemist and mineralogist, J. Ch. Ullmann (1771- 1821).

³⁰ Named after the mineral's chemical composition. Arsenopyrite crystal may resemble pyrite in handspecimen, but it are never real cubes, as arsenopyrite is triclinic.

³¹ **Löllingite:** named after Lölling, Hüttenberg, Carinthia, Austria

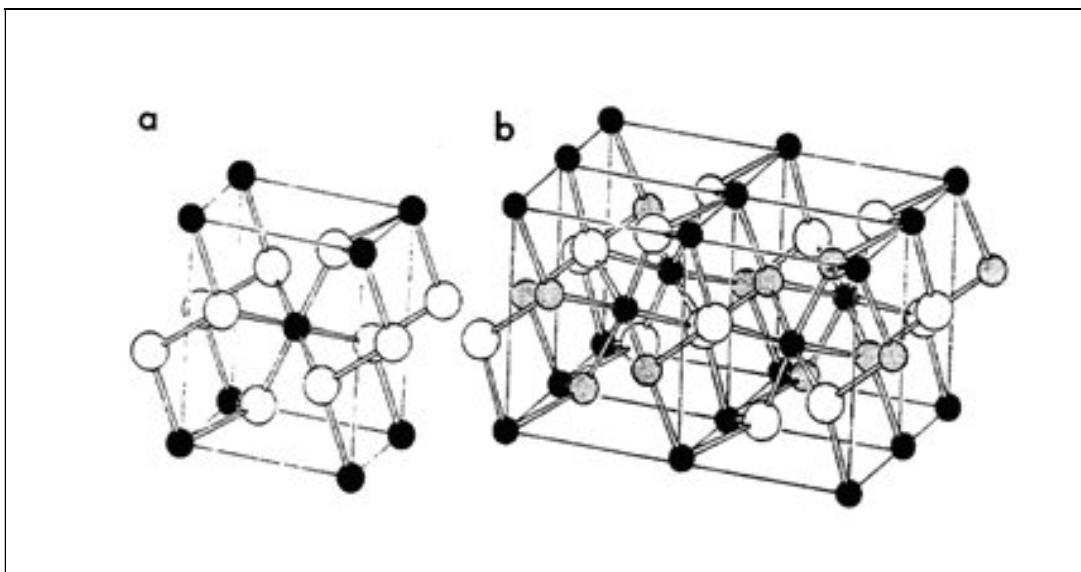


Fig 4.9. (a) The structure of marcasite, FeS_2 (closed spheres are Fe) (b) arsenopyrite, FeAsS . Grey spheres are As.

2.2.4. Other stoichiometries (M_xS_y)

a) Chalcocite³² structure and derivatives (digenite, djurleite).

The *chalcocite* (Cu_2S) structure is again an example of hydride metallic and covalent bonds in sulphides. Chalcocite has a complex structure which is based on a hcp stacking of S-atoms. The structure is distorted and not hexagonal.

At 104°C chalcocite transforms to a hexagonal modification, of which the unit cell is analogous to a hcp-stacking. This phase has a large diffusion for Cu and high electric conductivity.

At about 350°C this hexagonal chalcocite changes into a cubic form with a variable stoichiometry ($\text{Cu}_{1.765}\text{S}$ - $\text{Cu}_{1.79}\text{S}$), which is called *digenite*. Digenite has sulphur in a ccp stacking.

A small change in the stoichiometry of Cu in chalcocite leads again to new phase (orthorhombic), named *djurleite* ($\text{Cu}_{1.96}\text{S}$). Optically, *digenite* and *djurleite* are difficult to distinguish. However, the difference in optical properties between *chalcocite* on the one hand, and *digenite/djurleite* on the other hand is considerable.

Digenite and *chalcocite* are also important minerals in the pyrometallurgical processing of sulfidic Cu-Ni-ores. Both occur in an intermediate product.

Digenite often contains a little Fe, which can be admitted into the structure at HT.

³² Chalcocite from the Greek *chalkos*, meaning "copper". (Hence: **chalcopyrite** = copper pyrite). Cubanite: named after the location. **Digenite** from the Greek for "two kinds" or "sexes," in reference to the presumed presence of both cuprous and cupric ions. **Djurleite** for the Swedish chemist Seved Djurle (1928–2000), who first synthesized the compound later found in nature.

Digenite is therefore sometimes seen as a member of the Cu-Fe-S-group of sulphides, chemically related to chalcopyrite³¹ (CuFeS_2), cubanite³¹ (CuFe_2S_3), and *bornite*³³ (Cu_5FeS_4)

The tetragonal bornite (Cu_5FeS_4) is related to digenite. The structure of bornite, one of the most readily identified sulphides is based on a ccp stacking of S-atoms. Above 335°C there is complete solid solution between bornite and digenite. HT-bornite also has (limited) solid solution with chalcopyrite. The disintegration of these compositions results in the often peculiar, but common evolution-textures of chalcopyrite and bornite.

b) Stibnite structure and derivatives

In this group we find a large number of minerals where Group-V elements like, As, Sb, Bi, are bonded to sulphur. The metal-sulphur groups form rings or plates which are build of MS_3 trigonal pyramids or MS_4 tetragonal pyramids. The manner in which these metal-sulphur pyramids are connected determines the final M-S-stoichiometry.

