# TA3140 - Economic Minerals and Rocks

## An Introduction to Ores, Ore Minerals, Industrial Minerals, and Coal

Dr. J.H.L. Voncken
Dr. K.H.A.A. Wolf

Based partly on texts by Prof. Dr. M. Hale

TU Delft
Faculty of Civil Engineering and Geosciences
Department of Geotechnology
August 2011

# Table of Contents

# Preface

These lecture notes, belonging to the course TA3140, *Economic Minerals and Rocks*, are intended to present the subjects covered in this course in detail. To these lecture notes also belong *Powerpoint Sheets,* distributed via Blackboard to enrolled students. The lecture notes presented here, provide besides the contents of the course, also additional information or even sideways for those interested in the subject. For example, most of the mineral names used in this course are explained in this text (generally in footnotes), but it is not necessary to know these.

Chapter II is a modified version of the unpublished course notes *"The Geology of Ore Deposits - Economic Geology"* from *1996/1997* by *Prof. dr. M. Hale (ITC).* Also the book by *A.M. Evans (1993) Ore Geology and Industrial Minerals, An Introduction,* is frequently used.

The other information covered here is taken from books mentioned in the literature list.

The chapter on Coal (Chapter V) is by Dr. K.H.A.A. Wolf.

With respect to previous editions, this version is slightly modified and extended.

August 2011.

Dr. J.H.L. Voncken

# Chapter I. Introduction - Principles and Concepts.

Economic minerals and rocks are minerals and rocks with an economic significance. They may be used to man's advantage. The area of the Earth Sciences dealing with economic minerals and rocks is called ***Economic Geology***. The term commonly refers to metallic mineral deposits and mineral resources. This course will give an overview of the minerals and rocks that are mined for industrial uses. These rocks also comprise coal, oil shale and oil sands. Although **coal and oil shale/oil sand** are generally ranked among the fossil fuels, they are also sedimentary rocks (if not metamorphic – e.g. anthracite). In this course, we will look at the ore deposits and their minerals, industrial minerals and rocks, and at coal and oil shales/oil sands. First, however, we must deal with some general concepts and definitions.

## *I.1. Ores, Ore Minerals and Industrial Minerals.*

It is useful to define some of the terminology which is used in the field of Economic Geology and throughout this course. To start with, the term mineral is used in many different ways. The meaning is not always the same. In the health science and food and drink industry, *mineral* means something else than in the Earth Sciences. For example: "*the content of mineral constituents such as potassium, calcium, and phosphorus is very dependant on the type of honey…*" (quotation from a text on honey types). Such minerals are defined as follows: *inorganic elements that originate in the earth and cannot be made in the body.*

In this course we use the definition of a mineral as given by the International Mineralogical Association (IMA)[1]. This general definition is (Nickel, 1995):

- ***a mineral is an element or chemical compound that is normally crystalline, and that has been formed as a result of geological processes.***

In the field of Economic Geology, the useful components occur as ores, or (ore) deposits. The term mineral is subdivided into ***ore minerals*** and ***industrial minerals***. The subdivision is not entirely rigid, but in general they are used in the following sense:

- ***Ore is a solid naturally occurring mineral aggregate of economic interest from which one or more valuable constituents may be recovered by treatment.***
- ***Ore minerals are minerals from which metals or metallic constituents can be extracted.***

---

[1] ***IMA (International Mineralogical Association)***: An international committee of mineralogists, founded in 1958, which commits itself to the promotion of mineralogy as a science, takes care of the connections to neighboring scientific fields (e.g. materials science, inorganic chemistry), and sets rules for the mineralogical community in several scientific areas (e.g. mineral nomenclature, Commission on New Mineral Names), Definitions, etc.). There are national representatives, subcommittees, working groups, etc.

- ***Industrial minerals are any rock mineral or naturally occurring substance of economic value exclusive of metallic ores, mineral fuels and gemstones.***

See also Evans (1993), Nickel (1995).

In practice, **ore minerals** are in general found to be **opaque minerals**, which means they are **non-translucent,** even when cut and polished to a very small thickness. This however is only true to a certain extent, as many opaque minerals have a certain degree of translucency, occurring in general for long wavelengths of light (red, brown, etc.). In the microscopic study of ore minerals, conducted with a polarisation microscope in reflection mode, this aspect is generally referred to as “internal reflections”. An ore mineral may or may not have internal reflections. More of this will be told in the microscopy course on Ore Mineralogy. On the contrary, **industrial minerals** in general are **non-opaque, translucent minerals**, and may be studied in transmitted light. However, several industrial minerals have very high refractive indices, which makes microscopic study more difficult.

It is useful to elucidate the definitions with some examples:

<u>Ore minerals</u>: pyrite ($FeS_2$), galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), hematite ($Fe_2O_3$), magnetite ($Fe_3O_4$), goethite (FeOOH), orpiment ($As_2S_3$), native gold (Au), cassiterite ($SnO_2$).

<u>Industrial mineral</u>s: gypsum ($CaSO_4.2\ H_2O$), quartz, ($SiO_2$), calcite ($CaCO_3$), halite (NaCl) , barite ($BaSO_4$), fluorite ($CaF_2$), talc ($Mg_3Si_4O_{10}(OH)_2$ ), rutile ($TiO_2$). Often industrial minerals also include rocks, such as limestone (mainly $CaCO_3$), sandstone, granite, basalt**,** slate, gravel..

Sometimes confusion may arise: quartz is used <u>as such</u> in the glass industry, but in very pure form quartz is used to <u>extract</u> the metal silicium (Si) by a pyrometallurgical[2] reduction process. In this context, quartz would be an ore mineral. However, quartz is generally considered to be an industrial mineral, even when applied as “silicium ore”. Apatite ($Ca_5(PO_4)_3F$ ), the most common phosphorus ore, is laos considered by many geologists to be an industrial mineral, as phosphorus is not a metal. However, the production of phosphorus is reminiscent to a pyrometallurgical production process, common for metals. Hematite ($Fe_2O_3$) is a main iron ore minerals, but also constituent of many pigments, in which form it is actually an industrial mineral.

As to the relative importance of ores and industrial minerals: present day society cannot without either of them. On the one hand, metallic ores always have had an aura of romance, especially the ores of gold and silver, and they occur in many heroic tales, ranging from the mythic voyage of Jason and the Argonauts to recover the Golden Fleece, to the novels of Joseph Conrad and Jack London. Wars have been fought over metallic ore deposits, and new discoveries raised great public attention (for instance “gold rush in Klondike, Alaska”, or the like). Products from metallic ores are often considered to be more “tough”: for instance those made of steel. See the pictures below. This may suggest that metallic ores are more important.

---

[2] A metallurgical process involving heat

*Fig. 1.1.“Tough” products founded on metallic ores. (Iron).*

On the other hand, considering industrial minerals, no heroic stories were ever conceived concerning phosphate deposits, or rock salt, neither was there ever a talc rush, or a limestone rush. Many products of industrial minerals have no “tough” imago. Therefore they might seem less important. However, this is not so.

In many industrial activities and products, from the construction of buildings to the manufacture of ceramics (table ware, sanitary ware), the production of glass, the use as colouring agents in glass and synthetic materials, and the use in sanitary or cosmetic or nursing products (ranging from kitchen abrasives, to baby powder, or even tooth paste) industrial minerals are used. Below are four images which clearly show the commonness of industrial minerals (a fact which in general is overlooked). Therefore, we can safely state that ores and industrial minerals are equally important.

*Fig. 1.2.“Not-so-tough” products based on industrial minerals: baby talc powder (left), ordinary white “latex” wall paint with rutile ($TiO_2$) or chalk as a white pigment (right).*

*Fig.1.3. Bricks (left) en cement (right), also made of industrial minerals.*

## I.2. Important factors in the Economic Recovery of Minerals.

Mineral resources are natural occurrences of mineral bearing material in such a form, that economic extraction of a mineral commodity is possible. In order to access the exploitation possibilities of an ore body, a number of evaluations have to be made. How “rich” is the ore to be mined ? Which are the by-products ? What unwanted constituents are there ? In what form does the desired metal occur ? What is the location of the ore body: developed country, good infrastructure present, or is it “in the middle of nowhere” ? All these aspect are important to assess the quality of an ore body. Below these aspects will be dealt with. A commodity is a physical substance, e.g. a metal, which is interchangeable with another product of the same type, and which investors buy or sell, usually through futures contracts.
Although the text below deals with ores, it is to a large extend also of application to industrial mineral deposits and coal deposits. With respect to commodity, the term energy commodity is sometimes used when dealing with fossil fuels.

### I.2.1. Evaluation of an Ore Body

#### 1.2.1.1. Ore Grade

The concentration of metal in an ore body is called its ***grade.*** The process of determining these concentrations is assaying ( = making an assay[3]). Various economic, and sometimes even political factors determine the lowest grade of an ore that can be produced from an ore body. This termed the ***cut-off grade***. When the concentration of a valuable metal gradually decreases to background values in the confines of an ore body, may assays will have to be made. Cut-off grade is not geologically determined. If the price of a metal or commodity increases, it may be possible to lower the value of the cut-off grade, and thus increase the level of the ore reserves. The overall grade of the ore body will then be lowered, but for the same daily production, it will increase the life time of the mine. Grades vary from ore body

---

[3] A method to analyze or quantify a substance in a sample. An assay is an analysis done to determine the presence of a substance and the amount of that substance. It has a different meaning in the world of medicine.

to ore body, and the lower the grade, the greater the recoverable tonnage must be for a deposit to be economical. Technology may trans form waste into ore. In the Sudbury area in Ontario, old mine wastes can with modern technology be re-used as a low grade ore. Old mine wastes in the Witwatersrand in South Africa may still yield gold with modern technologies.

### 1.2.1.2.By-products

Sometimes several metals are present in an ore, and the sale of one may help finance the mining of the other. In times of changing metal prices, a mine may continue to exist for the production of a now (temporarily) uneconomic metal, because prices for one or more other stayed high. Nickel mines in the Sudbury area produce also copper and precious metals (platinum), which made them survive in past decades when the nickel price was low.

### 1.2.1.3. Mineralogical Form

The properties of a mineral govern the easy with which existing technology can extract and refine certain metals, and this may affect the cut-off grade. For instance, nickel can be better recovered from sulfide ores (*pentlandite* $(Fe,Ni)_9S_8$ ), *nickeliferous pyrrhotite* $(Fe,Ni)_{1-x}S$), then from silicate ores (*garnierite*, $(Ni,Mg)_4Si_6O_{15}(OH)_2\cdot 6H2O$). Sulfide ores can be worked down to 0.5 % Ni, whereas silicate ores must assay 1.5 % Ni. Tin (Sn) may occur in many minerals from which it is not recoverable (*andradite* $(Ca_3Fe(SIO_4)_3$, *stannite* $Cu_2FeSnS_4$), and in the one form from which it is recoverable (Cassiterite, $SnO_2$).Aluminium is abundant in many silicate rocks, but normally it must be in the form of hydrated aluminium oxides or hydroxides, a rock called bauxite, to be economically recoverable. The mineralogical nature of the ore will also put a limit on the grade. For instance, a copper ore containing only native copper can theoretically yield a concentrate with a 100 % Cu, but if the ore mineral was *chalcopyrite* ($CuFeS_2$), the concentrate would contain only 34.5 % Cu.

Industrial mineral may present different problems. A silica sand ($SiO_2$) for high quality glass production may contain 0.035 % $Fe_2O_3$. Some brown looking sands can be upgraded, if the iron oxide is present as a coating, but if the iron oxide is present as inclusions, this is not possible.

### 1.2.1.4. Grain Size and Shap*e*

The ***recovery*** is the percentage of the total metal contained in the ore that is recovered in a concentrate. A recovery of 90 % means that 90 % of the metal contained in the ore is recovered in the concentrate, and 10 % is lost in the tailings. One might think that when grinding an ore fine enough, complete separation must be possible. In theory this true, but in practice, many mineral processing techniques fail at small grain sizes. Moreover, milling and grinding is very expensive (as is has high energy consumption), so it might be cheaper to loose a certain percentage of the metal in the tailings, then to grind further to a smaller size.

Sometimes fine grain size and/or intergrowths and tiny inclusions may preclude a mining operation. The MacArthur River lead-zinc deposit in Australia, has not been mined since its discovery in 1956 because of the extremely fine grain size. Cu concentrations must be very low in the concentrate for pyrometallurgical zinc processing.

Grain sizes may also be of importance for the use of a number of industrial minerals. Aggregate in concrete is used in a number of grain sizes, depending on the end use. Different minerals for filler application require different often very small grain sizes. (The same for pigments). Grain shape may also be important.

### 1.2.1.5. Undesirable substances

Undesirable substances may be present in both ore and gangue minerals. Arsenic from *tennantite* ($Cu_{12}AsS_{13}$) may introduce unwanted As in a copper concentrate. *Chalcopyrite* inclusions in *sphalerite* may introduce copper in a zinc concentrate. If the amount of Cu is too high, the Zn-smelting process goes astray, and the ore cannot be processed. Phosphorus (e.g. from *apatite* $Ca_5(PO_4)_3F$ ) in iron ore concentrate (common in the famous Kiruna ores from N-Sweden) is unwanted for iron production etc. These unwanted substances cannot always be removed by separation processes. For instance, in the photograph below, the ZnS-host mineral contains numerous tiny inclusions of *chalcopyrite* ($CuFeS_2$), which cannot be removed. Milling must then be extremely fine, and separation techniques on such a particle scale often do not work. A concentrate of this type of sphalerite will yield a low price from a Zn-smelter (if accepted at all).

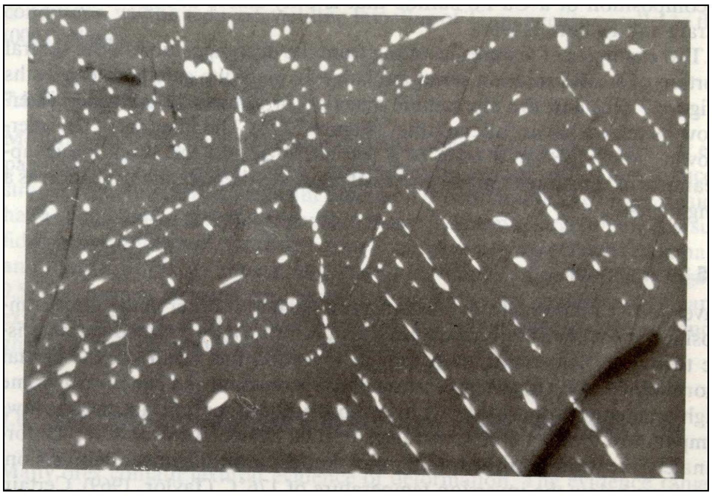


*Fig.1.4. Chalcopyrite blebs(white) in sphalerite. Reflected light microscopy. Width of field is 520 µm. From Craig and Vaughan, 1994.*

### 1.2.1.6. Size and shape of the ore bodies

The size, shape and nature of the deposit also influence the workable grade. Large low grade deposits that occur at or near the surface, may be worked with cheap open pit methods, whereas thin tabular veins deposits will have to be worked by more expensive underground methods. Ore bodies with regular shape can be mined at lower cost than irregular bodies with barren zones. In the latter ones the waste-to-ore ratio is higher.

*Fig.1.5. Open pit copper mine.*

### 1.2.1.7. Ore character

Loose unconsolidated beach sand can be mined cheaply by dredging and does not require crushing. Hard compact ore must be drilled, blasted and crushed. In hard rock mining, a related aspect is the strength of the country rocks. Badly sheared rocks in underground operations may require more roof supporting then less sheared ones. In open pit mining a gentler slope of the pit sides will be necessary, which will affect the waste-to-ore ratio. (Similar for coal or lignite mines).

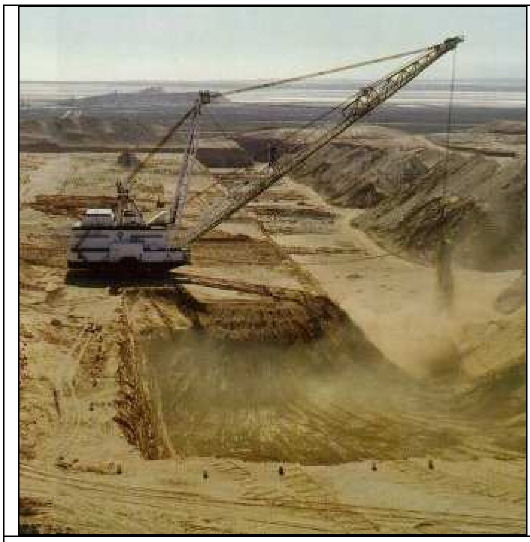
| | |
|---|---|
|  |  |
| *Fig.1.6a Excavator in an alluvial diamond mine.* | *Fig.1.6b. Hambach lignite mine (Germany) with a giant dredger in the foreground.* |

*Fig.1.7. Underground gold mine. Shaft 2 and shaft 3 (background) of the Western Deep Levels mine at Carletonville, South Africa.*

*Fig.1.8 Excavator in an underground mine.*

### 1.2.1.8. Cost of capital

Presently it is almost impossible to develop a large scale mining operation without external funding or capitalisation. Borrowed capital has to be repaid with interest. Revenues of the mine must cover running costs, taxes, royalties, profit to the shareholders etc. Therefore such factors also play a role in potential exploitation of a newly discovered ore body.

### 1.2.1.9. Location

Location also may determine whether an ore body is economically viable. In a remote location, there may be no electricity, roads, railways, schools, hospitals etc. All or some of these infrastructural elements will have to be build. Transport costs may be very high. Wages will have be high to attract skilled workers. This may preclude exploitation, and this often happens. But if the ore body is rich enough, exploitation may still be carried out at a profit. A good example of a mine in a difficult remote terrain is the Ertsberg copper deposit in Papua New Guinea, located at an altitude of 4,500 meters above sea level. The Freeport Mining Company started in the 1970's with the exploitation, and in the tropical jungle of the very mountainous Papua New Guinea (fig. 1.9, 1.10) everything had to be build from scratch. There was no infrastructure at all. Nevertheless the exploitation was a success, and after the Ertsberg was exhausted, the neighbouring Grasberg was taken in exploitation.

*Fig. 1.9. The location of the Grasberg mine (within red circle, invisible because of cloud cover), Papua New Guinea, Indonesia.* *Satellite Image by Google Maps.*

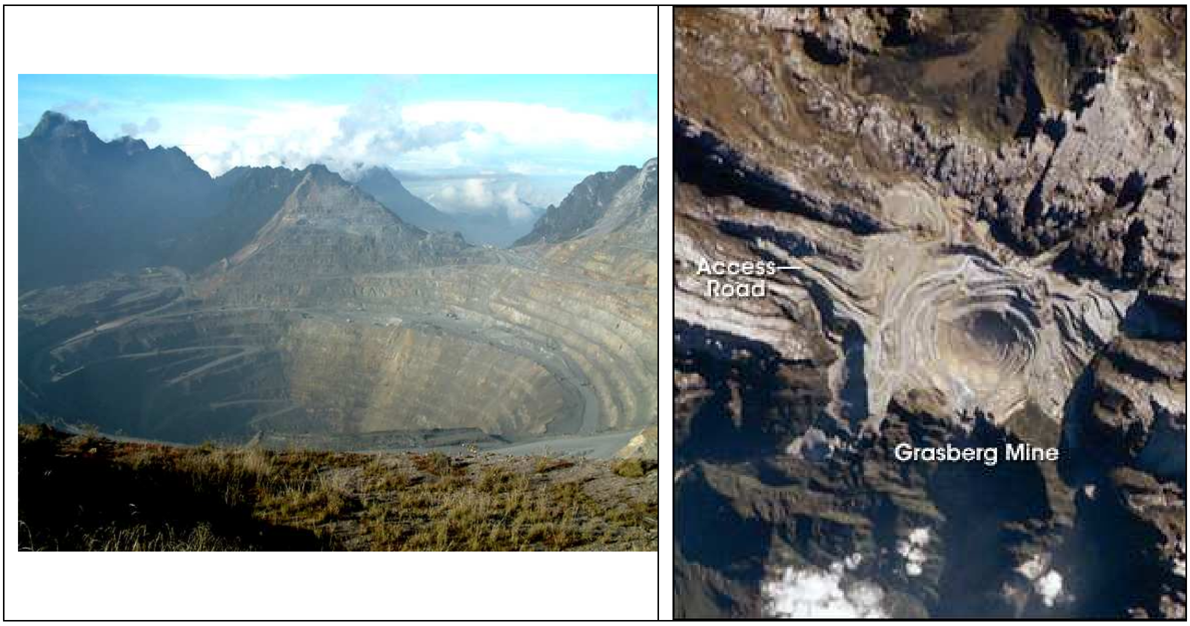


*Fig.1.10 .Grasberg Mine, Papua New Guinea. Left: near the mine itself. Right: view from space.*

### 1.2.1.10. Environmental Considerations.

New mines may bring prosperity, but inevitably will have an environmental impact. Conflicts with respect to environmental issues may involve the payment of compensation and the eventual costs for rehabilitating mined out areas. Stability of the overburden rock may be relevant in populous areas, where underground mining operations are carried out. Even the slightest subsidence of buildings at the surface may result in high costs.

### 1.2.1.11. Taxation

Governments may impose so much taxes, that a mining operation, economically viable in every other aspect, may be abandoned. On the other hand, mining may be encouraged by governments by financial bonuses, or mild taxes.

### 1.2.1.12. Political factors

The present and expected future stability of a country may influence the decision to start a mining operation, which will last in general for decades. Fear of nationalization may also play a role whether to start or to abandon exploitation.

## I.2.3. Ore reserve classification

***Reserves*** are that portion of the identified resources from which a usable energy or mineral commodity can be economically and legally extracted at the time of determination. The following terms are in their phraseology similar to that used for hydrocarbons (oil, gas), but in the latter field other definitions are used. (N.B.: coal is treated as if it were an ore or a rock).

In delineating and working an ore body, one must often classify the ore reserves into three classes: ***proven, probable, possible***. Frequently used synonyms are: ***measured or identified***, ***indicated*** and ***inferred***.

***Proven ore*** (***measured, identified ore***) has been sampled so thoroughly, that one can be certain of its outline, tonnage and average grade, etc., within certain limits. It is also called an identified resource. Elsewhere in the ore body, sampling may have been less thorough, but there may be enough information to be reasonable sure of its tonnage and grade. This is ***probable ore (indicated ore)***. On the fringes of the exploratory workings , there may be enough information to infer that the ore extends in some way into only partially explored areas, and that it may amount to a certain volume and grade. This is ***possible or inferred ore.*** Even lower in the ranking is ***hypothetical*** ore: undiscovered materials that may de expected to exist on the basis of broad geological knowledge and theory. Lowest in this scale is ***speculative*** ore.

In many countries these or equivalent words have nationally recognized definitions, and legal connotations.

### I.2.4. Mineral Resources

Mineral resources represent the total amount of a particular commodity (e.g. copper), and usually they are estimated for a nation as a whole, and not for a single mining company. They consist of ore reserves, uneconomical deposits and hypothetical deposits not yet discovered. The estimation of undiscovered potential can be made by comparison with well explored areas of similar geology.

## *I.3. Geochemical Considerations*

### 1.3.1. Classification of elements

It is traditional in the mining industry to divide metals into groups with special names. These are:
a) *Precious Metals* - gold, silver, **P**latinum **G**roup **E**lements or **PGE** (platinum Pt, rhodium Rh, ruthenium Ru, iridium Ir, osmium Os, and palladium Pd)
b) *Non-Ferrous Metals* - copper, lead, zinc, tin, aluminium. The first four are also known as *base metals*
c) *Iron and Ferroalloy Metals* - iron, manganese, nickel, chromium, molybdenum, tungsten, vanadium, cobalt
d) *Minor metals and related Non-metals* – antimony, arsenic, beryllium, bismuth, cadmium, magnesium, mercury, REE (elements La – Lu), selenium, tantalum, tellurium, zirconium etc.
e) *Fissionable Metals* - uranium, thorium.

## 1.3.2. Partitioning of elements between mantle and lithospheric crust

The evolution of the Earth has favoured relative enrichment or depletion. In both mantle and lithospheric crust, the elements Si and O dominate. Other abundant elements in the mantle (bulk composition) Mg > Fe > Al. Other abundant elements in the lithospheric crust are (bulk composition) Al > Fe > Ca > Mg. These are the major elements which are the main constituents of rock forming minerals. The remaining less abundant elements are trace elements. Geochemical behaviour of trace elements often follows chemically similar major elements. Thus Ga (gallium) behaves as Al (aluminium), Ge (germanium) behaves as Si (silicium), Hf (hafnium) follows Zr (zirconium), Te (tellurium) follows S (sulphur)

On this basis, trace elements are also partitioned between mantle and lithospheric crust. Examples of trace elements which partitioned into the mantle are : Ni, Co, Cr, Ti, V, PGE, Au.
Examples of trace elements which partitioned into the lithospheric crusts are : B, Be, Li, F, Cl, Sn, W, U.

## 1.3.2. Concentration ranges in the lithospheric crust

The lithospheric crust is spatially very inhomogeneous. Thus the amounts of each mineral and element show considerable spatial variations. Statistically, the distribution of an element has a very wide spread. Consider for instance the very common element Si. It occurs in concentrations ranging from zero tot 46.6 %. The higher concentrations show a higher frequency ( = more usual). The distribution of Si is called negatively skewed (Fig.1.9.). The upper cut-off is formed by the mineral richest in Si. This is quartz, $SiO_2$, containing 46.6 % Si. A rock can comprise pure quartz, and then contains the maximum amount of Si, or less, if it contains another silicate, or non-silicate minerals.

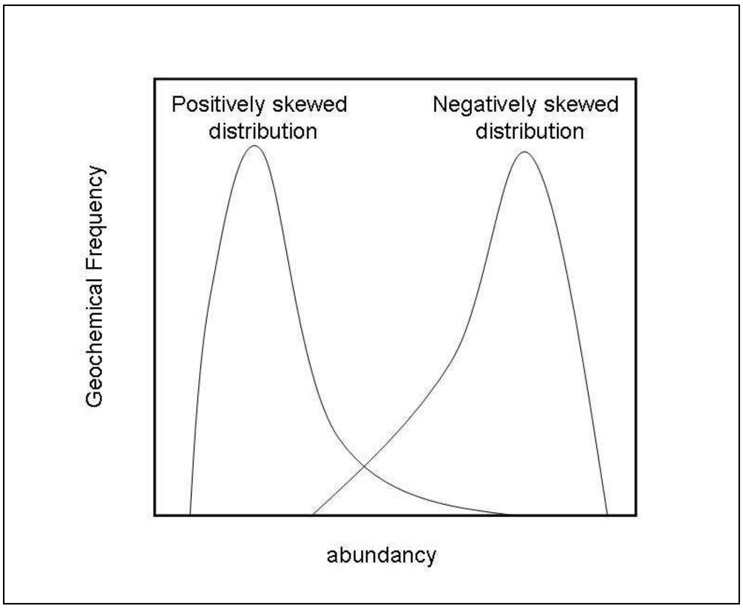


*Fig.1.11. Skewed element distributions.*

With decreasing abundance, element distributions become increasingly positively skewed. Trace elements have positively skewed distributions. Low concentrations are usual, as trace elements often substitute for a few atoms of a chemically similar element in the crystal lattice of rock forming minerals. An example is Sr (strontium) substituting Ca in calcite and dolomite. Trace elements sometimes form their "own" minerals, but in that case these minerals are very rare in the rock (accessory minerals). An example is zirconium (Zr), forming the mineral *zircon* ($ZrSiO_4$), or titanium (Ti) forming the mineral *rutile* ($TiO_2$).

Ore deposits usually have the following characteristics :

- Comparatively rare natural accumulations of metals
- Comparatively large natural accumulation of metals
- Typical enrichment factors relative to average abundances < 5 to > 5000

For instance, Fe and Al have a low enrichment factor ( 5 - 15 x crustal average), but ore grades are generally very high. For most other metals it holds that they are relatively scarce in the crust. The enrichment factors are 50 – 5000x crustal average. Ore grades are often low.

## *I.4. References*

Craig, J.R., Vaughan, D.J. (1994). Ore microscopy and Ore Petrography, Second Edition, Wiley, New York, 434 pp

Evans, A.M. (1993) Ore Geology and Industrial Minerals, An Introduction. 3th edition. Blackwell Scientific Publications, 390 pp.

Hale, M. (1996, 1997) The Geology of Ore deposits - Economic Geology. Lecture notes, Delft University of Technology, Department of Applied Earth Sciences, 149 pp.

Nickel, E.H. (1995) The definition of a mineral. The Canadian Mineralogist, 33, 689 – 690

# Chapter II. Types of Ore-Deposits

## *II.1. Introduction*

Ore deposits are classified in many ways. The type of classification depends generally on the persons using it: economists and mining engineers may classify deposits according to commodity (copper deposits, iron deposits) or morphology (stratiform, vein type, etc.). A more thorough classification can be made on basis of their genesis. The genesis of ore deposits may be very diverse, ranging from deposits directly related to volcanism, to sedimentary accumulation to weathering of rocks.

The most common subdivision is in:

- Magmatic ore deposits
- Hydrothermal ore deposits
- Uranium ore Deposits
- Autochthonous ore deposits
- Allochtonous ore deposits

These types can again be subdivided into smaller units, based on the specific processes that led to their concentration. Minerals are described in general in the more mineralogically oriented Chapter IV. In chapter IV also the origin of most of these mineral names can be found.

The following classification and description of the genesis of ore-deposits follows closely the text by *Prof. Dr. M. Hale (1996)* for the now obsolete lecture series on *Economic Geology, originally* coded *TA2900.* His text to a large extend follows the book by *A.M. Evans, Ore Geology and Industrial Minerals, An Introduction, Blackwell Scientific Publishers, 1993*, which was consulted also in many cases for this text, especially where there are significant deviations from the line of Hale's text. Many illustrations in this chapter also are taken from and modified after the book by Evans.

## *II.2. Magmatic Ore Deposits*

Magmatic ore deposits are all linked to magma (molten silicate). They are linked to the main stage of magma emplacement or crystallization. Sometimes the term orthomagmatic ores is used for this group.

The magmatic ore deposits can be subdivided into ores formed by a degassing of the Earth's Mantle, and ores formed by segregation in a magma chamber.

## II.2.1. Deposits related to mantle degassing

Some rocks are brought to the surface by the explosive degassing of the mantle. The main gaseous component is usually $CO_2$. The resulting rocks can be similar to the composition of the mantle (ultramafic rocks), or they can be highly altered by the emplacement and following processes, in interaction with volatiles and crustal rocks. Ultramafic (or ultrabasic) rocks are igneous and meta-igneous rocks with very low silica content (less than 45%), generally >18% MgO, high FeO, low potassium, and are composed of usually greater than 90% mafic minerals (dark coloured, high magnesium and iron content). The Earth's mantle is considered to be composed of ultramafic rocks.

### II.2.1.1. Diamonds

*Diamonds* (chemical composition C), are formed at very high temperatures and pressures: 1000 – 1600 °C, and 70 to 100 Kb). In the Earth, these conditions exist at 150 – 200 km below the surface. This corresponds to a condition in the upper mantle. Diamonds were formed in the Earth during two episodes: about 3.3 Ga, and between 1.5 and 1.0 Ga. Some diamonds were transported upward with mantle material, but many were not. Transport and diamond synthesis are not related.

The mantle material and diamonds must be transported to the crust very rapidly, otherwise the diamond would undergo a phase transformation, and change into graphite.

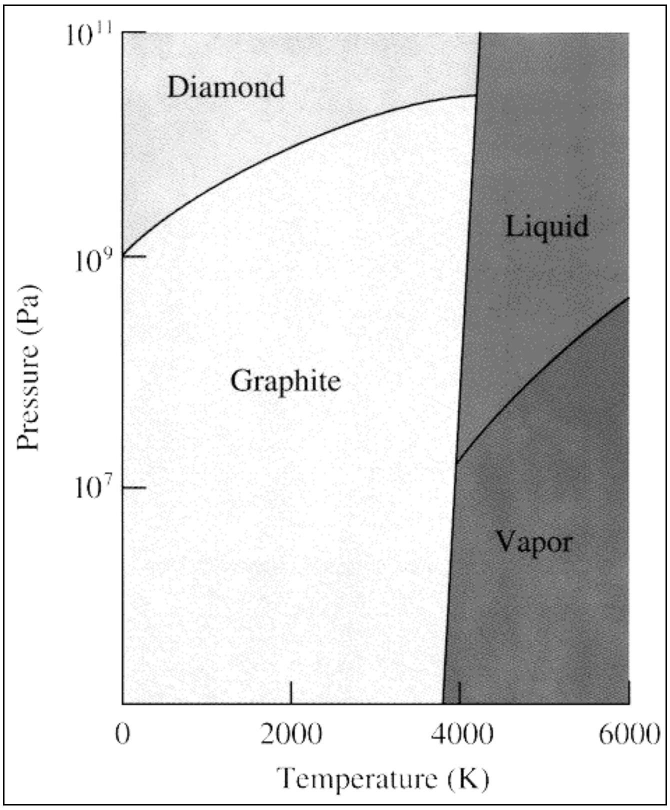


*Fig.2.1. The phase diagram of carbon.*

Rates of ascend are estimated to 70 km/h or even somewhat higher, in order to produce gem quality diamonds. Magma migrated from the mantle to the lower crust through deep penetrating fractures. From there on, points of weakness in the crust provided the way for these magma’s to rise further, and finally reach the surface. Carrying diamonds and other samples from Earth's mantle, the magma rises and erupts in small but violent volcanoes. Just beneath such volcanoes is a carrot-shaped "pipe" filled with volcanic rock, mantle fragments, and some embedded diamonds. This extension to the surface is called a diatreme (pipe), up to about 2 km in diameter, and with a downward extension of about 2 km. The diatremes become narrower with depth. The rock is called kimberlite after the city of Kimberley, South Africa, where the pipes were first discovered in the 1870s. Another rock that provides diamonds is called lamproite.

Kimberlite consists of mainly olivine, with minor pyroxene (chain silicate), phlogopite (a mica), garnet, minor calcite and serpentine. Lamproite consists of mainly olivine, with pyroxene, amphibole (a double chain silicate), phlogopite, sanidine (K-feldspar) and minor garnet. The search for diamonds has determined that most are derived from kimberlite pipes in the oldest, nuclear portions of the continents, where the basement rocks are older than 1.5 billion years. Such parts of continents are called cratons.

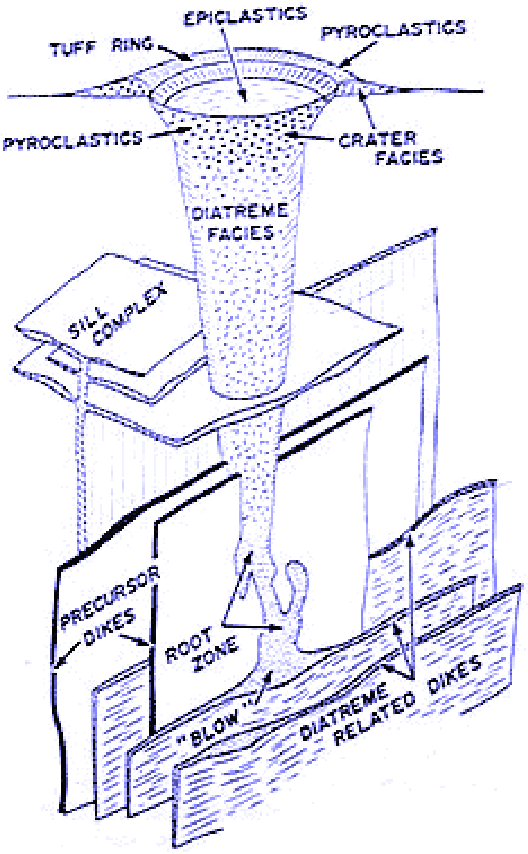


*Fig.2.2. Example of a Diatreme*

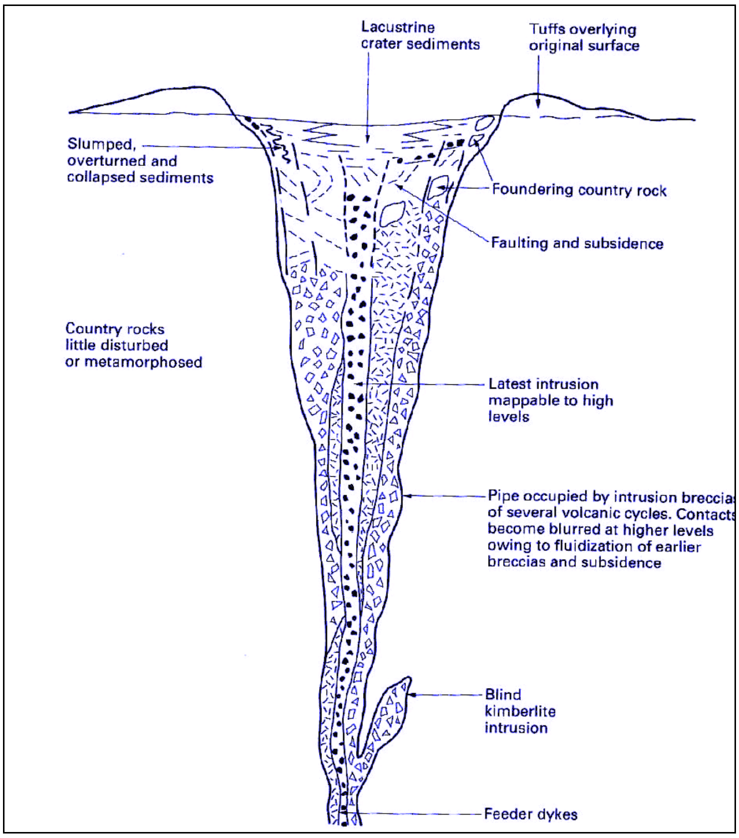


*Fig.2.3.Kimberlite-pipe. After Evans, 1993*

The diamond content of the kimberlite and lamproite is very low: about 1 carat (0.2 g/t). However quality and quantity of the gemstones is much more important than grade. Important diamond producing countries are; Australia, Congo, Botswana, Russia (Siberia), South Africa.

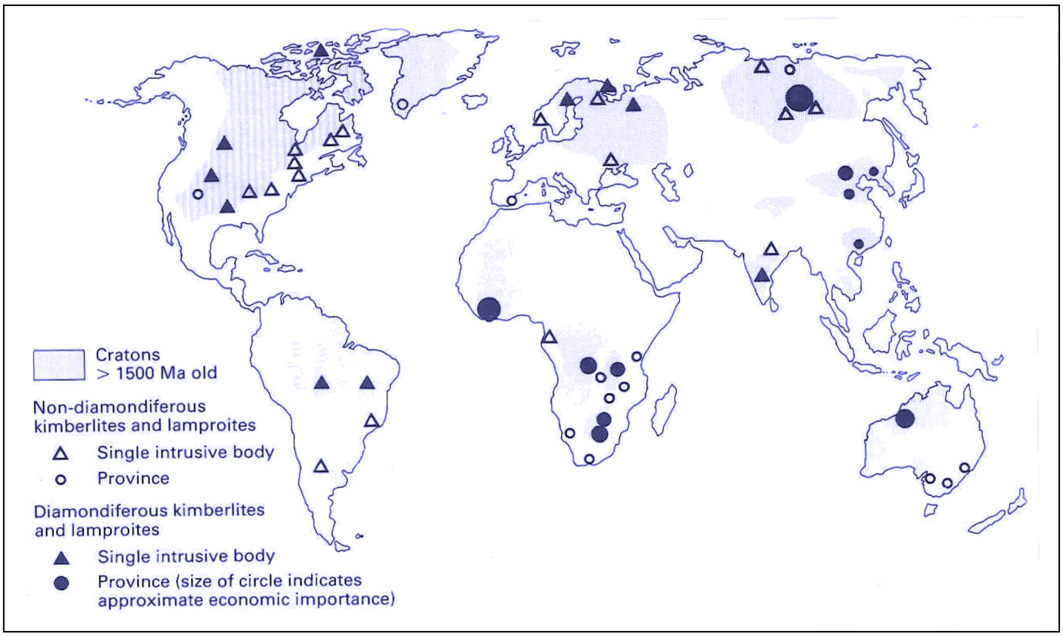


*Fig. 2.4.Kimberlite deposits and Lamproite deposits world-wide. After Evans, 1993.*

*Fig. 2.5. “The Big Hole”, Kimberley.*

### II.2.1.2. Carbonatites

Carbonatites are intrusive or extrusive igneous rocks defined by mineralogy that comprises more than 50 volume-% carbonate minerals. These rocks also form by explosive degassing of the mantle through deep fractures. They also reach the surface as pipes, usually a few km in diameter. They are, almost exclusively, associated with continental rift-related tectonic settings. Nearly all carbonatite occurrences are intrusives or subvolcanic intrusives. This is because carbonatite lava flows are unstable and react quickly in the atmosphere. Carbonatite lavas may not be as uncommon as thought, but have been poorly preserved throughout Earth's history. Only one carbonatite volcano is known to have erupted in historical time (and still does): Ol Doinyo Lengai (=”The Mountain of God”) in Tanzania. Ol Doinyo Lengai is a unique and extremely fascinating volcano that is located in the African Rift valley about 120 km NW of Arusha, Tanzania. It is the only volcano in the world that erupts *natrocarbonatite* *lava*, a highly fluid lava that usually contains *almost no silicon*. Natrocarbonatite lava is also much cooler than other lavas, being only about 510°C compared to temperatures over 1100°C for basaltic lavas. Natrocarbonatite is the most fluid lava in the world. Lava with a low gas content can flow like a whitewater stream, and actually has a viscosity near that of water.

Natrocarbonatite lava glows orange at night, but is not nearly as bright as silicon-based lavas since it is not as hot. During the day it is not incandescent; most flows look like very fluid black oil, or brown foam, depending on the gas content. Most newly solidified lava is black and contains crystals that sparkle brightly in the sun. Contact with moisture rapidly turns natrocarbonatite lava white because of chemical reactions that occur when the lava absorbs water. Eventually the water absorption process turns lava flows into brown powder

*Fig. 2.6. Ol Doinyo Lengai carbonatite volcano, altitude 2886 meters, northern Tanzania. The white deposits are weathered natrocarbonatite ash and lava.*

*Fig. 2.7. The crater of Ol Doinyo Lengai, with the solidified carbonate lava–lake turned white as a cause of absorption of moisture.*

Carbonatites may be of economic interest because they provide a source of lime (*calcite*), or *magnetite* (iron ore), *apatite* ($Ca_5(PO_4)_3F$, for phosphate fertilizers, or for *copper* ore (more rarely). In addition, carbonatites are important for the occurrence of (light) *Rare Earth Elements* (Y, La, Ce, Nd, Pr, Sm). Important economic minerals are *bastnaesite* $(REE)CO_3F$ and *monazite* $(REE)PO_4$.

Most important economic deposits are Palabora, South Africa, Mountain Pass, California, USA, and Bayan Obo, Inner Mongolia, China. Several sub-economic or non-economic deposits occur in Tanzania and Zambia.

Rare Earth Elements such as are used for a diverse range of applications. They comprise glasses with special refractive indices (Ce), magnets (Nd , Sm), colouring agents (Pr), high-tech ceramics (Y, Ce, La). Rare Earth Minerals are treated more extensively in the chapter on industrial minerals (Chapter III).

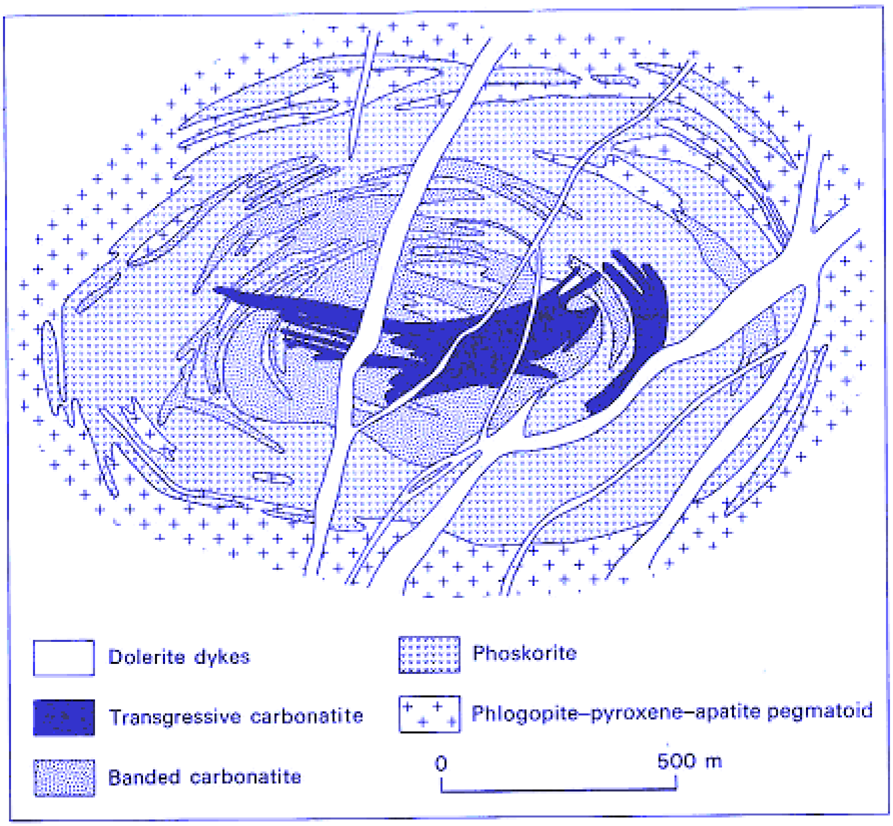


*Fig. 2.8. Simplified geological map of the Loolekop carbonatite at Palabora South Africa. After Evans, 1993.*

## II.2.2. Segregation deposits

These deposits form in the lower crust or upper mantle during the cooling and crystallization of a large –volume silicate melt. The deposits are associated with intrusive magmas of mafic or ultramafic composition. Ore minerals segregate as they crystallize, and accumulate within the magma chamber. The most important ore mineral is *chromite* ($FeCr_2O_4$). Ore grades vary between 30 – 6- % $Cr_2O_3$, depending on the iron content of the chromite. Chromite generally crystallizes along with olivine $(Mg,Fe)_2SiO_4$. Chromite is however denser (s.g. 5.0) then olivine, and settles faster under the influence of gravity. It forms a cumulate. These cumulates (e.g. 90 – 130 cm thick) may be quite extensive. The LG6 layer in the Bushveld Complex in South Africa extends over 70 km (!). Important deposits occur in South Africa (Bushveld Complex), and Zimbabwe (The Great Dyke).

Other chromite deposits are related to partially melted upper mantle, which is tectonically emplaced in the upper crust (ophiolites). These chromite bodies are generally lens shaped, and not by far as extensive as cumulates, but they are widely mined (Turkey, Philippines).

## II.2.3. Deposits associated with liquation.

Cooling and crystallization of pure silicate magma produces only silicate minerals. Magma with low sulphur content produces silicate and sulfide minerals. Magmas with more then a few percent sulphur undergo liquation. This means that two immiscible liquids separate. In this case this is the silicate liquid and the sulfide liquid. The sulphur liquid is denser than the silicate liquid, and sinks. Bodies of sulfide minerals crystallize, and in some instances constitute ore deposits.

### II.2.3.1. Magmatic Nickel Deposits

In a mafic/ultramafic magma, iron, nickel and copper partition into the sulfide liquid. This sinks into basal embayments whilst silicates crystallize higher in the magma. Below 1100°C, iron-nickel sulfides crystallize: *pyrrhotite* $(Fe, Ni)_7S_8$ and *pentlandite* $(Fe, Ni)_9S_8$. with further cooling, also *chalcopyrite* ($CuFeS_2$) crystallizes. Rarely, other Cu-Fe-sulfides, such as *cubanite* ($CuFe_2S_3$) crystallize. These sulfides form basal massive sulfides in their embayments. Upwards, the sulfides become intermixed with crystallizing and settling silicates. This leads to disseminated sulfides in a net of silicates. The deposits may be disturbed by later tectonic activities. Ore deposits range in size from a few million tonnes to several tens of millions of tonnes. Ore deposits grade from approximately 0.8 to over 3 % nickel. Copper is often produced as a secondary metal. There are two types of deposits: synvolcanic deposits, and large intrusions. Synvolcanic deposits occur in Archaean volcanic greenstone belts, and account for about 23 % of the magmatic nickel ores. Examples are Agnew, W-Australia, and Kambalda, W. Australia. The remaining deposits are related to large gabbroic intrusives. Examples are Sudbury, Ontario, and Noril'sk-Talnakh (Russia). In the case of Sudbury, it is believed that the origin of the magma generation is probably a meteorite/asteroid impact (astrobleme).