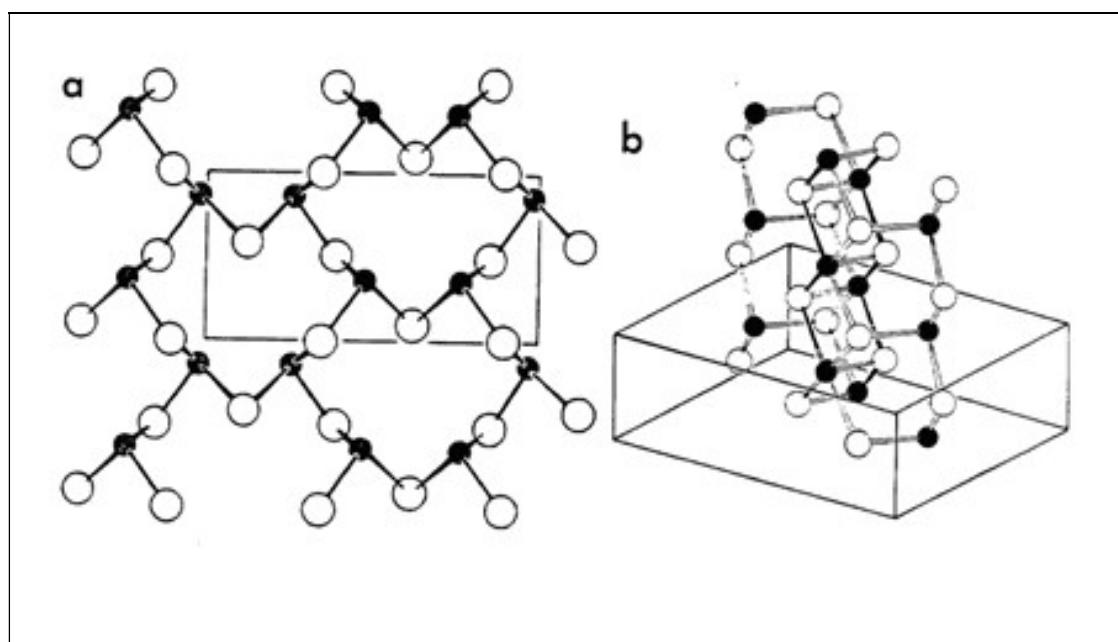


Fig 4.10 The layer structure of orpiment (As_2S_3) (a), projected along the b-axis, and one of the fourfold chains in stibnite (Sb_2S_3) (b). Open circles are sulphur.

³³ **Bornite:** named after the Austrian mineralogist, I. von Born (1742-1791).

Examples are:

- *stibnite*³⁴ (Sb_2S_3) (Synonym: *antimonite*)
- *bismuthinite* (Bi_2S_3)
- *realgar* (AsS)
- *orpiment* (As_2S_3)
- Cu-Bi-S minerals and Cu-Pb-Bi-S minerals (e.g. *bournonite*, PbCuSbS_3 ; *aikinite*, PbCuBiS_3 ; *emplectite*, CuBiS_2).

³⁴ **Stibnite:** From the Greek, *stimmi* or *stibi*, "antimony," thence to the Latin, stibium. Antimony: from the Greek *anthemon*, "flower" in allusion to the form of antimonite crystal druses. **Bismuthinite:** named after its composition. **Orpiment:** from the Latin, *auripigmentum*, in allusion to the vivid golden hue. **Realgar:** From the Arabic, *rahj al ghar*, "powder of the mine". **Bournonite** after French crystallographer and mineralogist *Jacques Louis, Comte de Bournon*. **Aikinite** after *Arthur Aikin* (one of the founders of the Geological Society of London). **Emplectite** from the Greek *emplektoς*, "interwoven."

3. OXIDES

3.1. Properties of Oxides

The mineralogy of oxides is different from that of sulphides because of the occurrence of ionic bonds. Oxides are because of these stronger bonds in general harder and more brittle than sulphides. Also they are often translucent. Magnetic properties are known from some minerals in the (inverse) spinel series (magnetite), ilmenite (FeTiO_3), wüstite³⁵ (Fe_{1-x}O) en hematite (Fe_2O_3). Often there are also interesting electric properties.

Many oxides are used in industrial applications, en they are manufactured on a large scale. Well known examples are cubic ceramic magnets (ferroxcubes), based on the structure of magnetite and related inverse spinels. Electronic applications are there for artificial materials with the perovskite structure, with famous examples like BaTiO_3 (dielectric), and Cu-Ba-Y-oxide ceramic superconductors.

3.2. General classification of Oxides

Most oxides are essentially ccp of hcp-stackings of oxygen, in which cations occupy tetrahedral or octahedral sites. In a ccp-cube there are 8 tetrahedral and 4 octahedral positions. In a hcp-stacking these numbers are 4 and 2.

Based on this, a number of basic structures can be recognised

- **NaCl-structure (MO)**

This structure is derived from a ccp-stacking where all octahedral cavities are filled with cations. Every cation and anion has 6 nearest neighbours.

Tetrahedral cavities are empty in stoichiometric structures. Examples of minerals with this structure are periclase (MgO), manganosite (MnO) and wüstite³⁴ (FeO).

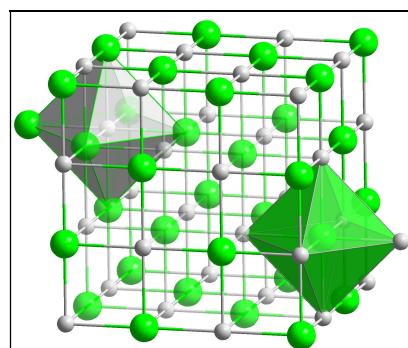


Fig. 4.11. The NaCl-structure.

³⁵ **Wüstite** (also spelled as wuestite): named after **Fritz Wüst** (1860 -1938), who first synthesized it.

- **Perovskite structure (ABO_3)**

In the perovskite³⁶ structure, also derived from the a ccp-stacking of oxygens, $\frac{1}{4}$ of the oxygen atoms is replaced by the large cation A, whereas $\frac{1}{4}$ of the octahedral cavities is filled with the smaller cation B. This leads to the ABO_3 -stoichiometry, with A in a 12-fold coordination. In fig. 4.15, the *perovskite* structure is shown. Perovskite .s.s. is CaTiO_3 , but natural perovskite is always impure: Na and REE for Ca, Nb replaces Ti. There are many synthetic varieties, for instance BaTiO_3 .

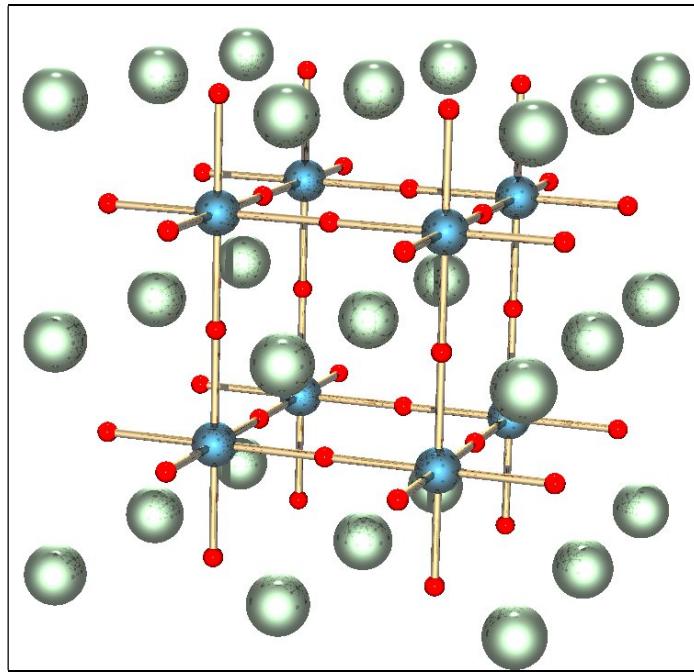


Fig. 4.12. The perovskite-structure, Red = O, Blue= Ti, Greenish = Ca

- **Fluorite structure (AO_2)**

Oxides with the fluorite structure (fig. 4.13) have a structure also derived from a ccp-stacking of oxygen atoms, but this time the A-cations go into the octahedral cavities, and the oxygen atoms go in the tetrahedral cavities. Thus the cations occupy the FCC lattice sites, while anions are located at eight tetrahedral sites. The four remaining octahedral sites in the FCC lattice remain vacant. A very well-known oxide mineral with this structure is *thorianite* (ThO₂). Related is the structure of *uraninite* s.s. (UO₂)

³⁶ Named after the Russian mineralogist, L. A. Perovski (1792-1856).

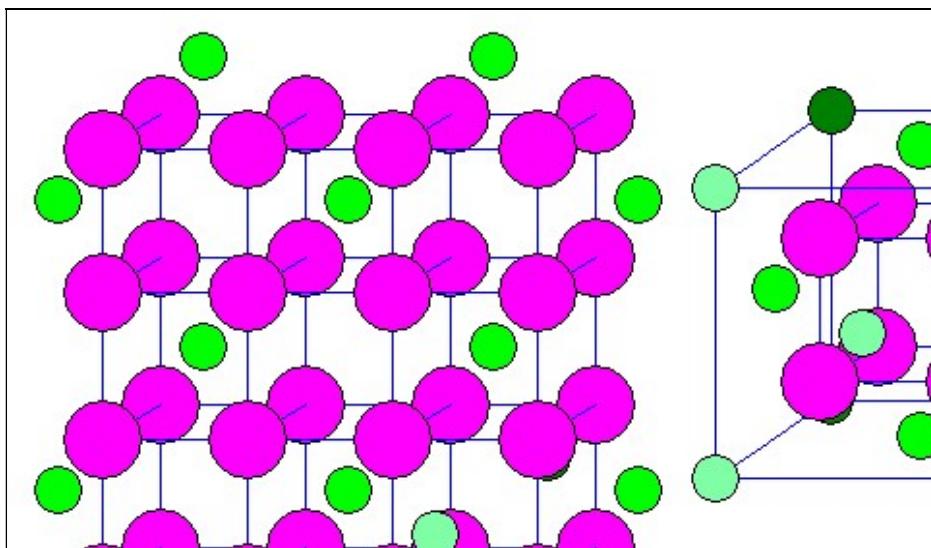


Fig. 4.13. The fluorite structure. In the derived oxides, oxygen takes the place of F and the cation takes the place of Ca.

- **Rutile structure (AO_2)**

The *rutile* structure is based on the hcp-stacking, but with considerable distortion, causing the symmetry to be tetragonal. Ti fills half of the octahedral cavities in an alternating pattern. Oxygen layers occur in a wave-like pattern. Rows of empty octahedral positions along $<001>$ form a kind of tunnels, which serve easy diffusion.