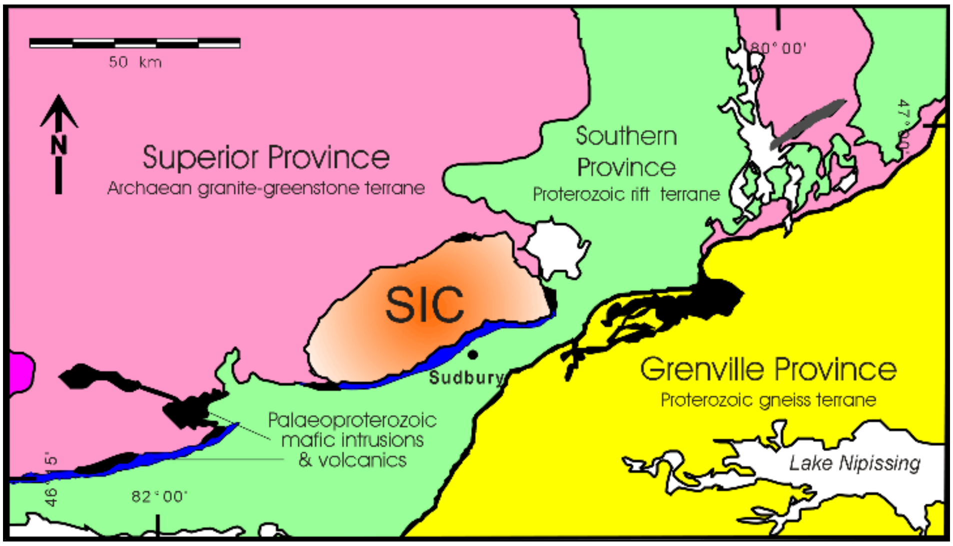


*Fig. 2.9. The location of the Sudbury Igneous Complex (SIC), Ontario, Canada*

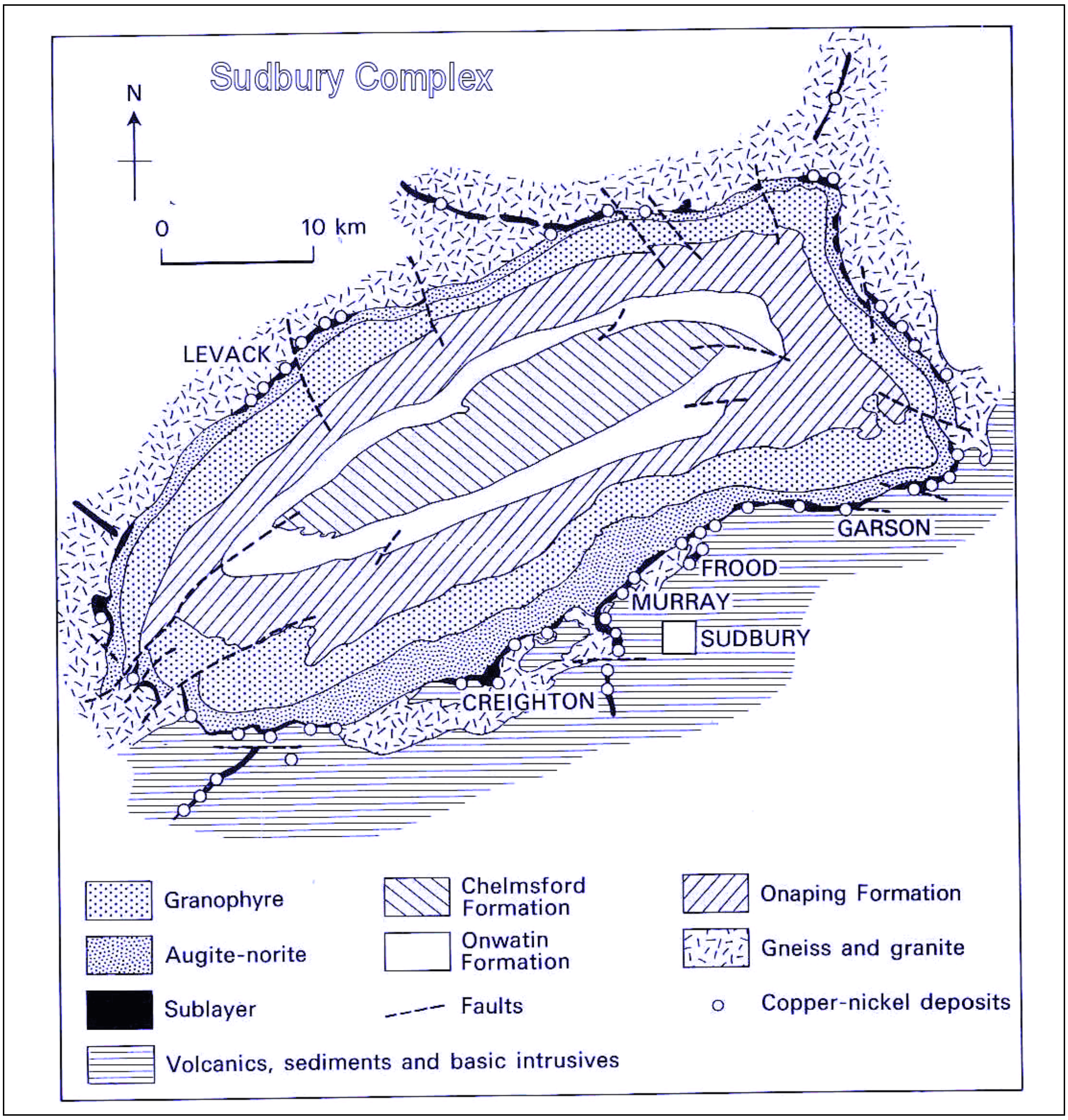


*Fig. 2.10. Geology of the Sudbury Complex, Ontario, Canada. After Evans, 1993.*

### II.2.3.2. Platinum Group Elements (PGE)

The Platinum Group Elements are : Platinum, Iridium, Rhodium, Ruthenium, and Osmium and  Palladium (Pt. Ir, Ru, Os, Pd).
Mafic/ultramafic magmas from the mantle contain low concentrations of  PGE. The PGE can not be accommodated in silicates, and remain in the liquid, while silicates crystallize. If the magma also contains sulfide, immiscible sulfide droplets may form. The PGE partition preferable into the sulfide liquid, where they may form PGE-sulfides. Minerals are *braggite* (Pt, Pd, Ni)S, and *laurite* ($RuS_2$).  Also arsenide's (sulfide analogues) form: *sperrylite* ($PtAs_2$), or *stibiopaladinite* ($Pd_3Sb$). PGE occur in ore grades in only two large mafic/ultramafic complexes The Bushveld Complex, South Africa, and the Stillwater Complex in Montana, USA. In the Bushveld Complex the so-called *"Merensky Reef"*  (0.3 – 0.6 m thick, strike length 110 km!) has acquired almost legendary fame. The Merensky and UG-2 (Upper Group-2)  reefs contain approximately 90% of the world's known PGE reserves! About 80% of the platinum and 20% of the palladium mined each year are produced from these

horizons. In Sudbury PGE are also produced, as a by-product from copper and nickel production.

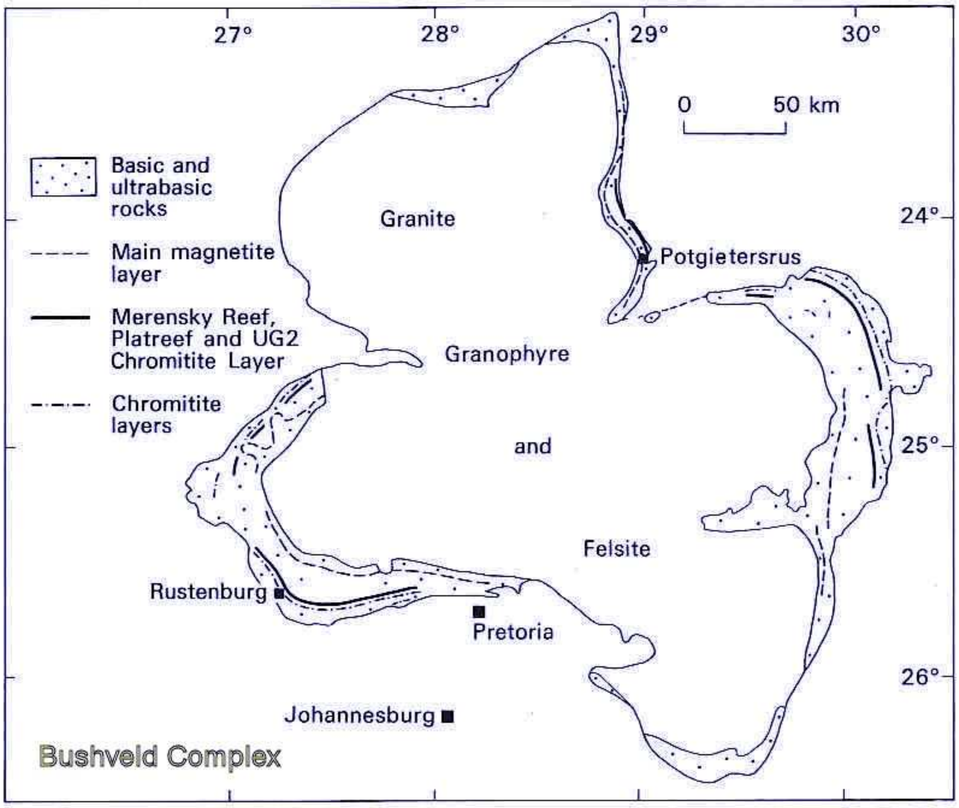


*Fig. 2.11. The Bushveld Igneous Complex, near Pretoria, South Africa. Note the scale. It is one of the largest igneous structures in the world. After Evans, 1993.*

### II.2.3.3. Magmatic titanium and vanadium deposits

More differentiated parts of magma's may have gabbroic or anorthositic composition. In these, iron (± titanium or vanadium) oxides may form immiscible droplets. These have higher density then the coexisting silicate liquid. These droplets physically separate and sink. Other mechanisms, such as changes in $fO_2$ may also trigger separation.

In some cases, these droplets accumulate as layers on the floor of the magma chamber. This may lead to stratiform ore deposits. Examples are the layers of vanadiferous magnetite in the Upper Zone of the Bushveld Complex., which constitute approximately 1 x $10^9$ tonnes of magnetite ore grading up to 2 % $V_2O_5$. In other cases, the droplets escape down fractures and crystallize in the underlying rock. This is a possible origin for the Tellness ilmenite deposit in southern Norway. Resources are 0.3 x $10^6$ tonnes of *ilmenite* ($FeTiO_3$) ore, grading 18 % $TiO_2$. The Tellness deposits are discordant (not stratiform), and occur in anorthosite.

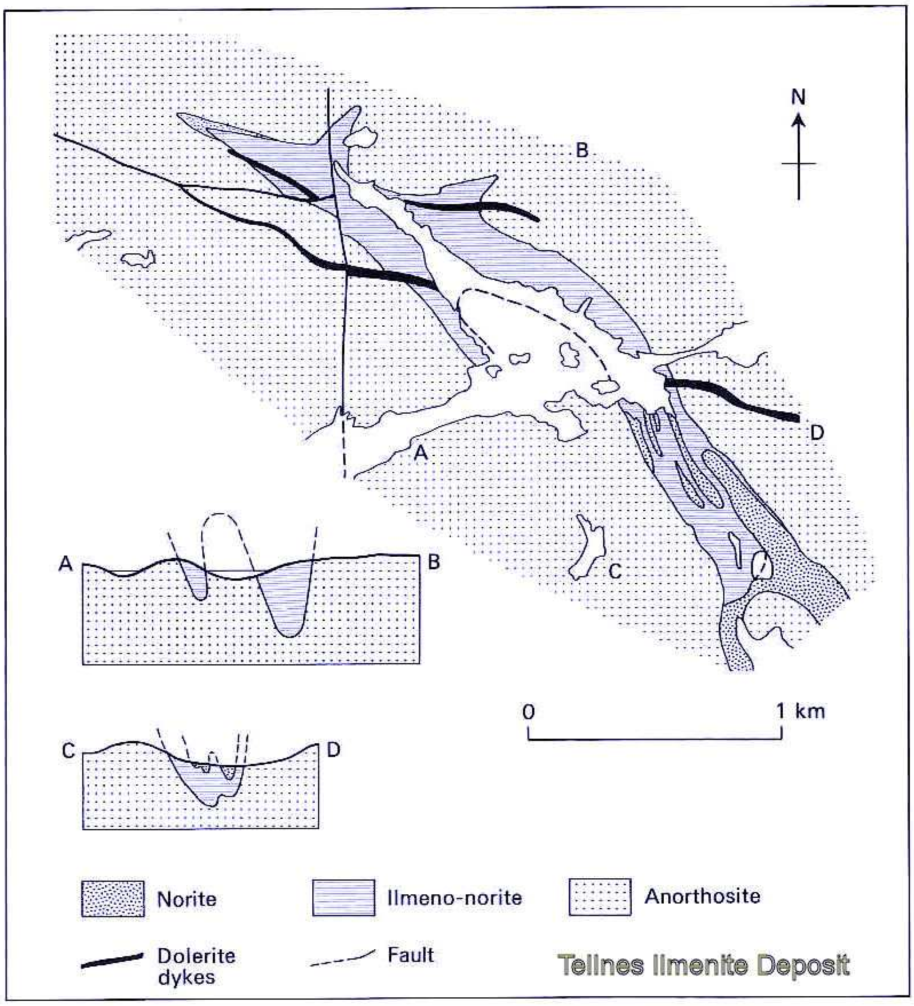


*Fig. 2.12. The Tellnes-ilmenite deposit, Southern Norway. After Evans, 1993.*

## I.2.4. Deposits associated with granitic magmas and pegmatites

Mafic and ultramafic magmas may originate in the upper mantle, but an other class of magmas can be generated in the Earth's crust. Crustal rocks, remelted at depth form magmas higher in $Al_2O_3$ and $SiO_2$, (more acidic), and crystallize to granitic rocks,. Granitic crystallize in the range 700 - 1000 °C. Due to their crustal origin, many of these melts contain dissolved $H_2O$. It is by the way the water that lowers the melting temperature of the silicate composition to a large extend. Some of the water may become trapped in hydrous minerals as OH. Such minerals for instance biotite, or amphibole. The remaining $H_2O$ remains in the fluid or gas phase of the melt. Many metals, which cannot be accommodated in silicate lattices follow the same trend. As the granitic rocks crystallize, the fluid phase becomes enriched in these metals. In some cases, the last silicate crystals form in a very aqueous fluid. In such fluids, because of high ion diffusion, large crystals can form. An essentially granitic rock with large crystals is a pegmatite. The last stage of the crystallization is also a phase with very high fluid pressure, and the fluid may be forced into the country rock of the granite itself by fractures. This gives pegmatites a vein-like appearance. The pegmatites themselves evolve, and sometimes are zoned. The composition of the silicate melt is now depleted in some major rock forming elements, but it is enriched in metals. These metals are often light or ultra light metals, such as lithium (Li), and beryllium (Be). Crystallization of magmatic silicates of economic interest may be the case. Examples of such silicates are *spodumene* ($LiAlSi_2O_6$), *petalite* ($LiAlSi_4O_{10}$), lepidolite (Li-mica), and *beryl* ($Be_3Al_2Si_6O_{18}$). Gem quality beryl, (containing some chromium which is responsible for the green colour) , is *emerald*. Examples of such deposits are Bikita, Zimbabwe, and Kings Mountain, NC, USA. Other mineralisations in pegmatites may be of tantalum and niobium minerals such as *columbite*, or *tantalite* (minerals series with general composition $(Fe,Mn)(Nb,Ta)_2O_6$).

Many other metals are concentrated in the last stage fluid phase of the granitic melt, but are not easily accommodated into silicates. They become the constituents of late stage magmatic fluids. These fluids produce hydrothermal, rather than magmatic deposits.

## *II.3. Hydrothermal Ore Deposits*

### II.3.1.Introduction

Hydrothermal ore deposits are a wide class of deposits, that owe their genesis to hot aqueous solutions. The origin of the solutions may be very diverse, ranging from magmatic to metamorphic, diagenetic, meteoric, and sea water. Solutions of different origin may mix. The metals may be constituents of the original solutions, but they may also be leached from other rocks, through which the solutions pass. Hydrothermal solutions range in temperature from 650 to 50 °C. pH-ranges are form acidic to near neutral. Metals are dissolved in the se fluids as complexes of $Cl^-$ and $HS^-$. In minor amounts, metals may be dissolved as complexes of $H_2S$ and $NH_3$. Ammonia concentrations are generally very low. In general Cl-species dominate over the others. $Cl^-$ only forms HCl at very low pH, but may form stable metal complexes at other pH. The bisulfide ion $HS^-$ may form very stable metal complexes too, and is predominant below 300 °C. At high temperatures, $Cl^-$ complexes dominate. Typical metal concentrations in such fluids are 1 – 10 ppb for gold, to > 1000 ppm for base metals.

There are up to 5 processes which cause such fluids to crystallize:

1. Rock-fluid interaction
2. Redox changes
3. Adiabatic expansion
4. Cooling
5. Saturation with respect to a compound

The crystallization may be due to one of these, or sometimes a combination of them. The following types of deposits can be recognized:

**Magmatic Type**

- *Greisen – tin deposits*

**Mixed magmatic groundwater type**

- *Skarn deposits (tungsten)*
- *Porphyry copper and molybdenum deposits*
- *Mesothermal deposits (tin, copper, zinc, lead, silver)*
- *Epithermal deposits (gold, copper, lead, zinc)*

**Metamorphic type**

- *Archaean lode gold deposit*s

**Seawater type deposits**

- *Vulcanogenic Massive Sulfide deposits (VMS-deposits), (copper, zinc, lead)*
- *Stratiform Sedimentary Exhalative Deposits (SEDEX-deposits), copper, cobalt)*
- *Missippi Valley Type Deposits (MVT-deposits) (lead, zinc)*

## II.3.2. Magmatic type–Greisen Tin deposits

An immiscible aqueous phase separates from crystallizing water saturated granitic magma below about 700 °C. The aqueous phase has a lower density than the silicates, and eventually collects in the apical regions of the intrusion. Where they disappear into fractures, and form veins, pegmatites develop. However, the solution may become in contact with the crystallizing upper part of the granite, and by metasomatic alteration and boiling, the minerals are converted to others. This produces a granoblastic aggregate of *quartz* ($SiO_2$), *muscovite* ($Kal_2Si_3AlO_{10}(OH)_2$), *tourmaline* ($(Na(Li,AlMg, Fe))_3A_{l6}(BO_3)_3Si_6O_{18}(OH)_4$) *topaz* $Al_2SiO_4(F,OH)_2$ and *fluorite* ($CaF_2$). A rock with this mineralogy is called a *greisen*. Greisens appear to be restricted to intrusions which are emplaced high in the crust, generally at a depth between 0.5 and 5 km, with upper aureoles which are sealed shut to prevent fluids escaping. This is generally required, as the boiling to produce greisenisation cannot occur deeper than about 5 kilometres. The rocks are often greyish in colour, which is the origin of the name, derived from the German language.

The greisen immediately below the roof of the granite is called and endogreisen. The fluids also break through the roof of the granite, and alter the adjacent silicate country rocks. This gives rise to an exogreisen. Granites derived from anatexis of the continental crust contain often tin, from the continental crustal protolith. In the silicate melt, this tin, in the form of $Sn^{2+}$ cannot enter the silicate lattices, and it is confined to the melt. $Sn^{2+}$ can however dissolve in aqueous solutions as a $Cl^{-}$complex. Thus tin is one of the minerals to become concentrated in the aqueous phase of the granite. Tungsten (W) often goes along with tin. During formation of the greisen, the soluble $Sn^{2+}$-complex is oxidized. This oxidation reaction produces *cassiterite* ($SnO_2$) . Carbonate country rocks have the same effect on the hydrothermal solution. The ore grades are low, 0.2 – 0.3 % Sn, although sometimes 1 % Sn is reached. Some

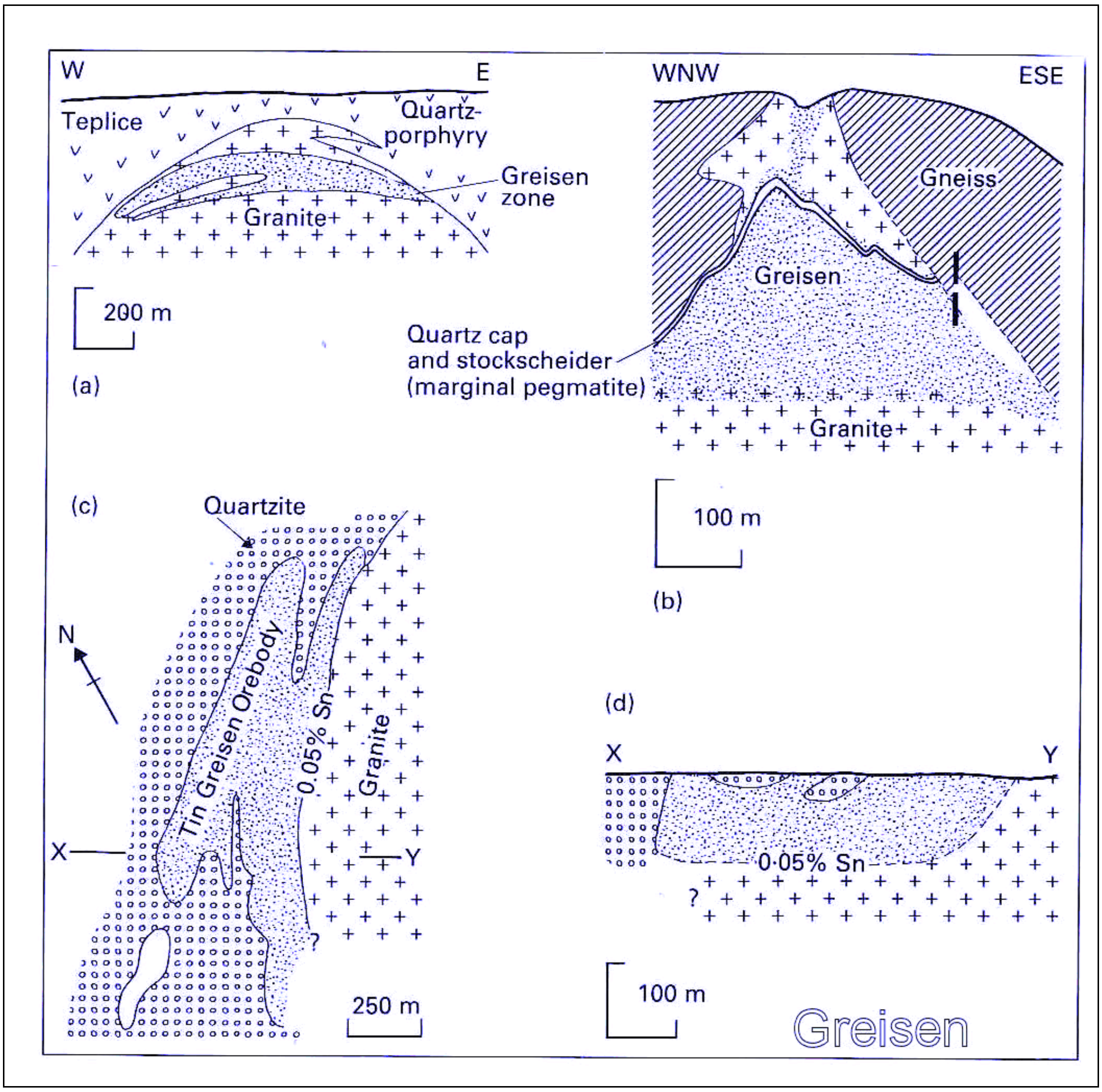


*Fig. 2.13. Some greisen-tin deposits. a) Cinovec, Czechia, b) Sadisdorf, Germany, c) and d): map and section of East Kempville deposit, Nova Scotia. After Evans, 1993.*

## II.3.3. Mixed Magmatic-Groundwater type

### II.3.3.1. Skarn tungsten deposits

Rising granitic magma intrudes pre-existing rocks deep in the crust. The heat of the intrusion transforms minerals in these pre-existing rocks. This process is called thermal metamorphism, or contact metamorphism. Silicate rocks are baked. Carbonate rocks are recrystallized. Often they become marble. The metamorphism is isochemical (nothing is lost or gained). Breakdown of carbonates may lead to formation of carbon and Ca. Ca reacts with silicates, forming e.g. diopside ($CaMgSi_2O_6$). Magmatic hydrothermal fluids concentrate in the apical parts of the granite. They break out along fractures and contact zones. They attack the remaining carbonate minerals in the metamorphosed carbonate rocks. These reactions release Ca and $CO_2$ into solution. The hydrothermal solutions contain dissolved metal and dissolved silica. The carbonate rocks is becoming metasomatically altered. Temperatures are around 500 °C. Calc-silicate minerals are formed: diopside, a pyroxene ($CaMgSi_2O_6$), grossularite, a garnet ($Ca_3Al_2(SiO_4)_3$), wollastonite ($CaSiO_3$).