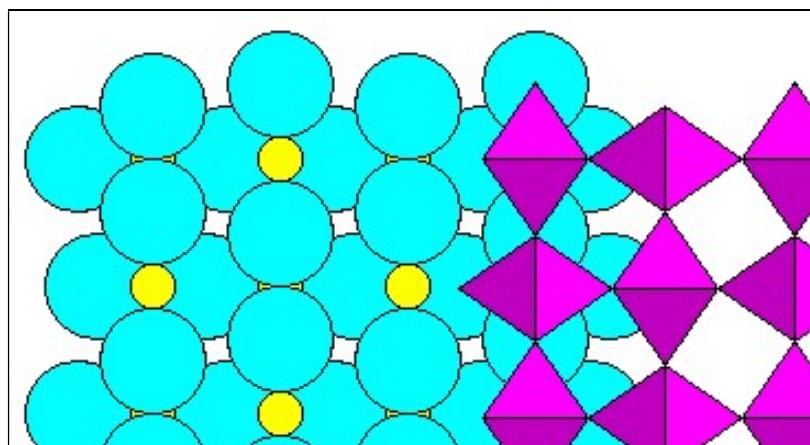


Fig. 4.14. Viewed down the fourfold symmetry axis, the rutile-structure looks like this. Octahedra with Ti at their centres enclose square tunnels.

Note that the purple octahedra are positioned in such a way that going around a square from the point of one octahedron to the next, we find ourselves spiraling up or down. This is a good example of a screw axis³⁷.

Examples of minerals with this structure are rutile³⁸ (TiO_2), *cassiterite* (SnO_2), *pyrolusite* (MnO_2). Cassiterite is the most important tin-ore mineral. Pyrolusite is the most important Mn-ore mineral.

- **Spinel³⁹ structure (AB_2O_4)**

The spinels are any of a class of minerals of general formulation AB_2O_4 which crystallize in the cubic (isometric) crystal system, with the oxide anions arranged in a cubic close-packed lattice and the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice. A and B can be divalent, trivalent, or quadrivalent cations, including magnesium, zinc, iron, manganese, aluminium, chromium, titanium, and silicon. When the cation in tetrahedral positions are labelled A, and those in octahedral sites B, the stoichiometry is AB_2O_4 .

All spinels have two cations (MgAl_2O_4) or two valences of the same cation (FeFe_2O_4) in a ratio 2:1. There are two kinds of spinels: normal and inverse.

When the most occurring cation (3+) is located in the octahedral position, the structure is called normal spinel. If the most occurring cation (3+) is divided over the two types of sites, the structure is called inverse spinel.

The spinel structure is given in fig.4.15.

³⁷ In crystallography, a screw axis is a symmetry operation describing how a combination of rotation about an axis and a translation parallel to that axis leaves a crystal unchanged.

³⁸ Rutile: from the Latin, *rutilus* - "reddish." Cassiterite: From the Greek *kassiteros* = "tin.". From the Greek, *pyro* and *louein*, "fire" and "to wash," because it was used to remove the greenish color imparted to glass by iron compounds.

³⁹ Name of uncertain origin, possibly derived from Latin, *spina*, for "thorn" in allusion to sharply-pointed crystals.