This assemblage is typical of a skarn. Tungsten is soluble in the hydrothermal fluids of the granite. The soluble tungsten may react with the released Ca to form $CaWO_4$ (*scheelite*)

When progressively the solutions cool, the metasomatism ceases. Groundwater at depth at temperatures of around 200 – 300 °C may eventually enter the skarn through late fractures. This causes retrograde reactions, and some of the scheelite may de dissolved, and redistributed. Examples of Skarn tungsten ores are Macmillan Pass, Northern Canada, King Island, Tasmania, Sandong, Southeast Korea. The deposits comprise several tens of tonnes of ore with grades up to 1 % $WO_3$.

Skarns may also be important for other metals associated with the hydrothermal solutions. Skarn iron deposits may acquire the metal from groundwater. Talc bearing skarns provide a large part of the worlds talc production.

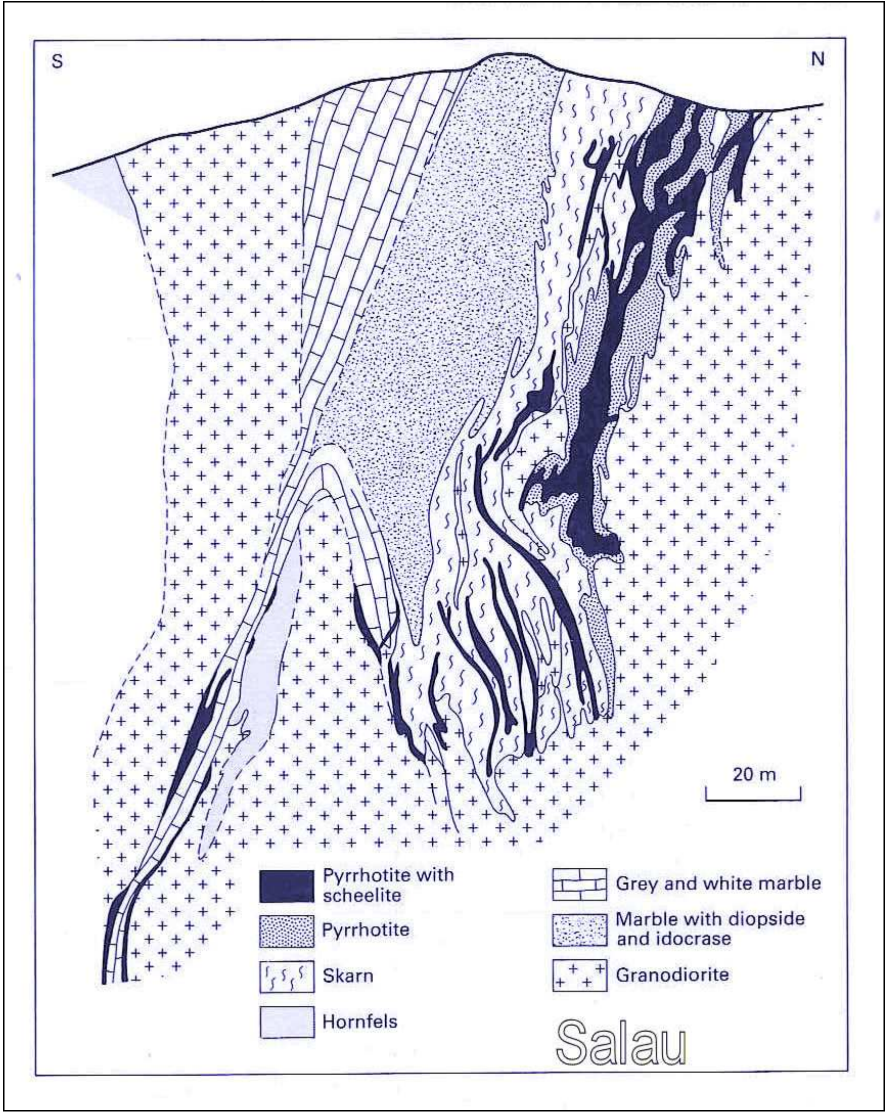


*Fig. 2.14. Cross section through the Salau tungsten deposit, France. After Evans, 1993.*

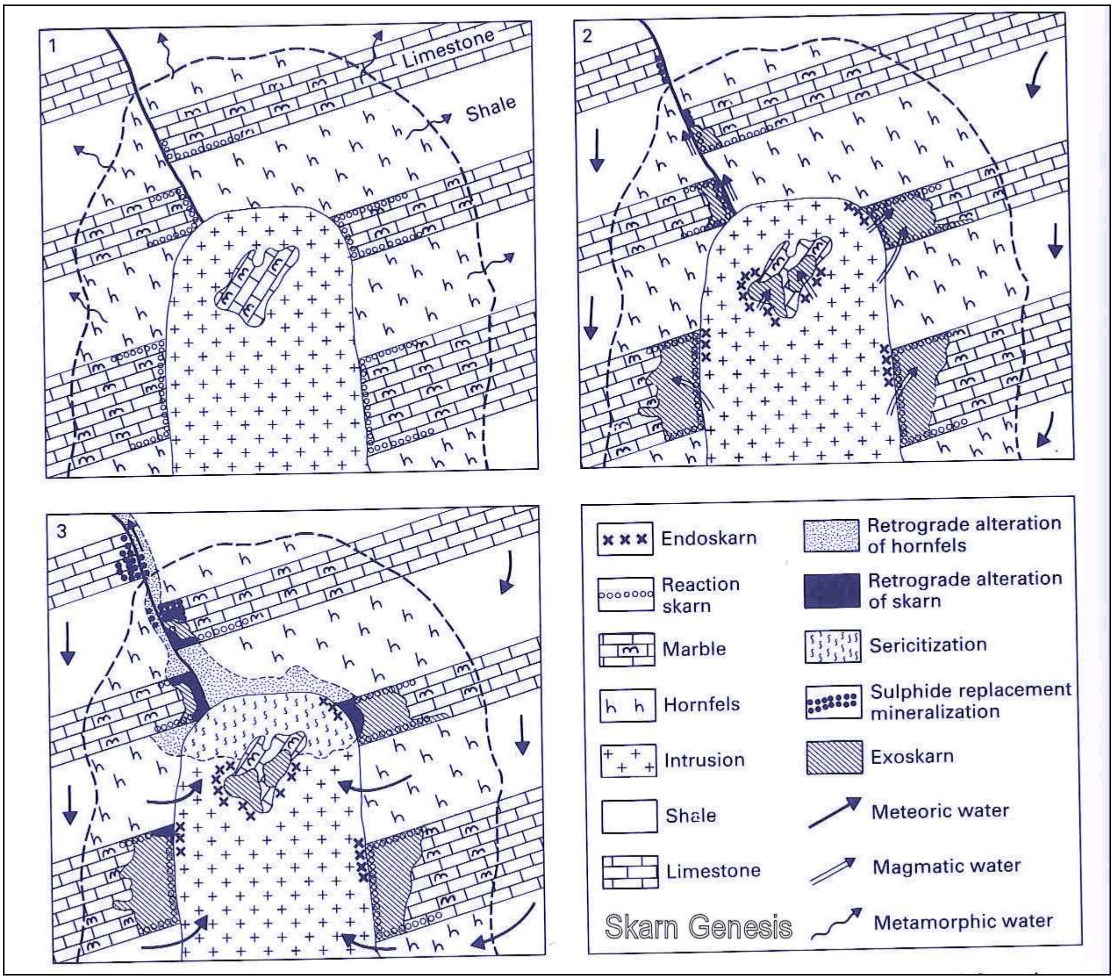


*Fig. 2.15. Genesis of a skarn. 1) The intrusion of hot magma drives out ground formation and metamorphic waters, produces a metamorphic aureole and reaction skarns. 2) Hydrothermal solutions exsolve from the crystallizing magma to form endo and exo skarns. Some sulfide formation may occur. 3) The system cools, permitting meteoric water to enter the intrusion and the skarn. Replacement reactions occur. Sulfide formation may occur. After Evans, 1993.*

## II.3.3.2. Porphyry Copper and Molybdenum deposits

These deposits are related to intrusions that have risen to a high level in the crust. The intrusions are subvolcanic and are at depths of one to four kilometres when mineralization occurs. They are found on the continental side of subduction zones. Due to their shallow depth formation, most preserved deposits are Cretaceous or younger. Aqueous fluids exsolved from the cooling magma accumulate in the apical region. Under retrograde boiling[4] they escape by hydro fracturing (Crackle

---

[4] Magma rise can lead to decompression and the formation of bubbles, much like the decompression of soda and the formation of CO2 bubbles when the cap is removed. This is sometimes referred to as the **first boiling**. As magma cools and anhydrous minerals begin to crystallize out of the magma, the residual liquid will become increasingly enriched in gas. In this case, the increased vapor pressure in the residual liquid can also lead to gas exsolution. This is sometimes referred to as ***second (or retrograde) boiling***.

brecciation) of the intrusion roof. Crystallization of the remaining silicate is accelerated, producing a porphyritic granite. The magmatic hydrothermal fluids contain some major elements and trace metals. The solutions cause potassium metasomatism of the surrounding rocks. Their soluble Cu, Mo and S precipitate as sulfides: *chalcopyrite* ($CuFeS_2$) and *molybdenite* ($MoS_2$).
Hydro fractures seal as a result of metasomatic mineral formation and sulfide crystallization. As a result the trapped fluids again undergo retrograde boiling. They again break out by hydro fracturing. Cyclical repetition of this process produces a *stockwork*[5] of sulfide veinlets and disseminated sulfides. As the system cools, convecting groundwater is entrained. This water produces a hydrothermal alteration envelope.

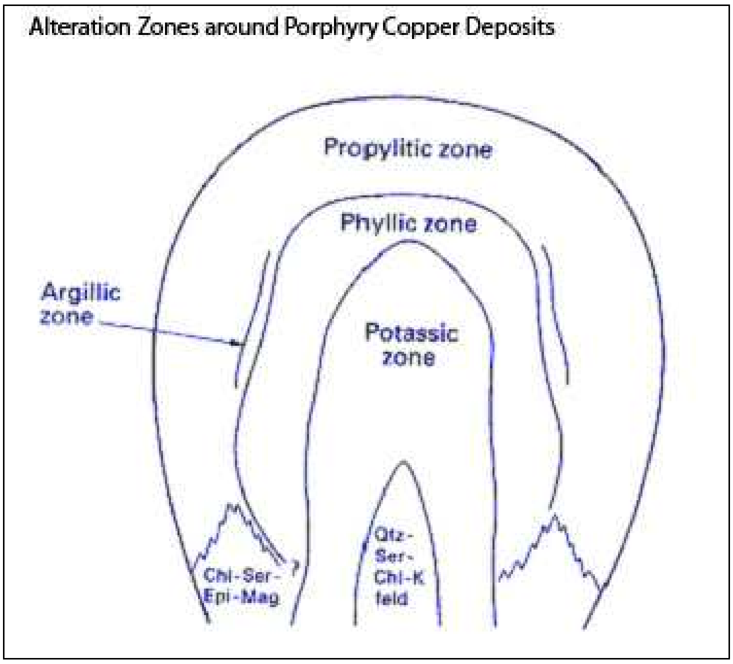


*Fig. 2.16. Hydrothermal alteration envelopes associated with a porphyry copper/molybdenum deposit. After Evans, 1993.*

First it alters the distal zones affected by the magmatic hydrothermal solutions. This produces the propylitic zone, biotite → chlorite. Later it causes argillic overprinting of the outer zones of the potassic alteration core. In this zone, biotite → clay minerals (kaolinite, montmorillonite). Finally, it causes overprinting of the intermediate zones of the potassic alteration core. In this zone, feldspar → sericite + quartz. These solutions also remobilize, redistribute and enrich the copper sulfides. The recognition of the zones is useful in exploration.

The ore grades of porphyry deposits are characteristically low: 0.5 – 1.0% Cu, 0.1 – 0.5 % Mo. Deposit sizes are always large, sometimes over a billion tonnes. Famous examples: Chuquicamata (Chile), 9.4 billion tones of ore grading 0.56 % Cu, Santa Rita, New Mexico, 500 million tones grading 0.95 % Cu, Climax, Colorado, 400 million tonnes 0.45 % $MoS_2$.

---

[5] A **stockwork** is an ore body formed by a mass of rock intersected by large numbers of small veins or stringers. Sometimes more or less parallel, sometimes crossing or interlacing in all directions.

*Fig. 2.17. The Chuquicamata open pit Copper mine, Chile.*

Porphyry deposits account for approximately 75 % of the worlds resources of copper. About 50 % of the world production of copper comes from porphyry deposits. Other important types of deposits for copper will be treated in the rest of this chapter. Among them are stratiform deposits and VMS deposits.

### II.3.3.3. Mesothermal Deposits

Mesothermal deposits are usually found in the country rocks around granitic intrusions. They are formed by aqueous solutions which migrated along faults, joints and bedding planes. These migration took place over a relatively long time. The resultant veins are generally larger than the original channelways, as replacement of the wall rock took place. The aqueous fluids may be of magmatic or meteoric origin, or a mixture. The heat of the intrusion forms a thermal gradient around the intrusion. These solutions precipitate quartz and metallic minerals along this temperature gradient. The temperatures of mesothermal systems are in the range 450 – 250 °C. There is a kind of zoning around the granitic intrusion. Closest to the granite (highest temperature), Sn-deposits are formed (*cassiterite*, $SnO_2$). Further away, in an intermediate zone, *chalcopyrite* ($CuFeS_2$) and *bornite* ($Cu_5FeS_4$), are precipitated. Farthest away from the intrusion (lowest temperature), *galena* (PbS), *sphalerite* (ZnS) and silver-compounds are precipitated. These zones are not perfectly separated, and there can be considerable overlap. Veins may vary from <50 cm to > 10 m wide. Their strike can extend up to several km. Wide veins may grade into replacement deposits, which can be elongated or massive.

Veins are at present day mines in a mechanical way, in which the vein swarms and stockworks are mined as a whole, taking into account the wall rock. Rarely are individual veins mined. Later, physical separation methods separate the ore from the *gangue* (non-ore material).

Tin deposits of this type are the vein deposits and disseminated deposits of the Bolivian tin belt. Bolivia possesses the greatest known reserves of tin outside the countries of south-east Asia.

Remobilization of low grade porphyry-type Cu-mineralization produces high grade mesothermal vein deposits. Examples are Butte, Montana, USA, and Bor, Serbia. Butte is mined from the 19th century, and produced approximately 7.3 million tonnes of copper.

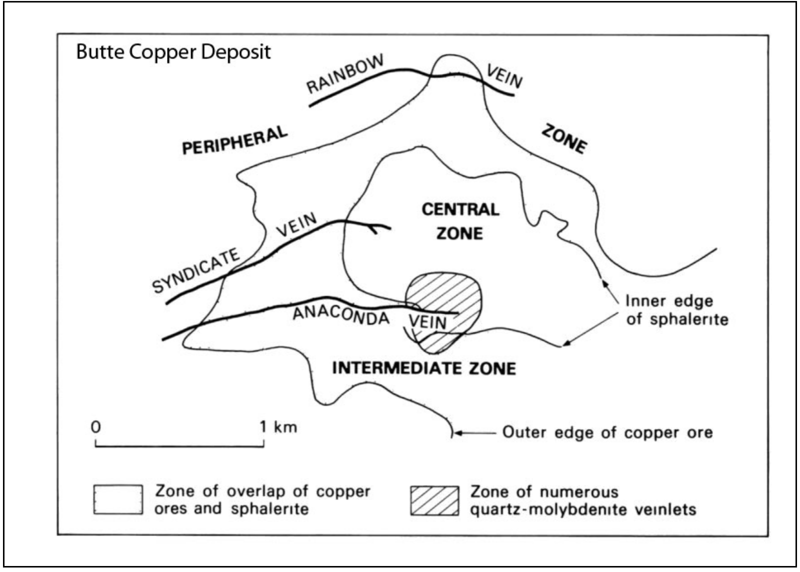


*Fig. 2.18. Butte, generalized map showing the zoning of the deposit.*

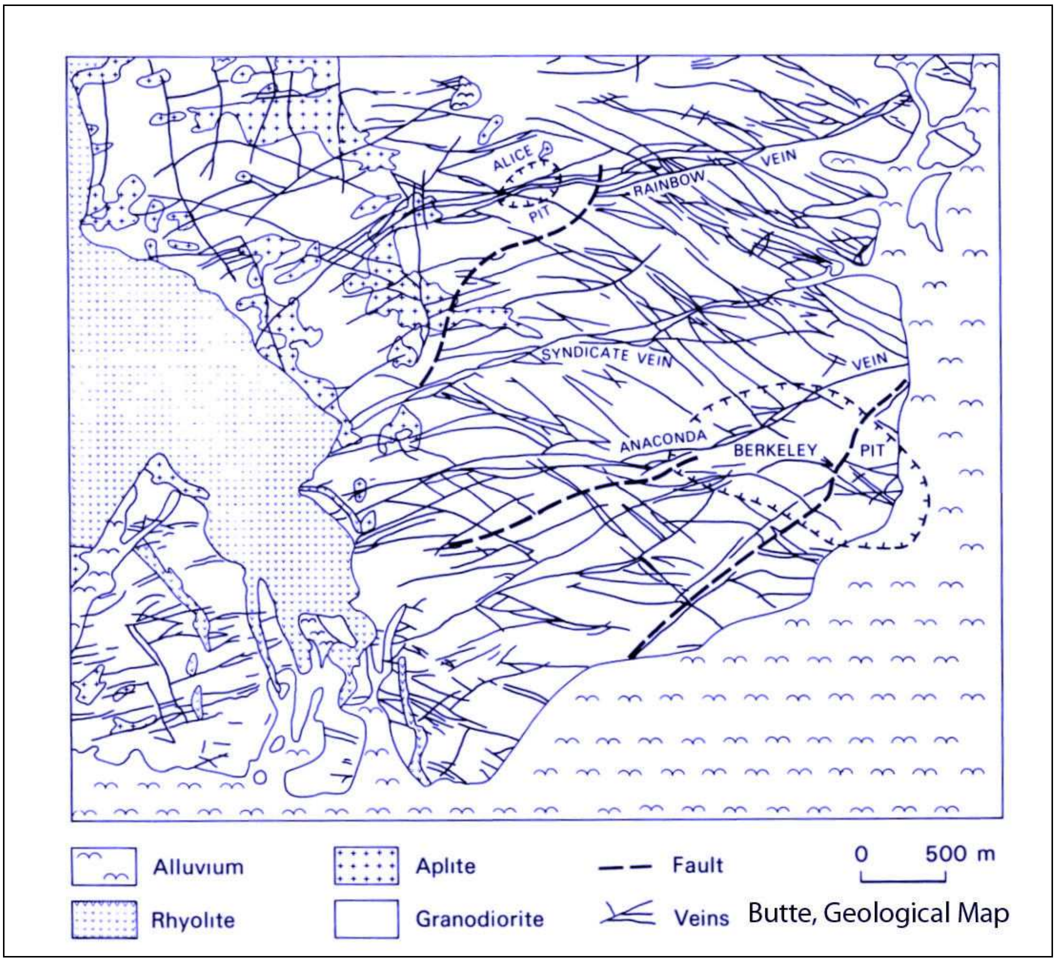


*Fig.2.19. Butte, generalized geological map showing the most important rock types and veins. After Evans, 1993.*

At Bor, mesothermal Cu-mineralization occurs as stockworks and replacement deposits. Several million tones of ore grading 1 – 6 % Cu occur in veins and replacement bodies. Ore minerals are *pyrite* ($FeS_2$), *chalcopyrite* ($CuFeS_2$), *bornite* ($Cu_5FeS_4$), *covellite* ($CuS$) and *enargite* ($Cu_3AsS_4$). Going downwards from the high grade mesothermal deposit, towards the intrusion, a porphyry deposits is encountered. The hydrothermal solutions that formed the mesothermal mineralization migrated from the porphyry. Lead, molybdenum, gold and zinc also occur. Bor is the largest copper deposit in Europe. The mesothermal Bor-deposit grades away from the intrusion into what is called and epithermal deposit.

Mesothermal veins rich in Ag and arsenides if Ni and Co are found at Cobalt, Ontario. Veins are about 200 m long, and 10 – 20 cm wide. There are about 100 veins. The mineralogy is very complex, and this makes mineral processing difficult and costly Ore minerals are: *cobaltite* CoAsS, *safflorite* $CoAs_2$, *arsenopyrite* FeAsS, *niccolite*, NiAs, *loellingite*, $FeAs_2$, *native Ag*. The grades are high, and this overcomes the high processing costs. The La Rose vein, found accidentally by blacksmith La Rose, was native silver over 30m’s. Magmatic water or heated groundwater associated with the intrusion of the nearby Nipissing diabase remobilized metals from the underlying Keewatin greenstones into the Cobalt sediments. Mining continued until the 1930's, then slowed down. Activity renewed in the 1950's then slowly dropped off, and there are no longer any operating mines in the area. The mine wastes, extremely high in arsenic, now pose an environmental threat.

### II.3.3.4. Epithermal Deposits

These deposits occur in volcanic or sedimentary rocks several km’s above granitic intrusions. Mesothermal deposits may grade into epithermal deposits. Epithermal deposits may contain for instance copper (chalcopyrite), lead (galena), zinc (sphalerite) and native gold. The hydrothermal solutions may be partly magmatic, but are mostly meteoric. The granite intrusive is mainly important as a heat source. The thermal gradient leads to convective circulation of the hydrothermal solutions, which reach temperatures up to 300°C. The solutions may remobilize earlier mesothermally deposited metals, or acquire new metals, from either the magma, or by leaching of volcanic country rocks. Gold is acquired from either the country rocks, or it has a magmatic origin. Gold is soluble in low temperature hydrothermal solutions as a bisulfide complex. However, complexes involving arsenic may also be important. Later destabilization of these complexes leads to precipitation of the gold. Ore deposits vary in size from about a million tones to tens of millions of tonnes. Ore grades are typically 2 – 10 g/t gold.

Famous examples of these deposits occur in Nevada, USA, where the Carlin-type disseminated gold deposit is the most well known. These types of deposits often feature several major arsenic minerals (*orpiment*, $As_2S_3$, *realgar*, AsS), some of them containing even thallium (Tl). These deposits occur in a so-called back-arc area, and are found also in other geologically similar places in the world (e.g. Zarshuran, NW-Iran).

Locally adiabatic boiling of these solutions precipitates gold over a narrow temperature range. This leads to the concentration of gold in very high grade "bonanza" deposits. Examples are Homestake, Nevada, and El Indio, Chile. The Nevada deposits are tertiary in age.

The epithermal deposits of Tennant Creek, Australia, are of Proterozoic age. Hydrothermal deposits of seawater origin deposited magnetite chlorite bodies in shales. Mixed formation water("evolved sea water" and interlayer water) /magmatic solutions carried Au, Cu and Bi in chloride complexes. Chlorite reduced the metals complexes to native gold, bismuthinite ($Bi_2S_3$), chalcopyrite etc. Another Bi-accompanying metal in the deposits is selenium (Se). The most famous mine was the Juno mine. Tennant Creek is now largely exhausted, but for many years it was one of the worlds principal resources of Bi.