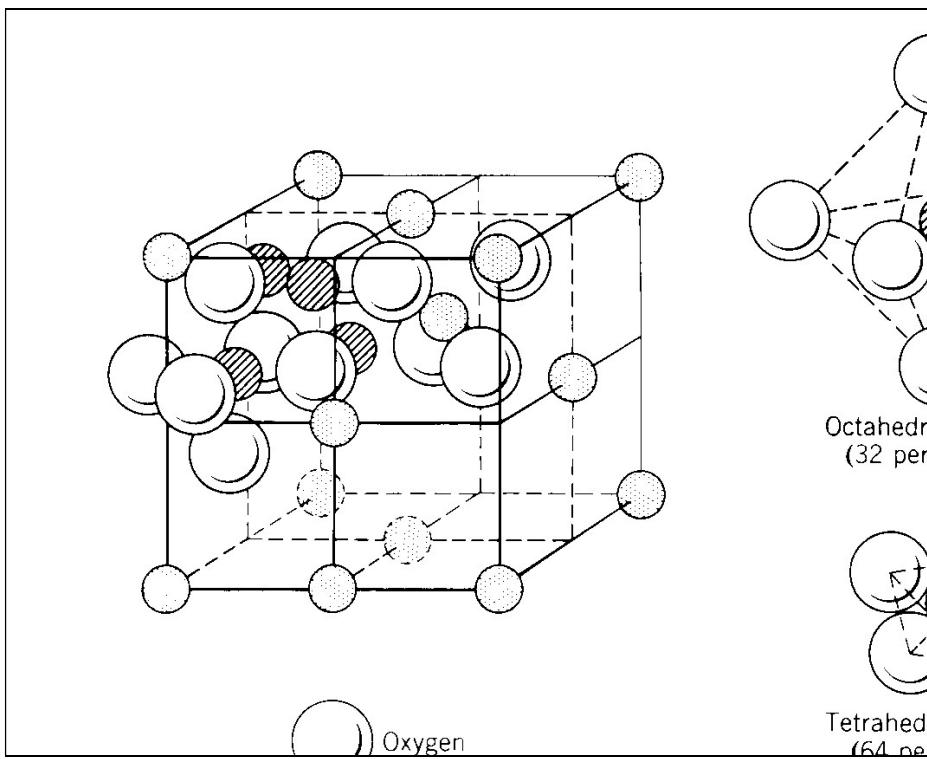


Figure 4.15. The spinel structure

Important examples are *spinel s.s.* (MgAl_2O_4 , normal spinel), *magnetite* (FeFe_2O_4 , inverse spinel), *chromite* ($\text{Fe}^{2+}\text{Cr}^{3+}_2\text{O}_4$, normal), and *ulvöspinel*⁴⁰ ($\text{Ti}^{4+}\text{Fe}^{2+}_2\text{O}_4$, special case). Magnetite forms solid solutions with many spinels, but the one with ulvöspinel is most likely the most important. This $\text{Ti}_x\text{Fe}_{3-x}\text{O}_4$ series is called *titanomagnetite*. Evolution Ti-rich phases of titanomagnetites gives rise to evolved ilmenite (FeTiO_3)-lamellae in magnetite.

Spinels are also very important because some of them (that is: some inverse spinels) exhibit **magnetic properties**. The typical example is *magnetite*. The type of magnetism displayed by magnetite is called **ferrimagnetism**⁴¹.

Electron spins of iron ions in the A and B-sites are directed contrary to each other, but because the iron is present in 2-valent state and 3-valent state, the netto magnetical momentum of the A- and B-sites does *not* cancel out.

Unpaired electron spins give rise to a magnetic moment. Hence the netto magnetism. If these unpaired electronspins do cancel with respect to their magnetic moment, the magnetism is of course not macroscopically noticeable. Such compounds are called **anti-ferromagnets**. Many industrial ceramic magnets are based on the magnetite structure. Such material are called ferroxcubes (magnetite and its related *ferrites* are cubic).

⁴⁰ The name is derived from **Södra Ulvön** island, Ångermanland, Sweden, and the **spinel group**.

⁴¹ **Ferrimagnetism** is different from the more common **ferromagnetism**. A detailed explanation is beyond this text. Above its Curie-point, for ferrimagnets called Neél-point, both types become **paramagnetic**.

- **Corundum structure (A_2O_3)**

The *corundum* structure is derived from a hcp-stacking of oxygen. The trivalent cations occupy 2/3 of the octahedral cavities. The distribution of occupied cation sites within a layer perpendicular to the six-fold axis (c-axis) is in the form of six-sided rings. Layers shift however in the direction parallel to the C-axis. (Fig.4.20). Repetition takes place after six layers of cations and anions. Examples are *corundum*, *hematite*, *ilmenite*. Hydrohematite is a defect solid solution, where OH takes the place of O and electrical neutrality is obtained with octahedral Fe^{3+} -vacancies. The formula becomes: $Fe_{2-x/3}(OH)_xO_{3-x}$, with x to approximately 0.5. Hydrohematite is formed by low temperature dehydrogenation of goethite ($FeOOH$).

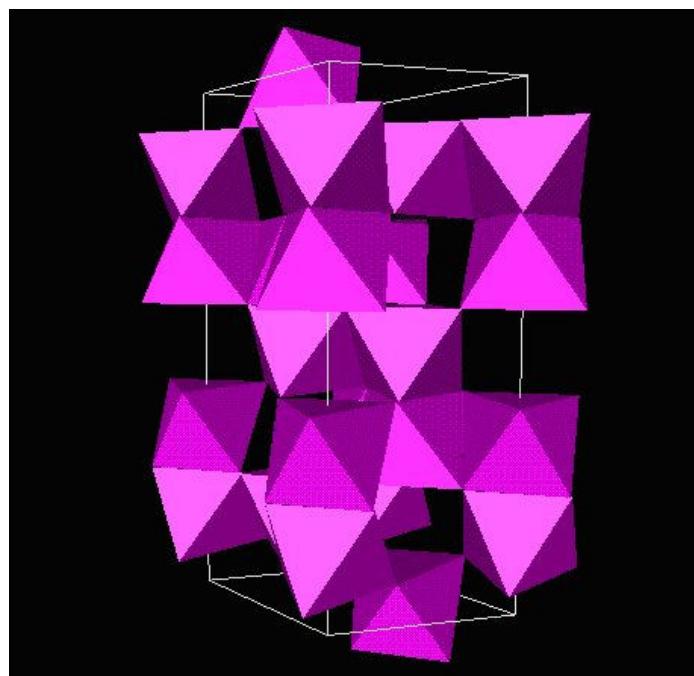


Fig. 4.16. The corundum structure

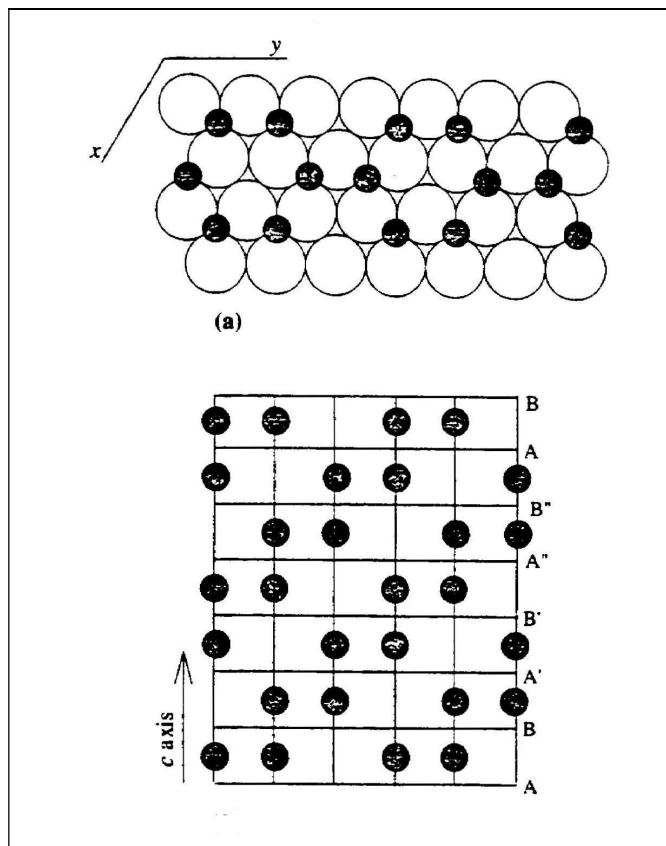


Fig. 4.17. The corundum structure.

4. HYDROXIDES (M-O-OH)

4.1. Fe- and Al-oxy-hydroxides

Goethite⁴² is the most common of the Fe-hydroxides and also the most stable one. The structure (fig. 4.21 14) is based on a hcp-stacking of oxygen and hydroxyl-ion, which resembles the rutile-structure. Fe³⁺-ions occupy the octahedral spaces in a series of double rows, alternated with a series of double rows without cation. Every double row with associated cations forms a double chain of tetrahedra which shares sides and which stretches along the c-axis. The chains themselves are connected by shared tops of the octahedra. The vacant rows of octahedral sites form “channels” fit for diffusion. In figure 4.21 they appear as “tunnels”, but they are better described as a series of vacant positions. They may enhance diffusion. At the surface these channels give rise to the formation of “grooves”, which are excellent places for the attachment of absorbed species. Goethite forms a restricted solid solution with *diaspore*⁴³ (α -AlOOH). Diaspore occurs in bauxites.

⁴² Goethite: named after the German poet and playwright J.W. von Goethe (1749–1832),

⁴³ Diaspore: the name is from the Greek for διασπείρειν, to scatter, in allusion to its decrepitation on heating.

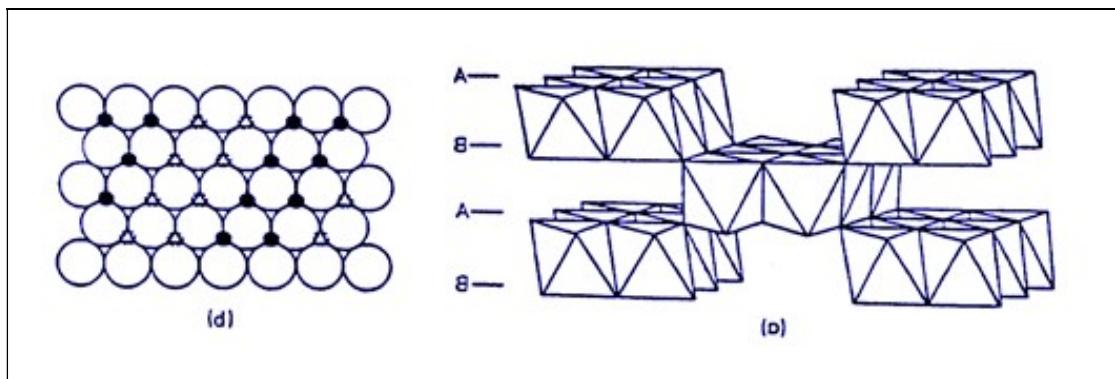


Fig. 4.18. The goethite structure.

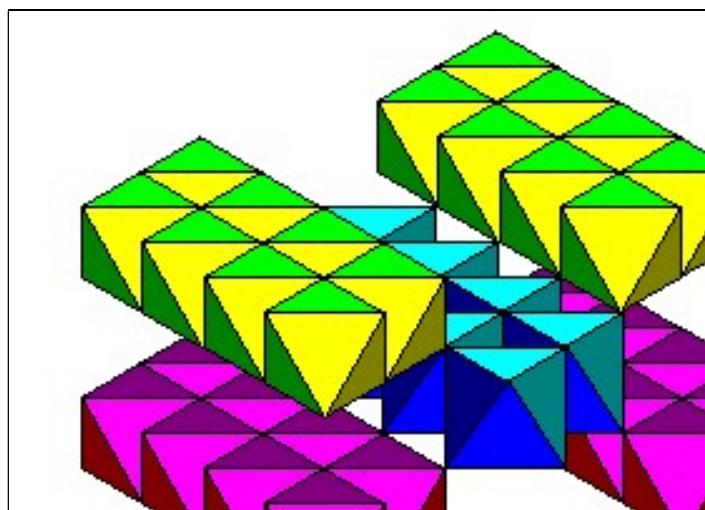


Fig. 4.19. The goethite structure in an oblique view.