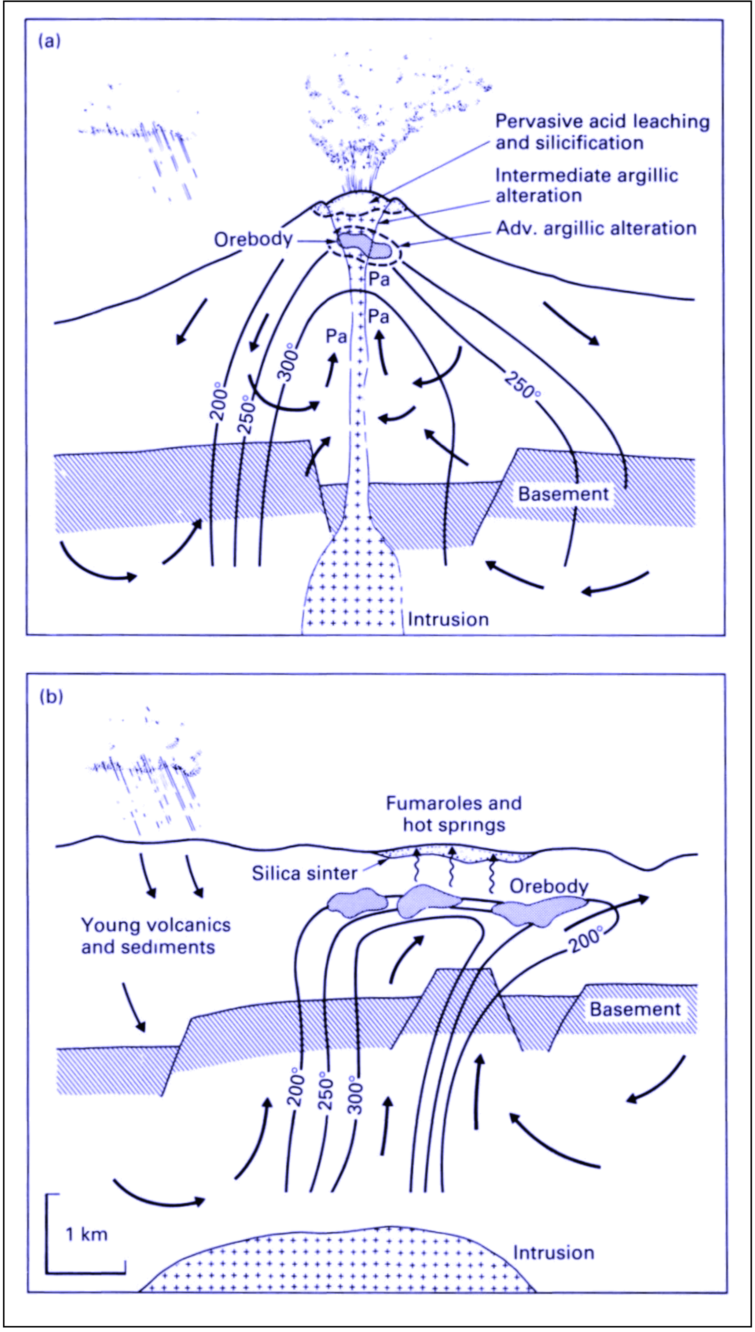


*Fig.2.20. Two schemes of formation of epithermal precious metal deposits, After Evans, 1993.*

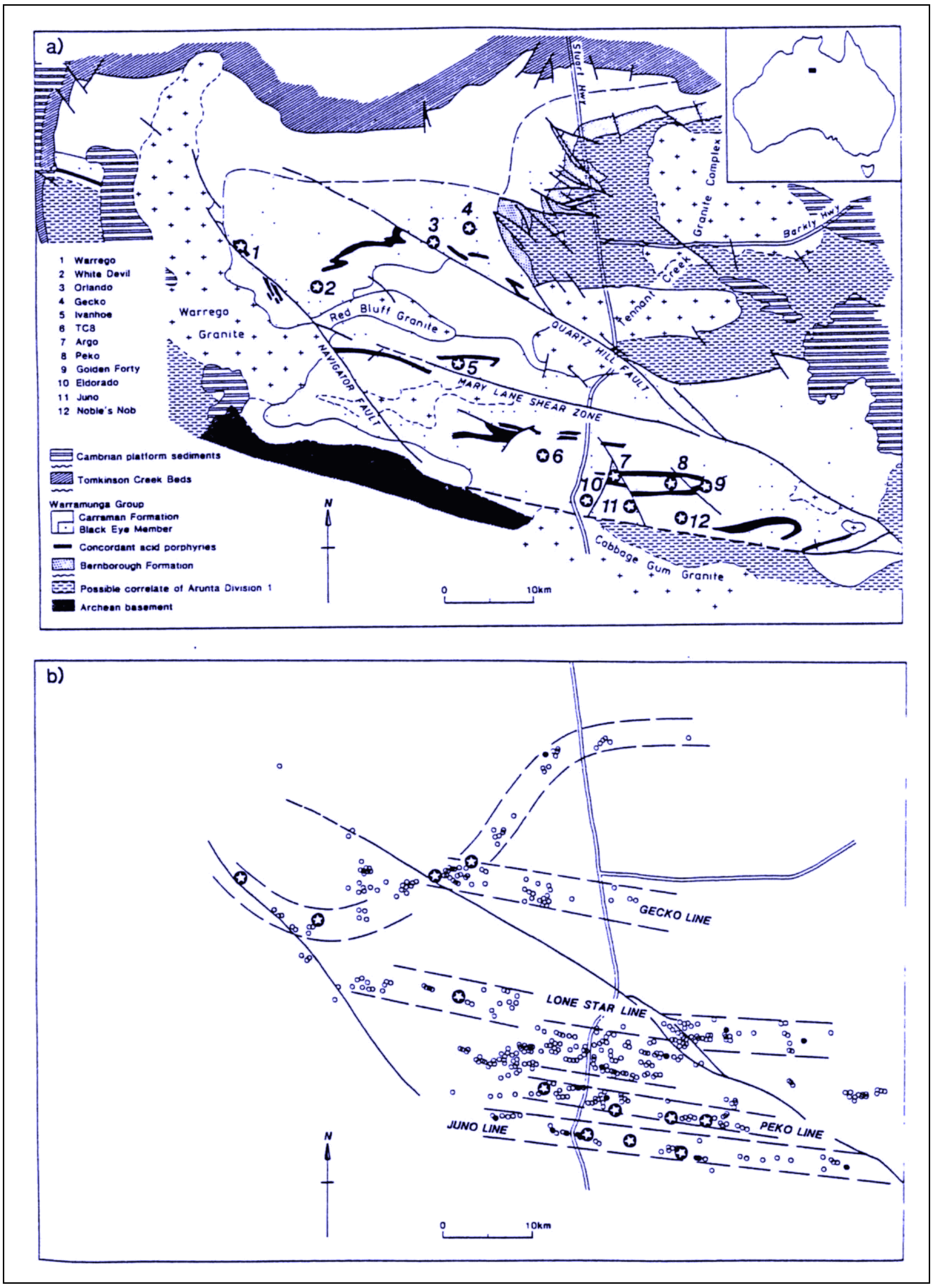


*Fig.2.21. The geology of the Tennant Creek, area, NW Territories, Australia. After Hale, 1996.*

## II.3.4. Metamorphic Type

### II.3.4.1. Archaean lode gold deposits

These precipitated from hydrothermal solutions of regional metamorphic origin. During regional metamorphism, rocks undergo deep burial, and experience high temperatures and pressures. Mineral transformations include loss of combined water or hydroxyl-groups. This results in a low salinity solution.

In the Archaean, the lower parts of volcano-sedimentary sequences underwent this type of dewatering (metamorphic dewatering). The resulting solutions leached gold from the volcano-sedimentary rocks. Gold was carried in solution as a bisulfide complex.

The solutions were channelled through shear zones, but did not reach the surface, they remained a depth. Sometimes the solutions found their way into smaller channel systems, where the bisulfide complex reacted with iron bearing wall minerals, and caused precipitation of *native gold* and *pyrite*.

Major Archaean lode gold deposits occur in Archaean greenstone (volcano sedimentary) belts. Important deposits are at Golden Mile, W-Australia, and the Porcupine District, Ontario, Canada.

## II.3.5. Seawater Type

### II.3.5.1. Volcanogenic Massive Sulfide Type (VMS-Type)

These deposits are the products of deeply penetrating submarine hydrothermal convection systems. The systems are driven by the heat of submarine volcanism. Being mainly seawater, the solutions are chloride bearing. Circulating in submarine rocks near heat sources, they may reach a temperature up to 350 °C. At this temperature, they leach the metals from the rocks through which they circulate. Also they may mix with late magmatic fluids, and acquire metals this way. The metals in which these solutions become enriched include Cu, Zn, and Fe. The metals are carried in solution as chloride complexes.

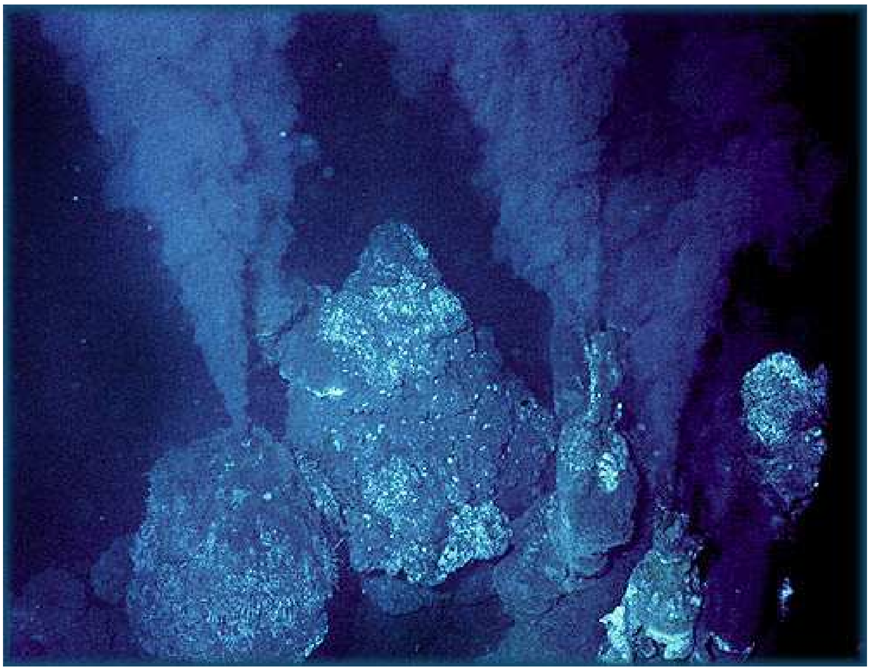


*Fig. 2.22. Sulfide structures build up as a result of precipitation and crystallization. This active sulfide structure is located on the Juan de Fuca Ridge, at 44°58' N & 130°14' W.*

The hydrothermal solutions are discharged through extensional faults onto the sea floor. Here rapid cooling precipitates *chalcopyrite* ($CuFeS_2$), *pyrite* ($FeS_2$), and *sphalerite* (ZnS).These accumulate as mounds and vertical chimneys venting fine grained sulfide. These structures are called *black smokers*.

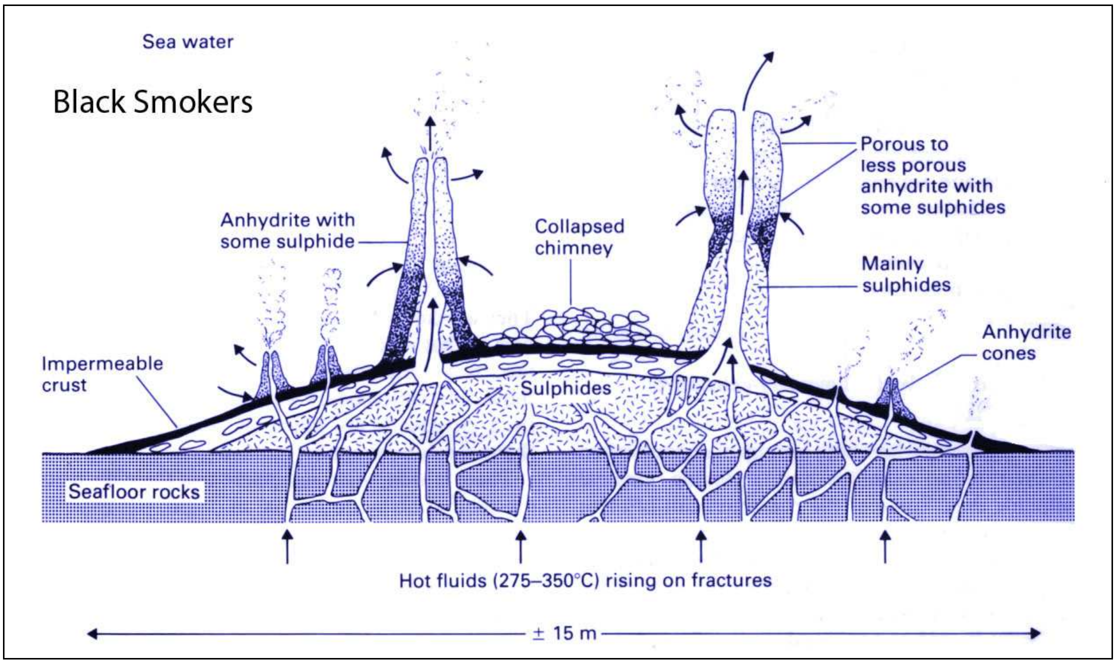


*Fig.2.23. Schematic picture of black smokers. After Evans, 1993.*

Black smokers provide an energy source for an ecosystem, founded on sulphur-reducing bacteria. A large group of other life forms thrive on this. Tube worms are common. Black smokers and their ecosystems were first discovered in 1977 by Ocean scientists diving near the Galapagos islands in the small research submersible ALVIN. One of the most notable scientist was Dr. Robert D. Ballard, who later discovered the tragic sunken ocean liner Titanic.

*Fig.2.24. Tube worms: Each of those tube structures is actually a worm. Tube worms are one type of life that is found near hydrothermal vents. Image by Dan Fornari, Woods Hole Oceanographic Institute*

Deep-sea hydrothermal vents support extraordinary ecosystems deep beneath the surface of the oceans. These ecosystems are the only communities on Earth whose immediate energy source is not sunlight. Life on Earth, and even possibly on other planets, may have formed in environments similar to these. The image below shows tube worms, living near the black smokers.

Periodic collapse of these chimneys contributes to the accumulation of a pile of sulfides on the ocean floor. This pile is subsequently emplaced into the upper crust as a **volcanogenic massive sulfide deposit.**

Most of these deposits are in size range of 1 million to 10 million tonnes of ore. Although relatively small, these deposits are attractive because of their very high grades. For instance Kidd Creek, eastern Canada, has ore grading 2.5 % Cu and 6.0 % Zn.

Another type of VMS-deposits is called the Kuroko-type, and is generated by submarine phreatic (steam) explosions for a submarine volcano. These types of deposits frequently contain also strata with *gypsum* ($CaSO_4.2H_2O$).

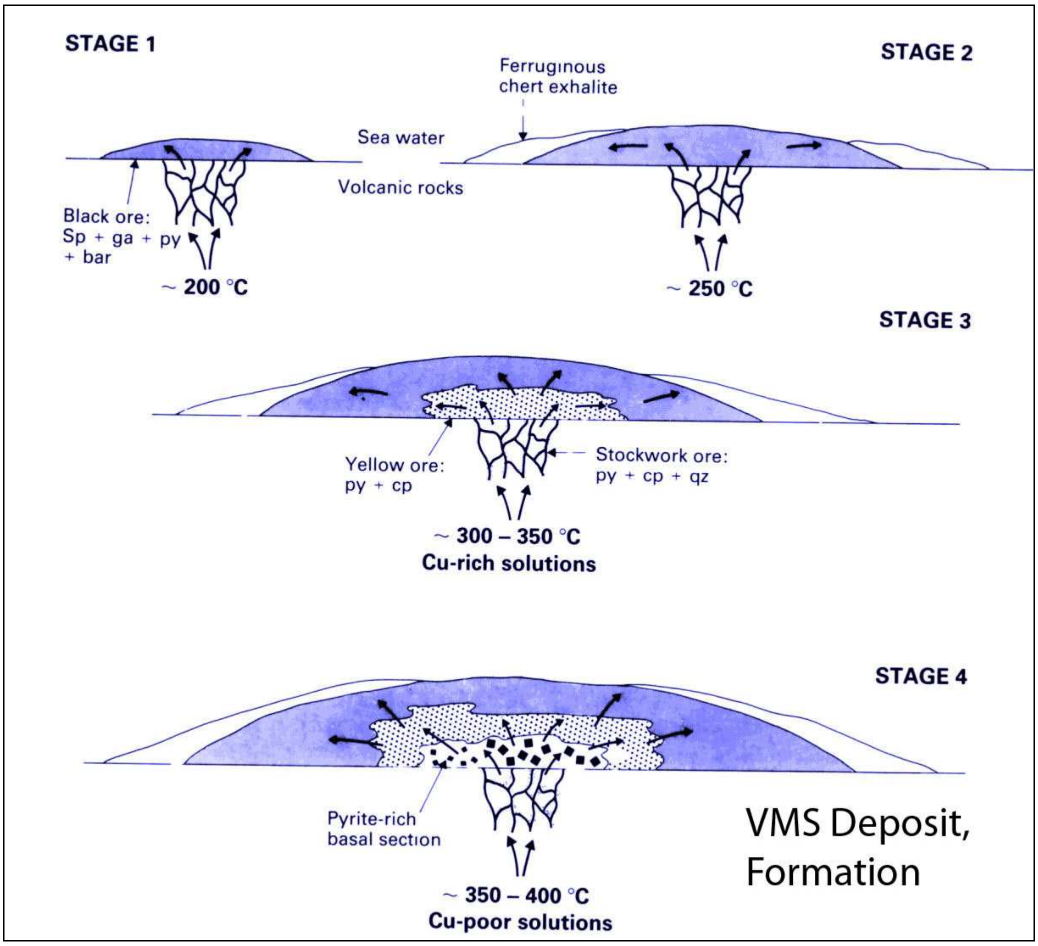


*Fig.2.25. Diagrams to illustrate the first 4 stages during the formation of a volcanogenic massive sulfide deposit. Bar = barite, Sp=sphalerite, ga=galena, py=pyrite, cp=chalcopyrite, qz=quartz. After Evans, 1993.*

### II.3.5.2. Stratiform and Sedex Deposits

*II.3.5.2.1. Stratiform Deposits*

These occur in rift associated sedimentary basins. The hydrothermal solutions originate from compactional dewatering of sediments. There may also be solutions originating from rift-related magmatism. Rift related heat drives the solutions in a convective circulation through the basin rocks.

During circulation these solutions may acquire metals by leaching them from the rocks through which they pass. The rocks may include sediments, volcanoclastic rocks, or crystalline basement. The metals are transported in solution as chloride complexes. A hydrothermal fluid that has a high chloride concentration is termed a **brine.**

Stratiform ore deposits occur when brines react with sulphur already present in the sediment. This may for instance be anhydrite, often found in continental clastic redbed aquifers. Reduction of anhydrite at approximately 250°C leads to the formation of sulfide. In other sediments, the source of sulphur may be diagenetic pyrite. Solutions experiencing shallow convection may become enriched in copper (Cu) and cobalt (Co). This may lead to the formation of *chalcopyrite* ($CuFeS_2$), *bornite* ($Cu_5FeS_4$), and *carrolite* $CuCo_2S_4$.

In the Central African copper belt, some twenty stratiform deposits comprise over $5x10^9$ tonnes of ore with grades of 2.5 to 4.5. % Cu and 0.2 % Co.

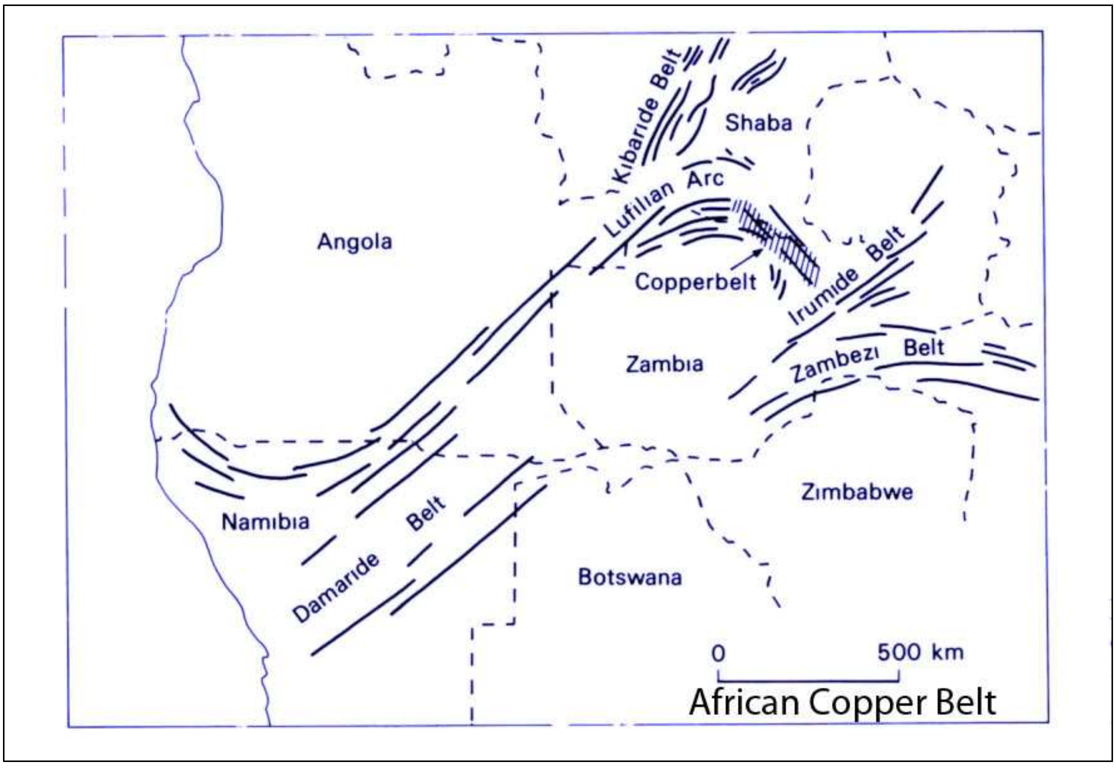


*Fig. 2.26. The location of the African Copper Belt, which is located mainly in Zambia. After Evans, 1993.*

#### *II.3.5.2.2. Sedimentary Exhalative Deposits*

Such ores are also called SEDEX deposits. The ores consist usually of *galena* (PbS) and *sphalerite* (ZnS). These ores are also found in sedimentary basins. The parent hydrothermal solutions are seawater that penetrates the basin sediments. With considerable depth penetration (about 10 km) they attain temperatures of 50 to 200°C. Gradually the chloride content increases.

As the temperature of the solution increases it rises, forming a convection cell. The solution acquires metal through leaching of the basin sediments during convective circulation. Metals are transported as chloride complexes. The metalliferous brines vent through rifting associated faults onto the seafloor. Being of higher density than seawater, they can flow into distal depressions. Here they lose heat and precipitate galena and sphalerite. The resulting deposits are large lead-zinc ore bodies. The most famous example is **Mount Isa**, Queensland, Australia, which has 87 million tonnes of ore, grading 7.1 % Pb and 6.1 % Zn.