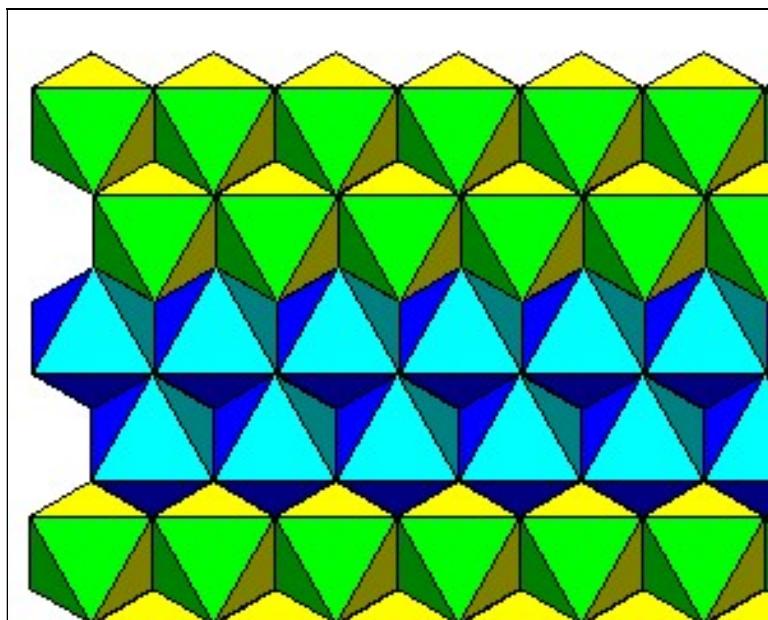


Fig. 4.20. The goethite structure, top view

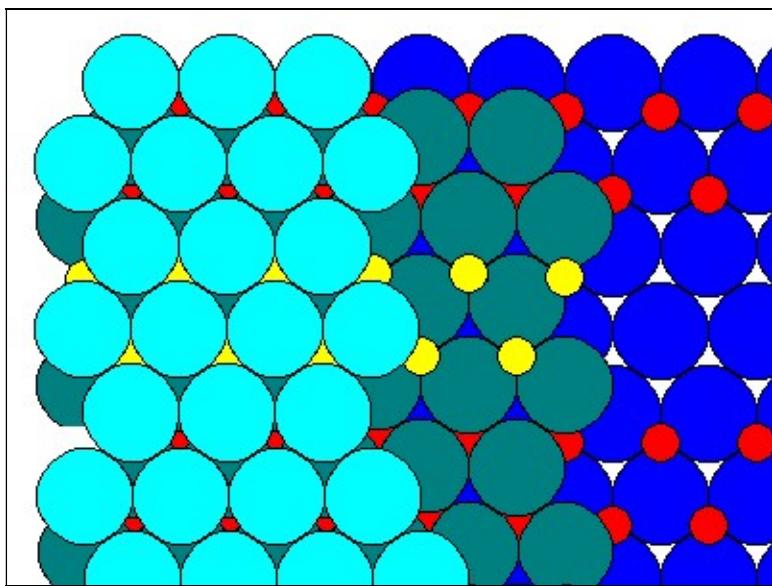


Figure 4.21. Ball model of the goethite structure. The octahedral layers are indicated in various shades of blue, cations in red and yellow.

A polymorph of goethite is the much more rare *lepidocrocite*⁴⁴ ($\gamma\text{-FeOOH}$). The analogous Al-oxyhydroxide is *boehmite*⁴⁵, which also occurs in bauxite. Boehmite has major industrial applications and is manufactured artificially. Lepidocrocite is based on a CCP stacking of anions (oxygen and hydroxyl) with intermittent rows of empty octahedral sites (fig. 4.25). The structure is such that step like layers of dioctahedral $\text{Fe}(\text{O},\text{OH})_2^-$ chains may occur.

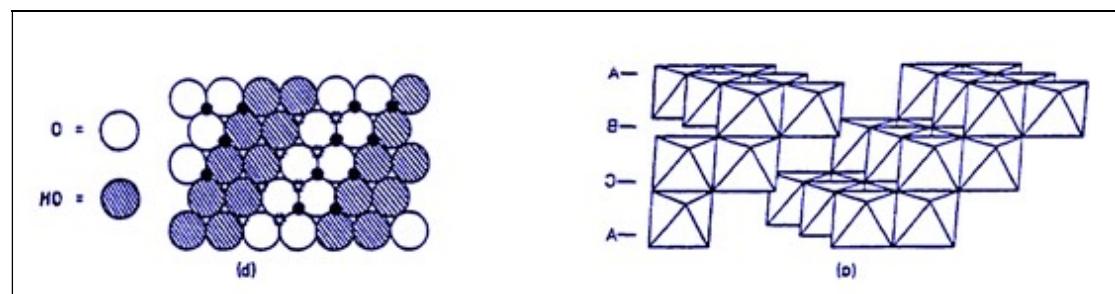


Fig. 4.22. The structure of lepidocrocite. Modified after Craig and Vaughan (1993).

⁴⁴ **Lepidocrocite:** name from the Greek lipis - "scale" and kroxis - "fibre."

⁴⁵ **Boehmite** (also spelled böhmite): named after the German geologist and paleontologist, Johannes Boehm or Böhm (1857-1938).



Fig. 4.23. Goethite, Minas Gerais, Brazil.

4.2. Mn-oxyhydroxides

Analogous to the Fe-oxyhydroxides and Al-oxyhydroxides, there are also Mn-oxyhydroxides. The number of Mn-oxides and hydroxides is very large. This is due to the large number of valences the Mn-ion may have, giving rise to a multitude of possible coordinations of O^{2-} and OH^- . Often the mineralogy of Mn-ore deposits is badly defined. (Sometimes a precise characterisation is impossible, as in Mn-nodules). Crystallinity often also is bad, The common mineral pyrolusite (β - MnO_2) is at a closer look often rather γ - MnO_2 or δ - MnO_2 .