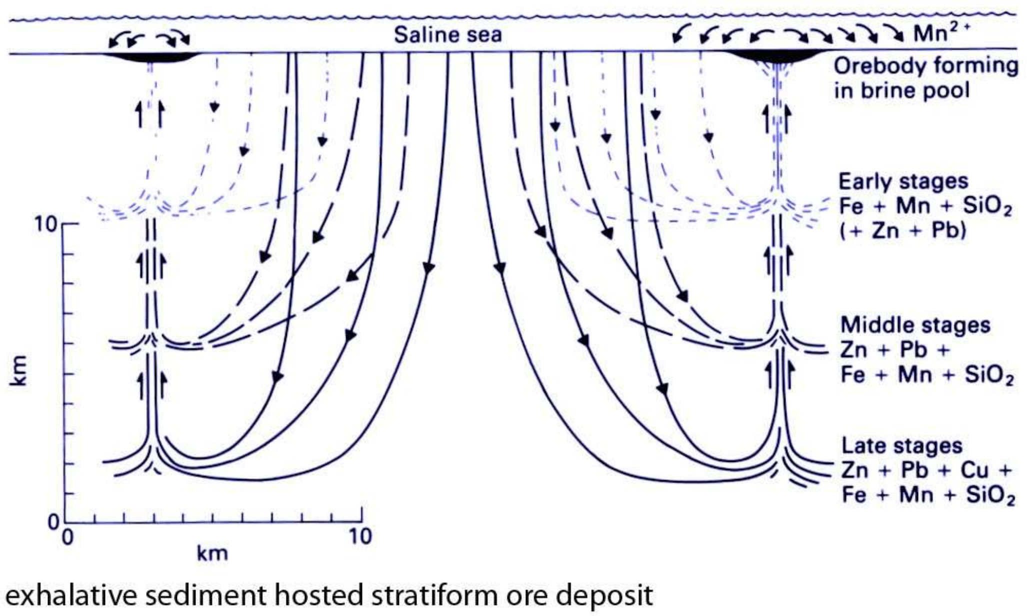


*Fig. 2.27. Diagram showing how seawater circulation through the crust might give rise to the formation of an exhalative sediment hosted stratiform ore deposit. After Evans, 1993.*

Many scholars consider the famous lead-zinc ores of **Broken Hill**, Australia to be a subclass of the SEDEX-deposits, being more or less a metamorphosed version of the SEDEX-mineralization.

### II.3.5.3. Mississippi-Valley Type deposits (MVT-type Deposits)

Formation water is expelled from sediments during compressional dewatering. This permeates argillaceous **(***montmorillonite*-bearing) sediments**.** At a burial depth of about 2 km, the montmorillonite is converted to *illite*. Montmorillonite and illite are two clay minerals. At this point the formation water leaches lead, and zinc from the sediment. Methane and oily components are also carried along with the fluid. The metalliferous solution migrates under the influence of gravity, or is driven by the heat from a nearby magmatic intrusion. It migrates to shallow water sediments around the basin margins. The methane carried along with fluid reduces gypsum and anhydrite in evaporites:

$CaSO_2.2H_2O + CH_4 = H_2S + CaCO_3 + 3\ H_2O$

The $H_2S$ is then available to precipitate the Pb and Zn as galena (PbS) and sphalerite (ZnS). This occurs in limestones of which the porosity is enhanced by processes like dolomitisation, karstification or brecciation. Acid dissolution according to the reaction

$ZnCl_2 + H_2S = ZnS + 2HCl$

where the HCl increases the dissolution of calcium carbonate leads to strata bound deposits of sphalerite and galena[6].

The type of deposits is named after deposits occurring in the valley of the Mississippi. Individual MVT-deposits tend to be small, but they occur in clusters. At Pine point, Northern Canada, there are $95x10^6$ tonnes of ore with an average grade of 2.5 % Pb and 6.2 % Zn, dispersed over 40 individual deposits in an area of 7000 $km^2$.

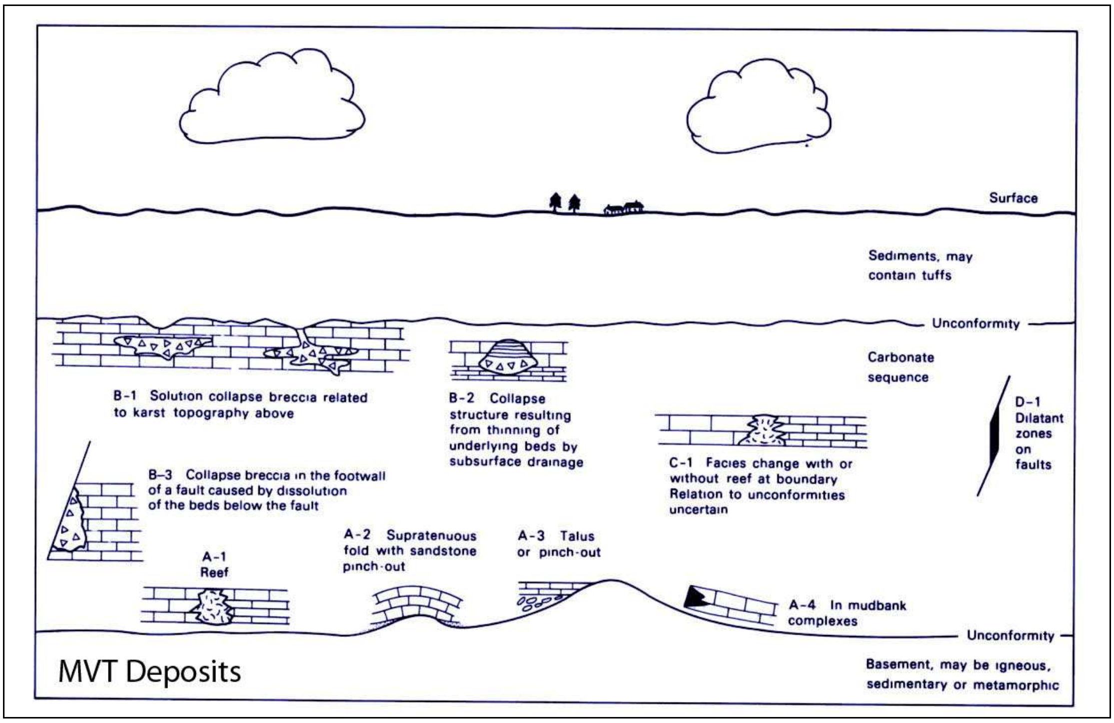


*Fig. 2.28. Idealized vertical section illustrating the range of geological situations in which carbonate hosted base metal de posits are known to occur. After Evans, 1993.*

---

[6] Strata bound = bound to one stratum (layer) or more strata (layers) . Stratiform = in the shape of a layer

## *II.4. Uranium Ore Deposits*

### II.4.1. Introduction

Uranium ores accumulate where hexavalent uranium is reduced to the tetravalent state. In the natural environment, the reducing agent may be pyrite, organic matter or graphite. As a result, uranium precipitates as *uraninite* ($UO_2$).

$$2UO_2(CO)_3^{4-} + 8\ H^+ + C = 2UO_2 + 7\ CO_2 + 4\ H_2O$$

Uranium is soluble as uranyl complexes in surface waters and oxidic groundwater.

### II.4.2. Unconformity type deposits

Uranium was originally leached from Archaean rocks. It may then have been incorporated into lower Proterozoic sediments. When the Earth's atmosphere became oxygenated during the middle Proterozoic, this uranium was remobilized by convecting hydrothermal solutions. These solutions were diagenetic or meteoric in origin and saline and $CO_2$-rich. These heated to up to 200 °C by a magmatic event, and driven along permeable formations until they reached redox boundaries. Some mid-Proterozoic sandstones rest unconformably on brecciated or faulted basement. The unconformity provides a good channel way. Faults and breccias act as reducing traps. There the soluble uranyl complex is converted into the insoluble oxide uraninite. Major uranium deposits occur at and below these mid Proterozoic unconformities. Examples are the Athabasca basin, Saskatchewan, Canada, or the Pine Creek geosyncline northern Australia.

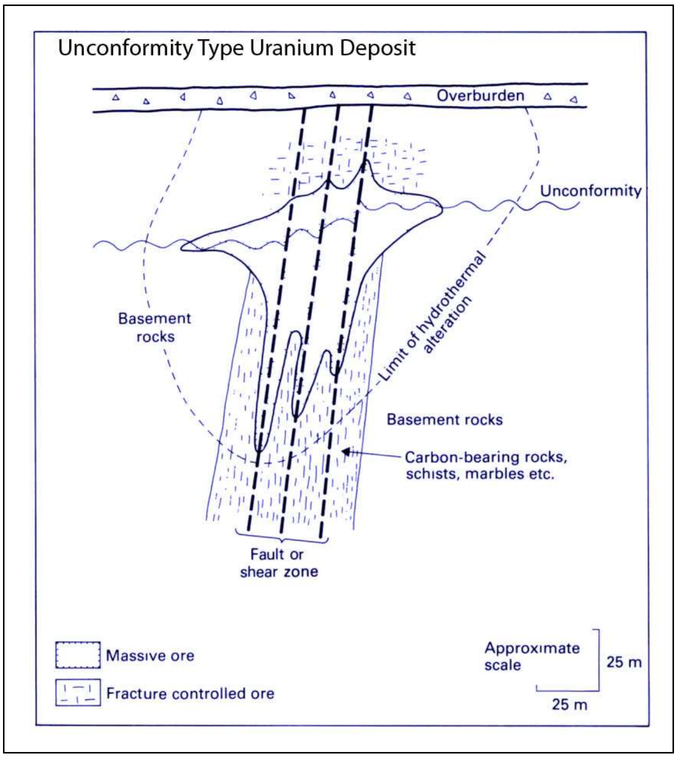


*Fig. 2.29. Generalized diagram of an unconformity type uranium deposit. After Evans, 1993.*

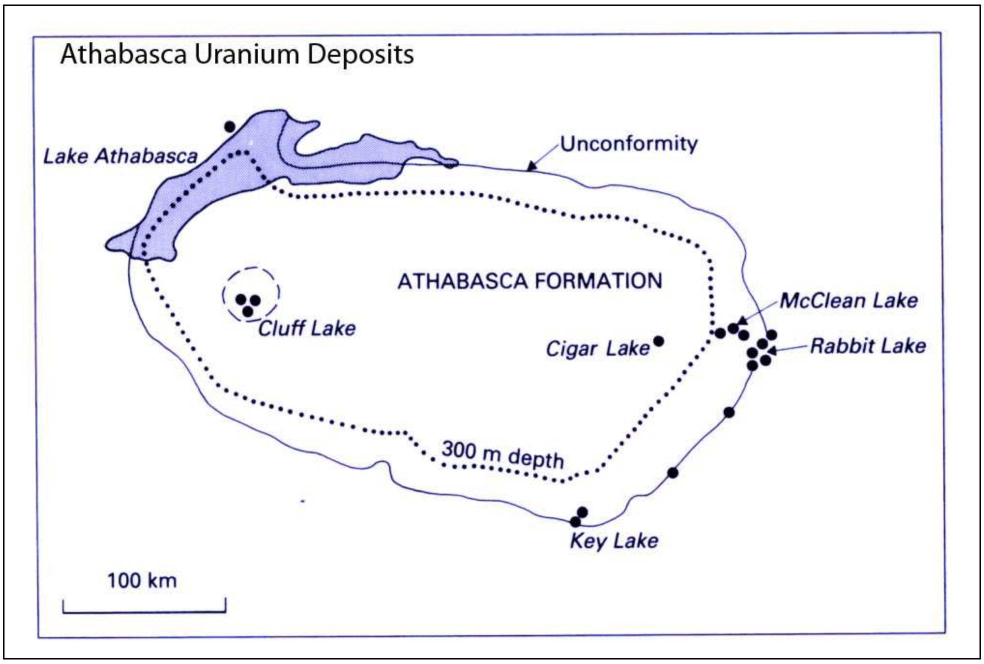


*Fig.2.30. Outline of the Athabasca basin, and the location of the associated uranium deposits. The basement rocks outside the basin are older Proterozoic or Archaean rocks. After Evans, 1993.*

### II.4.3. Sandstone deposits

More recent sediments contain smaller uranium deposits of somewhat similar origin. Uranium is leached from granites or volcanics by meteoric water at ambient temperature. The water flows through oxidizing sandstone channels or aquifers with hexavalent uranium in solution. When reducing conditions are encountered, the uranium is precipitated as uraninite. As more oxidizing waters flow through the channel or aquifer, the uranium is redissolved. It precipitates again if it again reaches the redox front further along the channel or aquifer. Deposits of this type occur in sandstone aquifers, and are therefore called sandstone hosted deposits. Because of their mode of genesis, they are also known as roll-front deposits.

These deposits occur in the Upper Paleozoic continental sedimentary basins of the western USA. Uranium ore bodies range in size from $50 \times 10^6$ tonnes and in grade from 0.1 to 9 % $U_3O_8$. They are generally small in size, and therefore have limited economic importance.

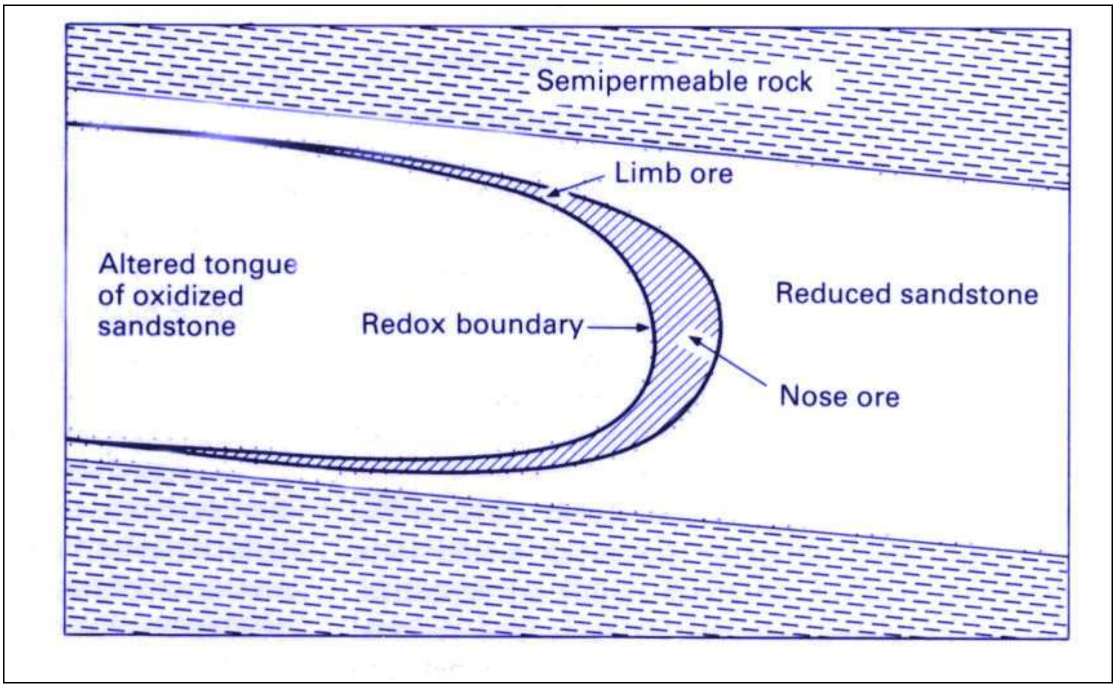


*Fig. 2.31. Idealized section of a roll-front uranium deposit. After Evans, 1993.*

These ores are formed at ambient temperatures and pressures. They are formed by selective precipitation in sedimentary or sub aerial (weathering) environment. Separation and concentration of metals results from different solubilities in aqueous systems. The solubilities depend on Eh and pH conditions.

### II.4.4. Quartz-pebble conglomerate deposits

Quartz pebble conglomerate hosted uranium deposits were the major source of primary production for several decades after WWII. Although up to eight different localities around the world have been identified, the most important deposits are in the Huronian Supergroup in Ontario, Canada (Elliot Lake) and in the Witwatersrand Supergroup of South Africa. These deposits make up approximately 13% of the world's uranium resources. The mining operations in the Elliot Lake area have closed in recent years because these deposits are uneconomic under current uranium market conditions.

Where uranium is recovered as a by-product of gold mining, the grade may be as low as 0.01% $U_3O_8$. In deposits mined exclusively for uranium, average grades range as high as 0.15% $U_3O_8$. Individual deposits range in size from 6000-170 000 t contained $U_3O_8$.

Quartz pebble conglomerate hosted uranium deposits formed as a result from transport and deposition of uraninite in a fluvial sedimentary environment. They are defined as stratiform and stratabound paleoplacer deposits (see also page 71). Host rocks are typically conglomerates and sandstones deposited in alluvial fan and braided stream environments.

Uranium minerals were derived from uraniferous pegmatites in the sediment source areas. These deposits are restricted to the Archaean and early Paleoproterozoic and do not occur in sediments younger than about 2200 million years. After that time, oxygen levels in the atmosphere reached a critical level, making simple uranium oxides no longer stable in near-surface environments.

## *II.5. Autochthonous Ore Deposits*

These ores are formed at ambient temperatures and pressures. They are formed by selective precipitation in sedimentary or sub aerial (weathering) environment. Separation and concentration of metals results from different solubilities in aqueous systems. The solubilities depend on Eh and pH conditions.

### II.5.1. Ocean Floor Nodules

The floors of the oceans cover 320 million km$^2$. The land area is just 150 million km$^2$. The ocean floor lies at depths $> 3.8$ km below the water surface, and comprises oceanic crust. This crust forms at mid-oceanic ridges, and is consumed by subduction at continental margins. Thus oceanic crust only survives during the migration from ridge to subduction zone. The "lifetime" of the oceanic crust is in the order of $1 \times 10^7$ year. During its lifetime, the oceanic crust experiences very little sedimentation, typically $< 7$ µm per year.

However the faecal pellets and remains of near surface biotica fall to the ocean floors. This biogenic debris is most prolific in the high productivity equatorial regions. The biogenic debris contains trace metals, which are liberated by diagenesis. Submarine volcanic activity, mainly at mid-oceanic ridges contributes additional metals. Dissolved Fe and Mn tend to precipitate as oxides on nuclei such as sand grains and shark teeth. The oxides auto catalyze further precipitation, and concentric layers form a ball of nodule. The diameter of nodules varies from a few millimetres to a few centimetres. Some are spherical, but in general they are asymmetric, with the most rounded surface upward.

*Fig. 2.32. Copper manganese nodule, central Pacific Ocean.*

The main Mn-oxides are *vernadite* ($\delta MnO_2$), *todorokite* $(Ca, Na)_2Mn_5O_{12}$, *birnessite* ($CaNaMn_7O_{14}$). The main Fe-oxides are different *amorphous ferric oxyhydroxide*, general formula FeOOH. The crystal structure of vernadite is suited to incorporate Co and Ce. The crystal structures of todorokite and birnessite may incorporate Cu and Ni.

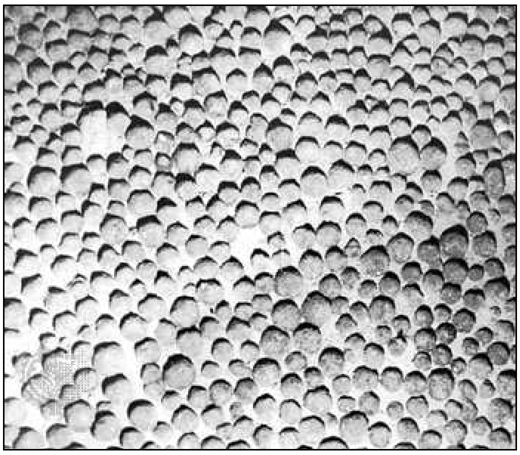


*Fig. 2.33. Image of nodules on the Pacific ocean floor*

Nodules are found on the ocean floor over much of the world. The total mass in the Pacific Ocean is estimated at $1.6x10^{12}$ tonnes. The nodules invariably rest on pelagic ooze, and are never stacked on top of each other. The distribution density is very variable. Also its composition differs from ocean to ocean.

The most promising area for deep sea mining of these nodules is between Hawaii and Mexico. It was for a short while attempted to dredge ocean floor nodules in the late 1970's and in the 1980's, but development costs were massive, and the deposits appeared in fact uneconomical. There has been little interest anymore in ocean floor nodules.

## II.5.2. Seawater sediments

### II.5.2.1. Iron Ore Deposits

These are iron-rich oxide facies of Banded Iron Formation (BIF). During the lower Proterozoic, BIF precipitated from shallow seas. Precipitation occurred over large areas on continental shelves and prograding coastlines. The oxide facies of the BIF is a seasonally varved alteration of iron oxides and chert. The varve layers are mm to cm scale. The iron oxides are *hematite* ($Fe_2O_3$) and *magnetite* ($Fe_3O_4$). *Chert* is $SiO_2$.The overall composition is about 30 % Fe and 45 % $SiO_2$.

*Fig.2.34. Banded ironstone. The rock is purplish red in appearance, caused by the hematite.*

*Fig. 2.35. Banded Iron Formation, "Tiger Iron", Western Australia. Layers are a few mm's to a cm thick.*

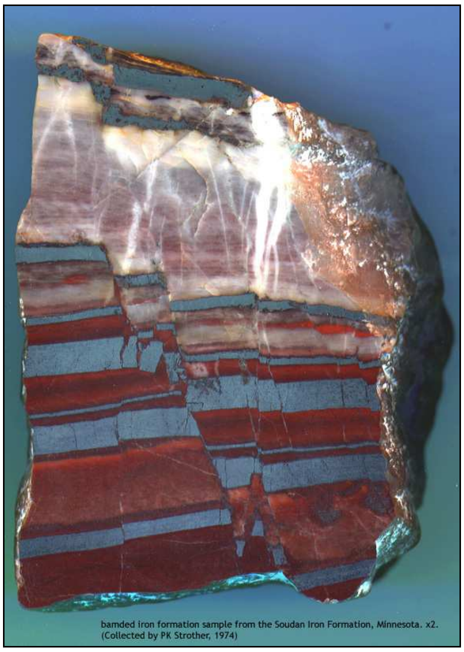


*Fig. 2.36. Banded Iron Formation sample from the Soudan Formation, Minnesota. 2x.*

Iron and silica were supplied by erosion form nearby landmasses. Surface drainage transported dissolved $Fe^{2+}$, soluble because of the then $O_2$-deficient, $CO_2$ rich atmosphere. Iron and silica were also supplied by seawater convecting through basin sediments. Seawater leached $Fe^{2+}$ from the underlying sediments at temperatures reaching ±300°C. In the Lake Superior district, North America, the Banded Iron Formation constitutes a low grade iron ore. Supergene enrichment during the Proterozoic sometimes lead to higher grade deposits. The supergene enrichment involved the oxidation of magnetite to hematite. There was limited remobilization of iron and its reprecipitation as *goethite* (FeOOH). Iron metasomatism of silicates also occurred. Subsequently, in the mid-Proterozoic, the enriched Iron Formation was again buried. This raised temperatures to ±100°C, and caused the conversion of goethite to hematite.

The Hammersley Basin of Western Australia contains $33x10^9$ tonnes of this type of iron ore. This tonnage has a grade of > 55%. Other large BIF deposits occurs in Brazil, e.g. in the Minas Gerais area.

### II.5.2.2. Manganese Ore Deposits

These are shallow marine and estuarine sediments. They were deposited during periods of marine transgression or high sea level stands. The sediment thickness is up to 10 m, and there is considerable lateral continuity. The source rocks are usually Precambrian shield rocks or similar, containing < 0.5 % Mn. Subaerial tropical weathering releases this Mn in 3 forms:

1) soluble $Mn^{2+}$
2) $Mn^{4+}$, adsorbed on the surface of clay minerals (which are themselves sub aerial weathering products
3) Pyrolusite ($MnO_2$), and similar insoluble minerals.

Soluble $Mn^{2+}$ and $Mn^{4+}$ adsorbed on clay minerals are carried down drainage channels to the sea. Some of the soluble $Mn^{2+}$ becomes a constituent of seawater. Some is oxidized to $Mn^{4+}$, which precipitates in stream beds as insoluble oxides.

The clay minerals with $Mn^{4+}$ are carried in suspension some distance form the shoreline. Then they settle, and form argillaceous sediments on the seafloor. These sediments are not enriched in manganese. They may contain even lesser manganese than the source rocks. Manganese ore deposits have grades 50 – 100 times higher. Also in general they contain little or no iron. The exact mechanism of separation is not well understood. Several theories have been put forward.

1) Segregation may take place at the source, owing to manganese being leached out of the source rocks more readily because of its low ionic potential. This however a process which would generate just a few percent difference in Fe and Mn in the extracted material with respect to the source rocks.
2) Iron may precipitate preferentially from hydrothermal solutions with respect to manganese. This observed hot springs which tend to produce more Mn than Fe.

3) Separation by differential precipitation. Chemical considerations suggest that in natural situations low pH ***may*** lead to a selective elimination of iron from iron-manganese containing solution.
4) The fourth possibility is that iron and manganese are becoming separated during diagenesis. The development of reducing conditions will cause both the manganese and iron to go into solution and move laterally and upward. When the solutions reach an oxidizing environment, the two are precipitated. However iron will be the last to be reduced and thus mobilized, and therefore the first to be oxidized and precipitated. In this way iron and manganese tend to become progressively separated in diagenetic solutions.

A number of researchers has proposed that anoxia may play a part in the formation of the giant deposits of shallow marine environments in intracratonic basins. Anoxia leads to an increase in manganese over iron in the deeper sea water of the adjacent shale basins. Following a transgression, the manganese can be transported to shallow oxidic waters where it precipitates.

Manganese deposits are divided into five classes, of which type II, discrete beds of manganese oxides or carbonates are intercalated with BIF. These are economically important deposits. Also important economically is the Type V, consisting of the above mentioned shallow marine deposits. The largest deposit known is the Oligocene age deposit of **Nikopol** in the Ukraine which forms 70 % of the world's manganese reserves. Other important deposits are Molango (Jurassic), Mexico, Groote Eylandt (Cretaceous), Australia, Imini (Cretaceous), Morocco, Kalahari (Precambrian), South Africa. Also northern Greece has manganese deposits.

In comparison with manganese nodules, which form in deep ocean environments, manganese deposits of economic importance are invariably shallow water deposits. Deep water deposits of older ages are unknown. This not well understood.

Manganese is used in steel making, in the manufacturing of batteries, and high strength alloys.

### II.5.2.3. Phosphate ore deposits

Deposits of phosphate occur mainly as marine sediments (phosphorite). Igneous deposits, related to carbonatites are of minor importance. The deep oceans constitute a reservoir of dissolved phosphorus. Ocean currents carry this dissolved phosphorus along continental margins. Upward movement may bring the Phosphorus rich water close to the surface. Near surface shoreward current bring this phosphorus-rich water onto the continental shelf. As the water becomes warmer, as happens in the tropics, it loses some dissolved $CO_2$, and its pH rises. At a certain moment, the solubility of Ca-phosphate is exceeded. This leads to the precipitation of *fluorapatite* $Ca_5(PO_4)_3F$ [7]. Apatite is by some considered to be an industrial mineral rather than an ore mineral.

Phosphorus is an essential nutrient for animal life. The plentiful supply of dissolved phosphorus on the continental shelf produces abundant biota. Phosphate is present in

---

[7] There are three forms of apatite, being fluor-apatite $Ca_5(PO_4)_3F$, hydroxyl-apatite $Ca_5(PO_4)_3OH$ and chlorine-apatite $Ca_5(PO_4)_3Cl$. Hydroxyl-apatite and fluor-apatite form in solid solutions. Chlorine-apatite is rather rare. With the name apatite as such, in general the fluorine end member is intended.

bone (Ca-phosphate) . When the animals die, they sink onto the sea floor, where the phosphate from bone accumulates. The decaying biota may produce low Eh conditions on the sea floor. In this environment, soluble phosphorus can replace the carbonate ion in limestone and dolomite. If clastic sediments are absent, deposits of fluorapatite (and other similar calcium phosphates accumulate. A subsequent marine transgression may rework the accumulations landwards. This produces ore grade phosphorite deposits. A fall in sea level allows their preservation on land. Ore grade phosporite deposits grade 35 -40 % $P_2O_5$. Major deposits and producers are in Florida USA, Morocco, Algeria, Jordan.

Phosphorus is produced in a more or less pyrometallurgical manner: it is reduced under strongly reducing conditions at very high temperatures in submerged arc furnaces, with the addition of cokes and silica (sand, gravel). This leads to the production of gaseous elementary phosphorus (P) accompanied by a silicate slag (general composition $CaSiO_3$). The cooled elemental phosphorus is in turn is converted into the secondary products, such as fertilizers, phosphoric acid (used in the food and drink industry), detergents, and medicals.

### II.5.2.4. Evaporites

Evaporites are precipitates of salts that are normally soluble in sea water or lake water. The most obvious and widespread is common salt, NaCl. Evaporite deposits form where

1) a body of water is not entirely open to a large sea,
2) the climate is such that natural evaporation of water exceeds rainfall.

#### *II.5.2.4.1. Marine evaporites: gypsum, anhydrite*

Evaporation of seawater leads to the following sequence of precipitation:

1) calcium carbonate, *calcite*, $CaCO_3$, limestone
2) calcium sulphate, *gypsum*, $CaSO_4.2H_2O$
3) Sodium chloride, *halite*, NaCl
4) Magnesium sulphate, *epsomite*, $MgSO_4$
5) Potassium chloride, *sylvite*, KCl.

Evaporation of seawater 1 km deep produces the following thickness of evaporites:

- Na-salts, halite, 12.9 m
- Mg-salts, mainly epsomite, 2.5 m.
- Ca-salts, limestone + gypsum, 0.7 m
- K-salts, sylvite, 0.4 m

In fact much thicker evaporite beds are common. Also the proportions of the salts vary considerably. Therefore simple evaporation alone does not account for evaporite deposits. Rather basins are open at the mouth to an open sea. Through this opening, influx of seawater brings in additional supplies of dissolved salts. This process has two variants: desiccated basin, and brine filled basin.

In a desiccated basin, substantial amounts of seawater in the basin, evaporate to evaporites. This produces successive layers (ideally concentric zones) of lime stone, then gypsum, then halite. Intermittently, there is an influx of seawater across the shallow mouth of the basin. This simple cycle is repeated many times.

A brine filled basin has a lower mouth that is continuously open to the sea. The salt rich brine produced by evaporation within the basin has a higher density then fresh seawater. The brine sinks to the lower levels of the basin. When the brine reaches a density of 1.2, it no longer mixes with in fluxing fresh seawater.  This means the waters in the basin are stratified. The brine layer acts as a mirror of radiated energy This radiated energy is concentrated in the upper layers of the water column, which then evaporates even more efficiently. Thick evaporite sequences can develop in large marine basins. Marine evaporites are common through geologic time.  A famous a example of a brine filled basin was the Permian Zechstein basin of North-Western Europe. It has five evaporite cycles, and the evaporites total 3 km in thickness. . It is mined in England, Germany and Poland for halite, gypsum, epsomite and sylvite. Locally is also mined in the Netherlands, by solution mining. Near Veendam, Groningen, Nedmag mines $MgCl_2$, KCl and NaCl by solution mining.  The $MgCl_2$ is partly used for the production of MgO, an important raw material for the ceramics industry.

The Zechstein evaporite deposits also form an impermeable layer above the porous lower Permian redbed sandstones, which are the reservoir rock for the enormous gas field of Slochteren. The gas, formed from heated Westphalian and Stephanian coal seams at depths > 4 km, forms one of the largest gas fields in the world, and is already for decades the major source of the great wealth of the Netherlands. The salt prevented the gas from leaking away, and as a result it was captured in the sandstone.

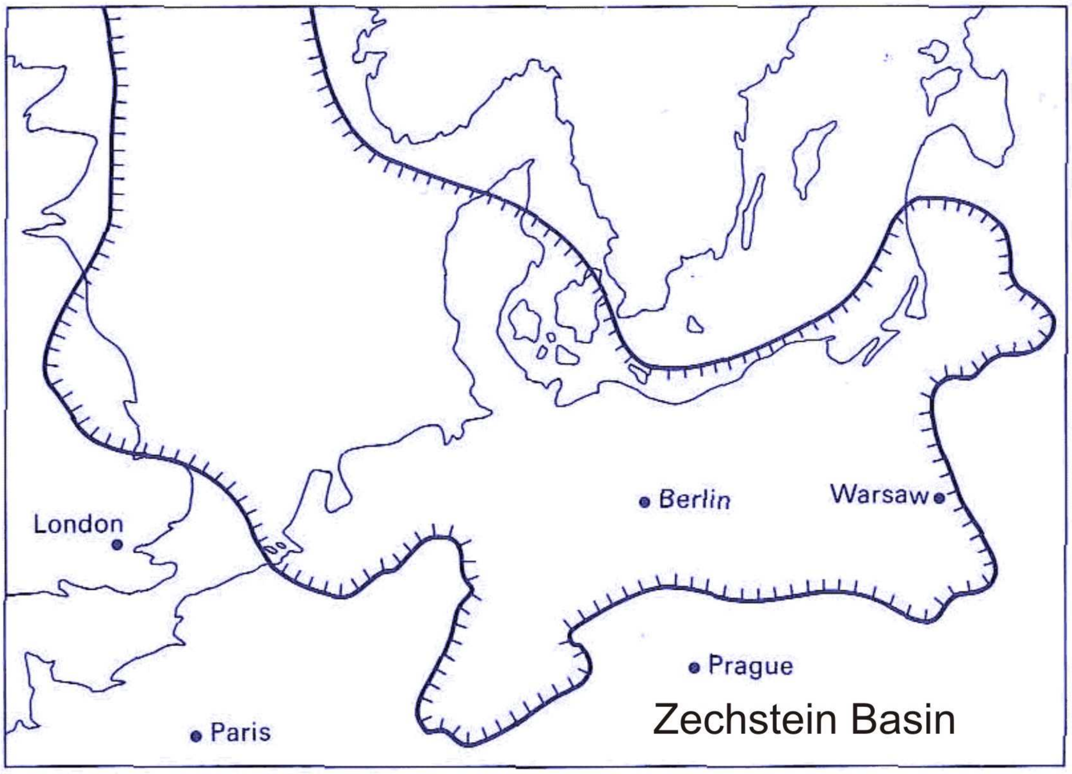


*Fig. 2.37. The Zechstein Basin. It was intermittently open to the sea in the North-West.*

*II.5.2.4.2. Continental evaporites: borates, lithium.*

These precipitate by evaporation of waters of continental (inland) drainage basins. These lakes may be fed by surface streams and or subsurface groundwater. Limestone and gypsum precipitate, but sodium carbonate (*trona*, $Na_3(CO_3)(HCO_3)\cdot 2H_2O$ ) and magnesium sulphate dominate. Examples are the Dead Sea, Jordan, and the Great Salt Lake, Utah, USA. In very arid climates these basins become seasonally dry. In these conditions even the most soluble salts precipitate. These include borate minerals: *borax*, $Na_2B_4O_5(OH)_4\cdot 8(H_2O)$, and *colemanite*, $Ca_2B_6O_{11}\cdot 5(H_2O)$. These minerals are mined for instance in Death Valley, California, and in South-West Turkey. Lithium brines occur in the Salar de Atacama, Chile. These contain up to 1000 ppm Li.

The last salts to precipitate are of course also the first to redissolve. Most evaporite deposits are Tertiary or Quaternary in age, as they are easily destroyed.

## II.5.3. Supergene Deposits

### II.5.3.1. Bauxite Deposits (Aluminium ore)

These are the residue of sub aerial leaching of aluminous, usually volcanic or intrusive parent rock. Conditions for bauxitisation include:

1) a warm tropical climate
2) alternating wet and dry seasons
3) gently undulating relief
4) good downward drainage.

The climate promotes the growth of vegetation which supplies organic acids to percolating rainwater. This low pH-solution dissolves rock-forming minerals such as feldspar, leaving clay minerals. For example feldspar is altered to kaolinite:

$$2KAlSi_3O_8 + 2H^+ + 9\ H_2O = Al_2Si_2O_5(OH)_4 + 2K^+ + 4\ H_4SiO_4$$

Free downward drainage removes soluble alkalis and silicic acid. The resulting overburden is then mainly residual clays. Residual clays are altered by percolating rainwater to amorphous aluminium hydroxides and oxides, mainly *gibbsite*:

$$Al_2Si_2O_5(OH)_4 + 5H_2O = 2\ Al(OH)_3 + 2\ H_4SiO_4$$

During the dry season, metastable amorphous gibbsite is concerted to crystalline gibbsite. This is stable over a wider pH-range. The world largest bauxite deposit is at Sangaredi, Guinea. Ore reserved are 180 x $10^6$ tonnes of ore grading 60 % $Al_2O_3$. The ore deposits form a plateau of approximately 30 m thick.

Bauxite is the most important aluminium ore. It consists largely of the minerals *gibbsite* $Al(OH)_3$, *boehmite* $\gamma$-AlO(OH), and *diaspore* $\alpha$-AlO(OH), together with the iron oxides goethite and hematite, the clay mineral *kaolinite* and small amounts of *anatase* $TiO_2$. It was named after the village **Les Baux-de-Provence** in southern France, where it was first discovered in 1821 by geologist Pierre Berthier.

In the history of the Netherlands, the bauxite deposits of **Suriname** also acquired some fame. ALCOA, Aluminium Company of America, is present in Suriname from 1916. In 1915, experts from this company had already discovered large bauxite deposits in Eastern Suriname, at the Cotticariver, near the village **Moengo**. In 1941, at the Parariver, the first plant for aluminium production was opened. The facility, called **Paranam**, produced most of the aluminium for the Allied Forces during the Second World War, making the Surinam bauxite deposits a most strategical issue. Presently, the production of bauxite in Suriname is carried out by Suralco, a subsidiary company of ALCOA. The mining at Moengo has now come almost to a halt. The deposit is now largely depleted. Production and mining still continues at **Lelydorp** and **Paranam**. However, the major role of Suriname in the world production of aluminium seems to have come to end, unless new deposits are found.

*Fig. 2.38. Bauxite. Reddish colours indicate iron hydroxides such as goethite. Very pure bauxite is white.  The iron content of bauxite is one of its critical parameters.*

*Fig. 2.39.Lelydorp Bauxite Mine, Suriname. It is now abandoned.*

There are also bauxite deposits where *boehmite*, γ-AlOOH, is the predominant mineral. These occur on karstified limestone and dolomite. These rocks themselves are not aluminium-rich, and the bauxite has another origin. Clays of Aeolian (wind) origin were deposited and accumulated in the karst cavities. These then experiences bauxitisation in the same way as residual bauxite deposits. This type of bauxite is found in the Halima Basin, Hungary.

### II.5.3.2 Lateritic Ni-deposits

Olivine $(Mg,Fe)_2SiO_4$ (a solid solution between fayalite and forsterite), is relatively easily hydrolyzed by hydrothermal or meteoric waters. An early alteration product is serpentine:

$$3Mg_2SiO_4 + H_2O + SiO_2 = 2Mg_3Si_2O_5(OH)_4$$

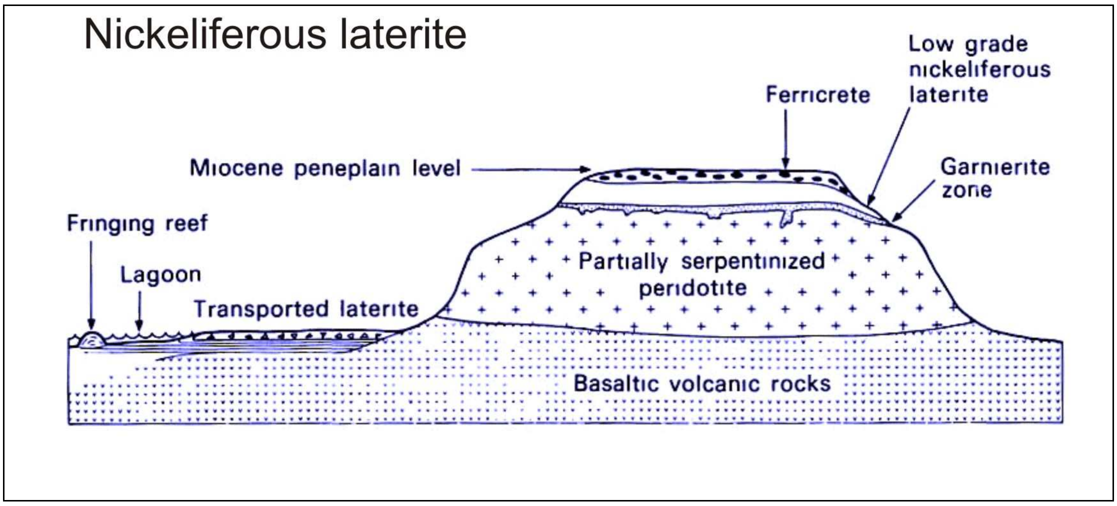


*Fig. 2.40. Section through nickeliferous laterite deposits. After Evans, 1993.*

Peridotite and other ultramafic contain much olivine. Olivine of ultramafic rocks contains typically 0.2 % nickel ($Ni^{2+}$) in its crystal lattice.

Peridotite may be exposed to weathering by warm tropical (not necessarily seasonable) rainfall. This produces rich vegetation and low pH percolating ground water. Olivine then breaks down to leave smectite clays (or at higher pH, quartz). There are also soluble products of weathering. Provided there is free downward drainage, these are initially flushed down the weathering profile. Soluble $Mg^{2+}$ is mainly lost into the groundwater. A few m below the surface, $Fe^{2+}$ precipitates in the limonitic[8] horizon as *goethite* (FeOOH). Some $Ni^{2+}$ is adsorbed on the freshly precipitated goethite. However, most $Ni^{2+}$ reacts with serpentine in the saprolite[9] to form garnierite.

---

[8] Limonite is not a true mineral but a mixture of similar hydrated iron oxide minerals. Most of limonite is made up of goethite.

[9] Disintegrated rock that lies in its original place. Contains mostly clay minerals and quartz, besides relics of parent minerals.

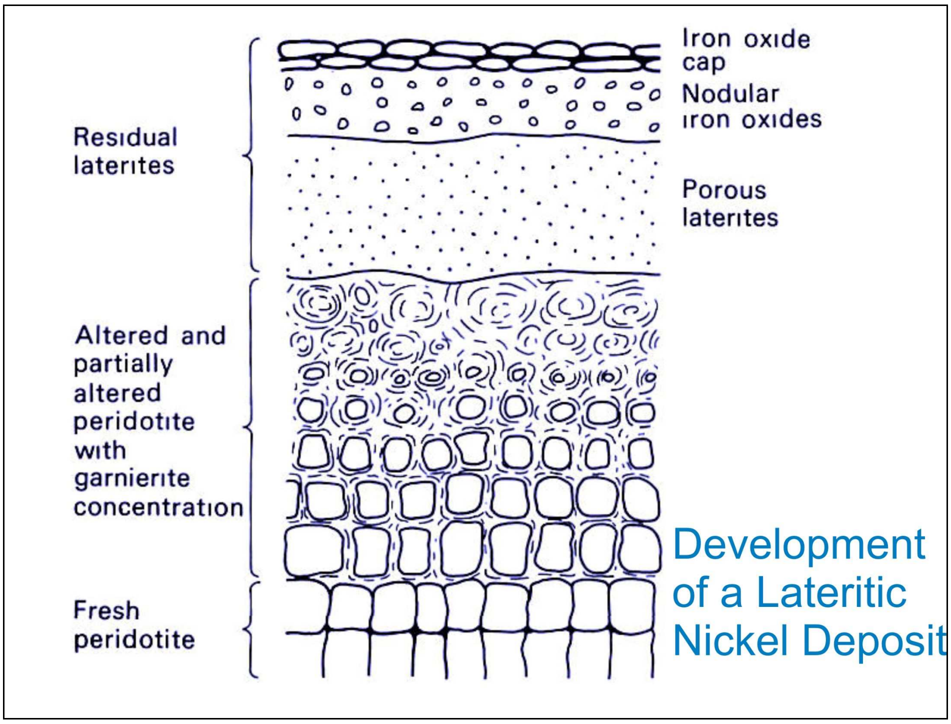


*Fig. 2.41. Diagrammatic profile of a peridotite occurrence in New Caledonia, showing the development of a lateritic nickel deposit. (After Evans, 1993).*

Garnierite is by some described as a mineral, with formula $Ni_3Si_2O_5(OH)_4$, but by most people as a mixture of minerals, consisting of Mg-rich phyllosilicates like serpentine, talc, chlorite and smectite in which a high percentage of magnesium is substituted by nickel. Also rare silicates like nepouite, a nickel rich member of the serpentine group, and similar minerals like falcondoite and willemseite are part of garnierite rock. Garnierite is a bright, but pale (apple) green material, readily distinguished from the other clayish material it is part of. Garnierite accumulation peaks at approximately 10 m below the surface.

*Fig. 2.42. Garnierite ore. The green material is garnierite.*

Gradual uplift of the land surface leads to dynamic (re-)weathering of the profile. The zone of garnierite accumulation is partly dissolved, migrates downward, and is reprecipitated. At the same time, more garnierite is added by weathering of olivine. In this way, the garnierite zone attains thickness and ore grade. Lateritic nickel deposits may grade up to 1.5. to 2 % Ni. A common by-product of lateritic nickel ores is Co (0.1 %). A large portion of the world's nickel is mined form lateritic deposits. However, the energy required to process lateritic nickel ore is much higher then the energy required for sulfide ore.

Lateritic nickel ores are found in New Caledonia, the Solomon Islands, Western Australia, Brazil, the Dominican Republic, etc.

## *II.6. Allochtonous Ore Deposits*

### II.6.1. Introduction to Placers Deposits

These are ore deposits containing minerals that have been transported, and concentrated by processes involving transport. Streams transport yearly approximately 23.5 x $10^9$ tonnes of sediment per year.. This sediment comprises rock fragments and mineral grains derived from the erosion of land surfaces. Erosion varies form place to place, but reaches up to 1 mm per year. Ice, wind and sea currents also transport rock fragments and mineral grains, but in smaller quantities. During transport minerals grains experience sorting. Sorting is due to effects of gravity, and to hydrodynamic properties of the minerals grains and rock fragments. Minerals with similar properties become separated from those with different properties. The properties of minerals that influence gravity are density and grain size. The properties that influence hydrodynamic behaviour are shape and density. Flakes will behave different from spheres in a water stream, even is the density is the same.

Minerals with little or no cleavage (quartz, garnet) retain their original grain size, usually coarse. Minerals with good cleavage (feldspars, clays) are reduced to fine grain size. Sorting leads in some cases to the accumulation of mineral deposits. Deposits of this type are always accumulations of minerals with the following properties:

- High density
- Poor cleavage (resistance to grain size reduction)
- Chemical stability in the weathering environment

Minerals with these properties are oxides or naturally occurring native elements :

- *Gold*, Au, s.g. 16 - 19.3 (because of varying amounts of silver)
- *Cassiterite*, $SnO_2$, s.g. 6.9
- *Zircon*, $ZrSiO_4$, s.g. 4.7
- *Rutile*, $TiO_2$, s.g. 4.2

- *Platinum*, Pt, s.g. 14 – 22 (because of varying amounts of other PGE[10], like palladium, Pd en Rhodium, Rh)
- *Monazite* (REE)$PO_4$, s.g. 4 – 6.5 (depending on composition)
- *Ilmenite*, $FeTiO_3$, s.g. 4.7
- *Diamond*, C, s.g. 3.5.
- *Chromite*, $FeCr_2O_4$, s.g. 4.8

The minerals mentioned in the list above (gold to chromite) are often classified as *heavy minerals.*

Sulfide minerals have high density s.g. 4 – 8) but lack chemical stability in the weathering environment. They do not occur in placers.

A few deposits accumulate in situ, by removal of less dense minerals and soluble rock constituents. These are *eluvial* or *lag* deposits.

Most economic deposits accumulate as a result of sorting during stream and sea current transport. These are called *alluvial or placer deposits.* These include modern (actively forming) and ancient (paleoplacer) deposits. Sites of placer accumulation can be classified by scale:

- River meanders, sand bars, km scale
- Braided river, channels, deltas, 10 km scale
- Slow filling intra-cratonic basins, 100 km scale.

Initially, for the later concentration of mineral grains, there is a prerequisite that the mineral grains should survive erosion, weathering and transport. Only minerals that enter the fluvial system in appreciable amounts are likely to form a deposit of economic importance. In situations that are ideal for placer formation, there would be a high degree of connectivity between the source and deposition areas. An example might be the delivery of material to the river across an alluvial debris fan, and the provision of a comparatively low energy environment for deposition. Linked to this condition of connectivity are enhancing conditions: easily accessible heavy mineral grains; competent overland (sheet) flow, and streamflow with the ability to selectively sort grains. In addition, a degree of repeated reworking of the local sediment deposits will help to concentrate the heavy minerals to form relatively small lenses within larger bodies of less-dense ‘host’ sediments. On the one hand, short-term degrading conditions may favour the development of lag concentrations of heavy minerals, on the other hand, longer-term aggrading conditions are required for the preservation of concentrated deposits of heavy minerals. Thus systems with varied flows, variable stream competence and capacity, and high sediment yields are ideally suited to the formation of exploitable placers. Such system characteristics are often obtained in locations close to the heavy-mineral source. Specifically, if sediment yields are high then the possibility of large economic placers developing is enhanced. However high sediment yields alone may produce rapid aggradation and so suppress sorting processes, so leading to poor concentration of placers.