Pyrolusite has a rutile-structure but the other MnO_2 -polymorphs have mixed structures. Ramsdellite⁴⁶ ($Mn-O-OH.xH_2O$) has a goethite structure, but nsutite ($Mn-O-(O,OH)$) has a mixed goethite-rutile structure. In these structures the large open channels are often occupied by H_2O , but also other large cations occur.

Psilomelane⁴⁷ is actually not a mineral. The name is discredited by the International Mineralogical Association in 1982. The material, $Mn-O-OH$, actually consists mainly of romanechite⁴⁸ and cryptomelane. Psilomelane is now a general term for hard, black Mn-oxides, with variable amounts of barium and potassium. It is a common and important ore of manganese, occurring under the same conditions and having the same commercial applications as pyrolusite.

⁴⁶ **Ramsdellite:** MnO_2 named after the American mineralogist, Lewis S. Ramsdell (1895-1975), of the University of Michigan, who first described the mineral. **Nsutite:** named after Nsuta, Ghana. Empirical formula: $Mn^{4+}_{0.85}O_{1.7}Mn^{2+}_{0.15}(OH)_{0.3}$

⁴⁷ **Psilomelane:** named in 1758, from the Greek psilos - "smooth" and melas - "black."

⁴⁸ **Romanechite:** Romanche, Saone-et-Loire, France. Psilomelane is often now used as a synonym for romanechite. Empirical formula: $Ba_{0.7}Mn^{3+}_{4.8}Si_{0.1}O_{10}\cdot 1.2(H_2O)$. **Cryptomelane:** from the Greek for hidden and black, as the identity of this common, black mineral is lost in the group of other black Mn-bearing oxides. Empirical formula: $KMn^{4+}_{6}Mn^{2+}_2O_{16}$.



Fig. 4.24. Banded massive psilomelane, Compton, Virginia, USA.

Cryptomelane, the commonest of the hard, black, fine-grained manganese oxides formerly called psilomelane, has not a goethite, but a hollandite-structure. This will not be discussed here. Romanechite is second of the most common species. The Mn-oxides have an enormous capacity for the adsorption of heavy metals. It is often difficult to give a rigid composition for these minerals. Also the physical properties are diverse.



Fig. 4.25. Psilomelane.

5. STRUCTURE SUMMARY

In this paragraph, we will give an overview of the different mineral structure groups treated and the most important minerals belonging to them.

Mineral group	Structure type	Subgroup	Examples	Remarks
Sulphides	Monosulphides	Sphalerite structure	sphalerite, chalcopyrite, luzonite, tennantite, tetrahedrite	Sphalerite is the most important Zn-ore. Chalcopyrite is the most important Cu-ore
		Wurtzite structure	wurtzite, cubanite, enargite	
		Nickeline structure	Nickeline, pyrrhotite, troilite	Pyrrhotite may exhibit magnetism
		Millerite structure	millerite	
	Pentlandite structure	pentlandite		
	Galena structure	galena, cinnabar		Galena is the only important Pb-ore
	Covellite structure	covellite		Minor Cu-ore. Widespread alteration product of chalcopyrite. First discovered natural superconductor
Disulphides	Molybdenite structure	Molybdenite structure	molybdenite	
		Pyrite structure	pyrite-subgroup, cobaltite-subgroup, gersdorffite-subgroup, ullmanite-subgroup	Very extensive group. Many sulphide minerals crystallize in one of these structures
	Marcasite structure	marcasite, arsenopyrite, löllingite		
Other Stoichiometries	Chalcocite structure	chalcocite, digenite, djurleite, bornite		
	Stibnite structure	stibnite (=antimonite), bismuthinite, orpiment, realgar		

Mineral group	Structure type	Subgroup	Examples	Remarks
Oxides	NaCl-structure		periclase, manganosite, wüstite	
	Perovskite structure		perovskite, BaTiO_3	Important industrial applications for many compounds with this structure.
	Fluorite structure			thorianite, uraninite
	Rutile structure		rutile, cassiterite, pyrolusite	Cassiterite is the most important Sn-ore. Pyrolusite is the most important Mn-ore.
	Spinel structure	Normal spinel	spinel s.s., ulvöspinel	
		Inverse spinel	magnetite, chromite	Magnetite and chromite are important ore minerals for respectively Fe and Cr. Magnetite is the archetypical cubic <i>ferrimagnet</i>
	Corundum structure		Corundum, hematite	Hematite is the most important Fe-ore mineral
Mineral group	Structure type	Subgroup	Examples	Remarks
Oxy-Hydroxides	Fe-Al-Oxyhydroxides		Goethite, lepidocrocite, boehmite, diaspor	Important minerals in respectively iron oxides and bauxites. Boehmite has also many industrial applications.
	Mn-oxyhydroxides		Cryptomelane, romanechite, “psilomelane”	Common in many Mn-ores

6. REFERENCES

The following works were frequently used in this chapter.

- Craig, J.R., Vaughan, D.J. (1994). Ore microscopy and Ore Petrography, Second Edition, Wiley, New York, 434 pp.
- <http://www.uwgb.edu/dutchs/MPNOTES.HTM>. Internet files of Earth Science 492: Crustal Materials Class Notes by Prof. Steven Dutch, Univ. Wisconsin, Green Bay, USA. Many (coloured) crystal structure drawings were taken from these lecture series.