---

[10] PGE = Platinum Group Elements: Pt, Pd, Ru, Rh, Ir, Os

Sorting leading to accumulation of a mineral occurs when the transport stops (deposition), or transport of other minerals begins (erosion)
These factors are determined by the setting velocity of grains in the suspended load, and the entrainment[11] sorting of grains in the bedload. In placer development, for the settling velocity, despite of the boundary conditions Stokes Law appears to apply very well. This means that particles with small radius and high density settle together with particles of large radius and low density. So for instance, gold grains of 0.05 mm radius may settle together with quartz grains with a radius of 0.165 mm

Minerals on a sand bed in a stream respond to the shear stress exerted by the water (± other moving grains). As the stress rises, first the grains are moved in a bouncing way along the bed (saltation). As the stress rises more, they are transported through the water (entrainment). Grains that respond to the same shear stress have entrainment equivalence. This leads to some important general findings:

1. Low density minerals are moved at lower shear stress than high density minerals of the same radius
2. Small radius minerals are moved at lower shear stress than large minerals of the same density.
3. Low density minerals are carried away and high density minerals remain
4. Fine grained minerals are carried away, and coarser grains of the same mineral remain.

Thus: *entrainment causes sorting by size and density.*

The shape of the grains is important in entrainment (and subsequent sorting) when the shapes differ a lot: for instance flakes versus spheres.

In short: settling velocities sort minerals by sufficiently fast-flowing water. Entrainment sorts minerals in insufficiently fast-flowing water to allow them to go selectively in suspension. The two mechanisms are complementary in concentrating heavy minerals in placer deposits.

## II.6.2. Placer Tin Deposits

Erosion of tin-bearing greisens and veins produces cassiterite placers downstream. The most important example is Kinta Valley, Malaysia, belonging to the South-Asian Tin belt, which stretches from Burma to Indonesia. Granites of varying Mesozoic ages intruded and more or less surround Lower Paleozoic limestones. The granites had greisens and veins at similar topographic levels. The region has experiences deep tropical weathering during the Pleistocene. Weathering products including cassiterite were carried downstream onto the limestone plateau. The limestone has a weathered karst surface. This is an excellent trap for transported sediments and cassiterite. Cassiterite occurs in the Pleistocene alluvium of the Kinta valley. Post Pleistocene sea level rises mean that some deposits are offshore. The shallow sea offshore Malaysia and Sumatra is called the Sunda shelf.

---

[11] Entrainment: being carried along by a fluid stream

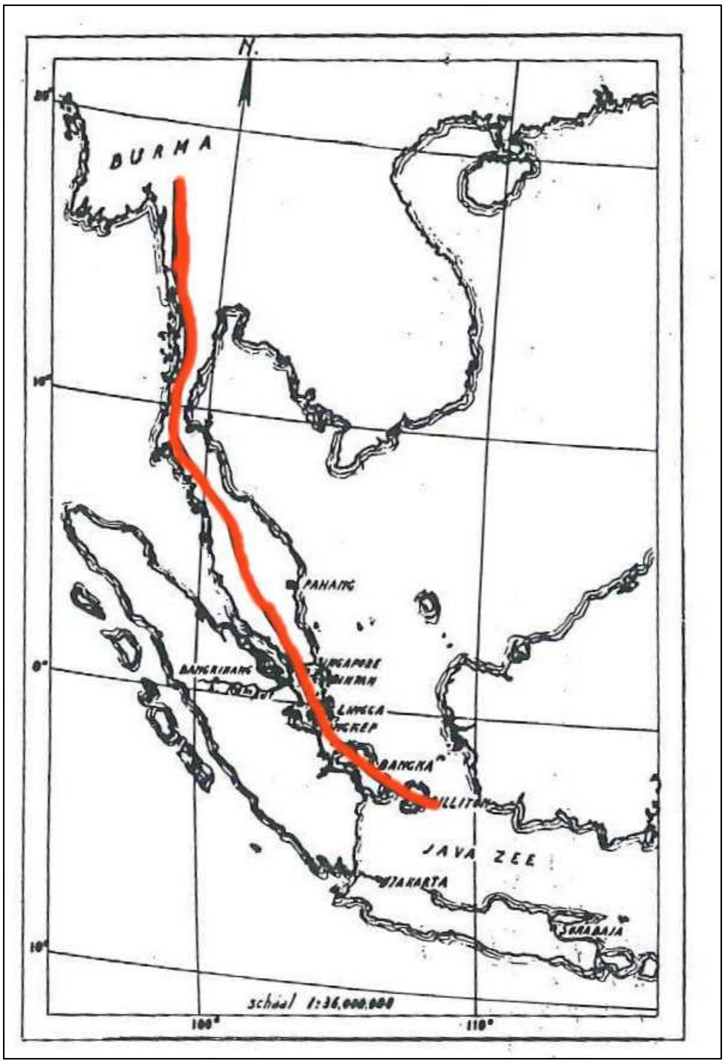


*Fig. 2.43. The South-Asian Tin Belt.*

*Fig. 2.44. The Sunda Shelf. The stippled area was dry land in the Pleistocene.*

Also famous are the tin deposits of the Indonesian islands Singkap (Singkep), Bangka and Belitung (Billiton). The islands are also part of the South-Asian Tin belt. Mesozoic (Cretaceous) granite and granodiorite intrusions in Paleozoic sandstones and shales on Bangka and Belitung lead to veins and alteration zones (greisens), which locally formed rich tin ores. *Cassiterite*-bearing veins and greisens were partly eroded, and similarly to the situation in Malaysia formed large placer deposits in valleys in the Paleozoic sediments, which were submerged due to Pleistocene sea level rises. Locally eluvial tin deposits were formed on the islands, in hill slopes and water sheds. Extensive underground tin mining (e.g. the Klappa Kampit mine, northern Belitung) took place on the islands, but also there was extensive mining of the submarine placers in the shallow sea around the islands. The submerged placer cassiterite was mined by dredging.

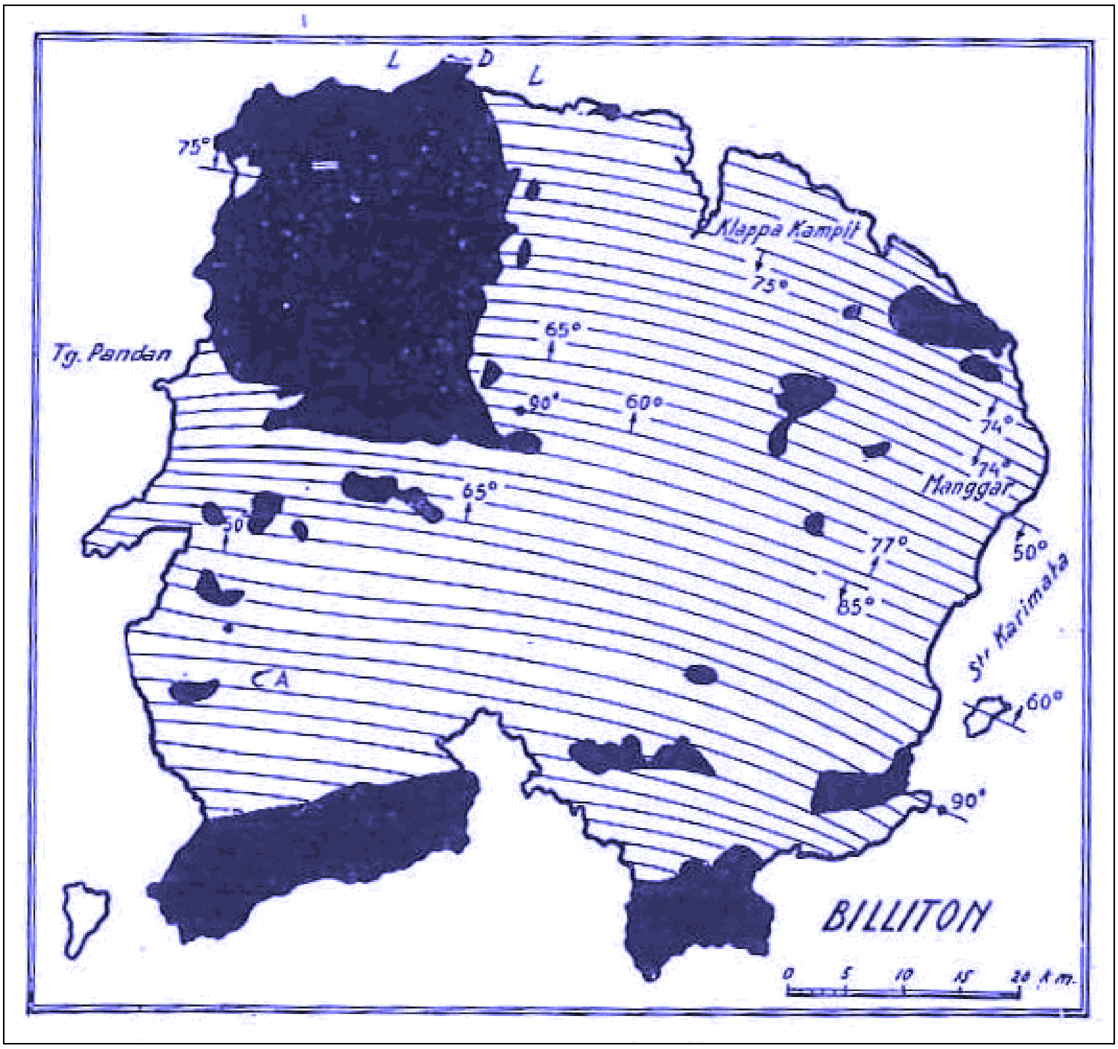
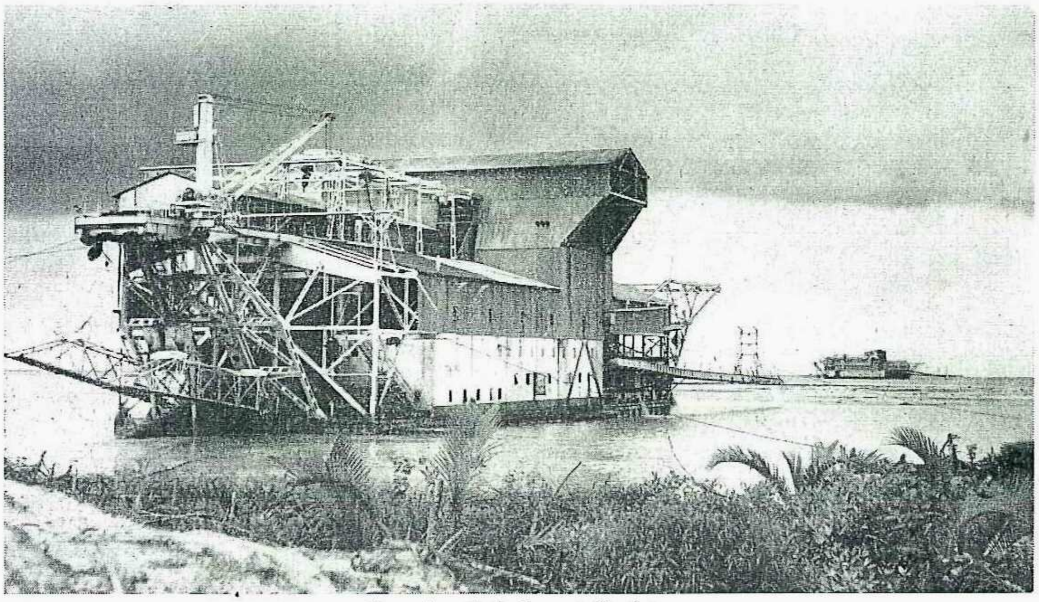


*Fig. 2.45. Billiton (Belitung) island. Black areas are intrusive granitic rocks. Other areas are Paleozoic sediments.*



Sea-going tindredges at Singkep

*Fig. 2.46. Sea going tin dredges at Sinkep, northwest of Bangka, 1950's.*

## II.6.3. Beach Placer Deposits

Sediment reworked by wave action is sorted where waves break. Heavy minerals settle, whilst lighter minerals are carried into the sea by the backwash. Best accumulations occur where wide ocean produces large storm waves.

Longshore current and subparallel ocean swell transports beach placer parallel to the coast. A curvature of the coastline may make the angle between current and swell oblique. This slows water flow, and promotes differential settling of heavy minerals.

Shoreline placers are almost constantly reworked by wave and current action. Deposits are preserved when the sea level falls. They are then found inland from the shoreline, on what can be recognized as a paleo-shoreline.

### II.6.3.1. Beach Placer Titanium Deposits

Beach placer titanium deposits are found along the east and west coast s of Australia, and on the East Coast of South Africa. Deposits are typically 10 m thick, 1 km wide, and over 5 km long. The minerals encountered in such placers are *ilmenite* ($FeTiO_3$) and *rutile* ($TiO_2$).Quaternary beach placers of New South Wales contain up to 3 % rutile. A Pleistocene beach placer at Eneabba, Western Australia, is 20 km long and contains approximately 10 % ilmenite. Most of the world's titanium production comes from beach placers. Their contribution to the world production is about $3 \times 10^6$ tonnes $TiO_2$

### II.6.3.2. Beach Placer Diamond Deposits

*Diamonds* have been transported from kimberlites across Southern Africa by the Orange river. Where this meets the Atlantic Ocean, wave action has concentrated diamonds close to the shoreline. Longshore currents carries the diamonds northwards along the coast. Locally the sea floor was a Precambrian schist. In places, wave action eroded the surface of the schist to a wave cut platform incised by gullies. As waves break, gullies in the schist trap diamonds. Light minerals are removed in the backwash. Fall of sea level during the Pleistocene left such beaches above sea level (raised beaches). Then windblown sand covered the deposits.

The grades of these Namibian diamond deposits are a commercial secret. When first discovered, the diamonds were *handpicked* in the field…..(!). At present, grades are estimated to be 0.5 – 10 carats[12] per tonne. Since the initial discovery of diamonds here in 1908, this regional composite placer deposit has yielded well over 100 million carats of +90% gem quality stones. The bulk of these stones have been derived from the south-western corner of Namibia, known as the *Sperrgebiet* (forbidden territory). Most of this diamond production has been recovered from a variety of placer types that range in age from contemporary deposits to those that are some 40 million years old.

In recent years, it has been attempted to mine the corresponding offshore placers. Nearly one half of Namibia's total annual production is mined from the sea and this proportion is set to increase in the years ahead.

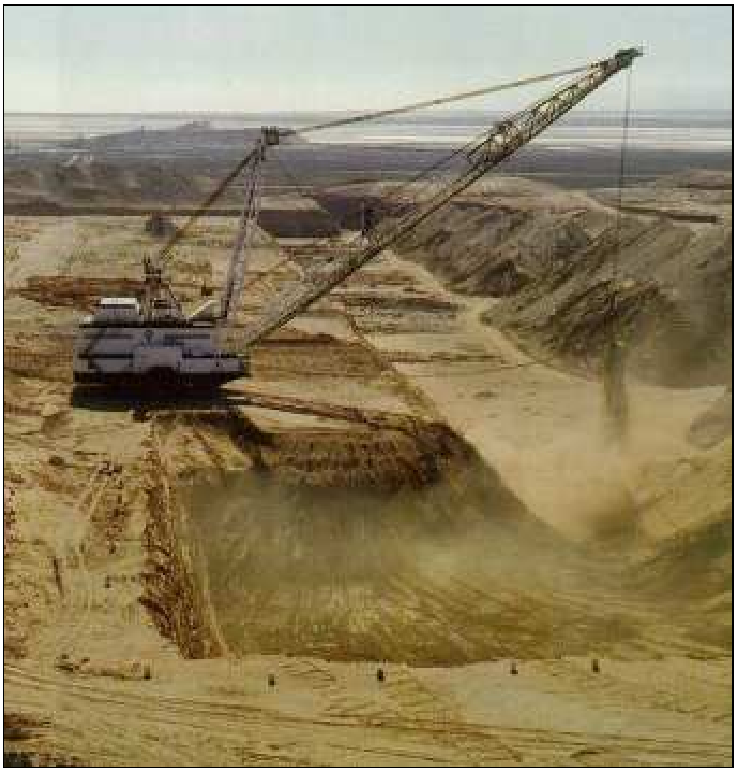


*Fig. 2.46. Alluvial diamond mine.*

---

[12] Carat: in the world of gemstones, a carat is a unit of mass for gemstones, equal to 0.2 gram

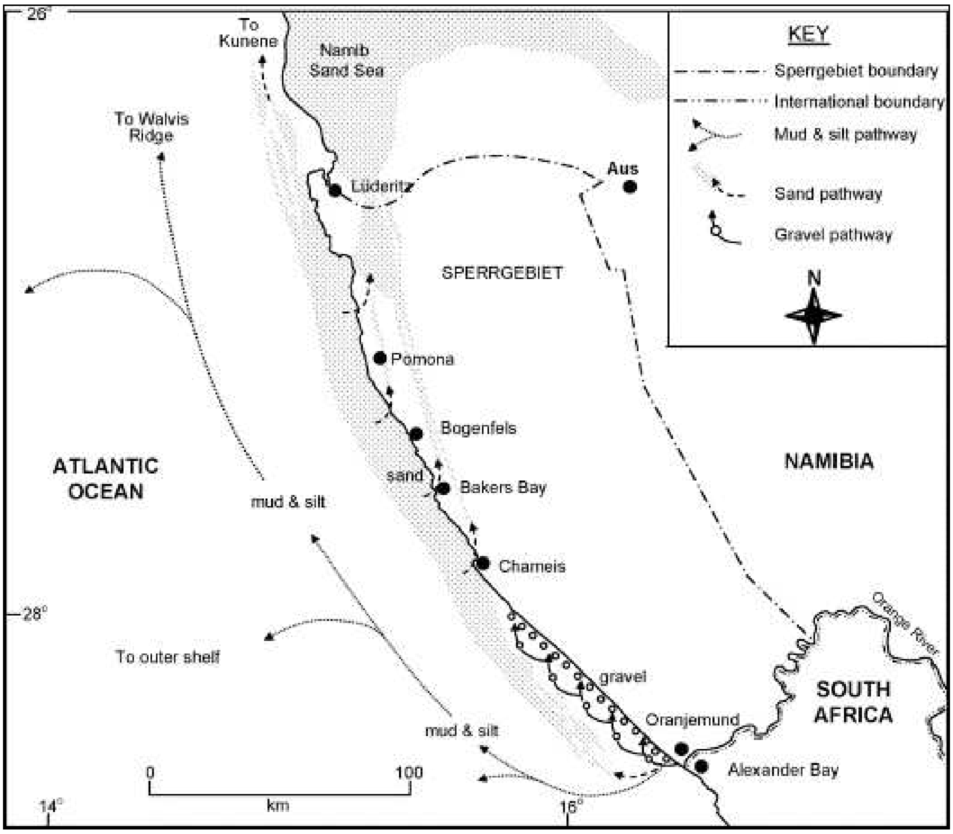


*Fig. 2.47. Map showing the sediment dispersal paths for gravel, sand and finer sediment on the continental shelf.*

*Fig. 2.48. Namibian Beach Placer Diamond deposit: "Mining Area. Keep Out". This is the so-called "Sperrgebiet".*

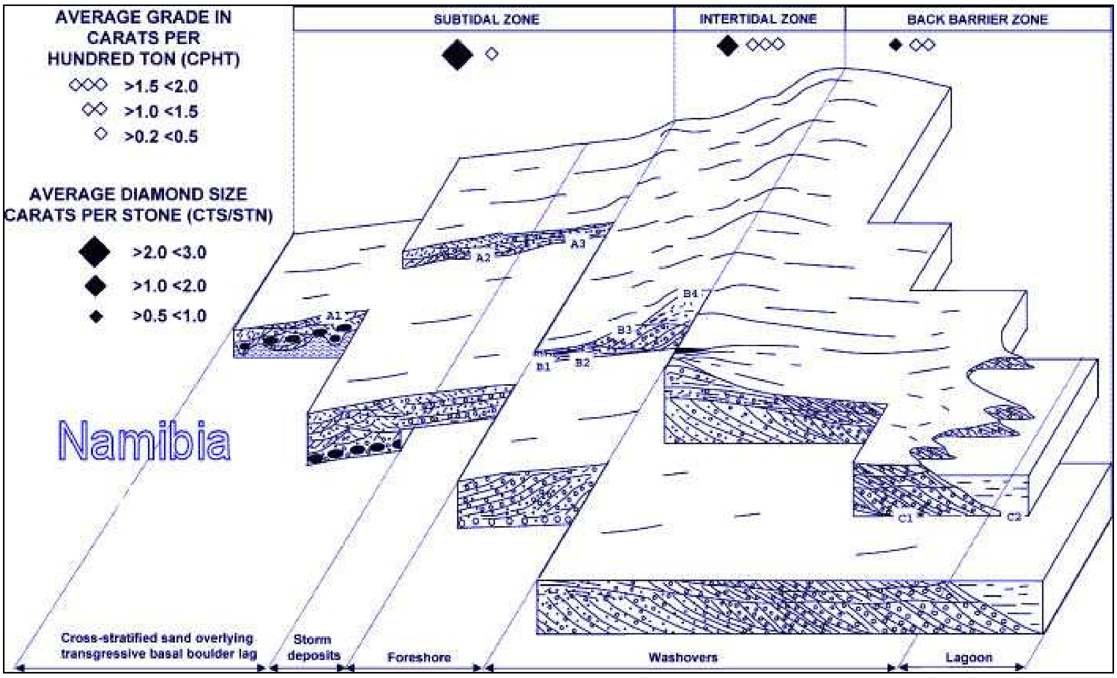


*Fig. 2.49. Average diamond grades of Namibia.*

## II.6.4. Paleoplacer Gold Deposits

These are found in intracratonic basins in South Africa, Ghana, Canada and Brazil. By far the most important, and most well known is the *Witwatersrand* basin of South Africa. This is possibly the first basin on the Earth to be filled mainly with sediments. The age is Archaean, 2.7 – 2.5 Ga[13]. Other basins with paleoplacer gold deposits are Lower Proterozoic (approximately 2.5 Ga - 1.5 Ga) in age. The Witwatersrand is a low chain of hills, at an elevation of 1700-1800 meters above sea-level, that crosses the Gauteng province of South Africa. It serves as a watershed. To the North, water flows to the Limpopo and therefore to the Indian Ocean. Water to the South flows to the Vaal river and Orange river, and therefore to the Atlantic Ocean.

Gold in Archaean greenstone belts was eroded from the surrounding land and carried by streams. As these entered the basin, the gold settled in deltaic fans around the basin margins. Longshore currents may have carried away lighter minerals. Gold in solution was assimilated by algae mats just beyond the deltas. During basin evolution, deltas silted up, and new deltas formed. Therefore there are gold-bearing deltas at different stratigraphic horizons. Also there was almost continuous uplift of deltas along basin margin faults. Thus the deltaic sediments were reworked by erosion and shoreline processes a number of times.

The deltaic fan sediments are mainly quartz pebble conglomerates. They are called "reefs"[14] in the Witwatersrand mining terminology. Gold grains are typically 0.005 – 0.5 mm. The quartz pebble conglomerates contain grains of 0.015 – 1.5 mm and larger. The gold is accompanied by *detrital* *pyrite* ($FeS_2$) and *uraninite* ($UO_2$). This was possible because the atmosphere of the Earth was $O_2$-deficient. Therefore pyrite

---

[13] 1 Ga = 1 billion years (Giga annum).

[14] The term "reef" in the South African mining geology has nothing to do with the general term reef.

did not weather, and simple uranium oxides were stable in near-surface environments. Also garnet and zircon are found in the conglomerates.

*Figure 2.50. Gold bearing quartz pebble conglomerate with pyrite. All the yellow material is pyrite!! The gold is not visible with naked eye.*

An exceptionally large source of gold is required to account for all the detrital gold in the Witwatersrand area. There is more gold in the Witwatersrand basin than in all known greenstone belts together !! Gold grades are typically 5 – 10 gr/t, much higher than any modern gold placer deposit. As a result of this, a hydrothermal origin of (a part of the) the Witwatersrand gold deposit is also suggested. The discussion is still not settled.

The Witwatersrand gold reefs are mined at different sites around the margin of the basin. The basin produced about 40 x $10^3$ tonnes of gold. Currently the basin produces about 30 % of the world's gold production.

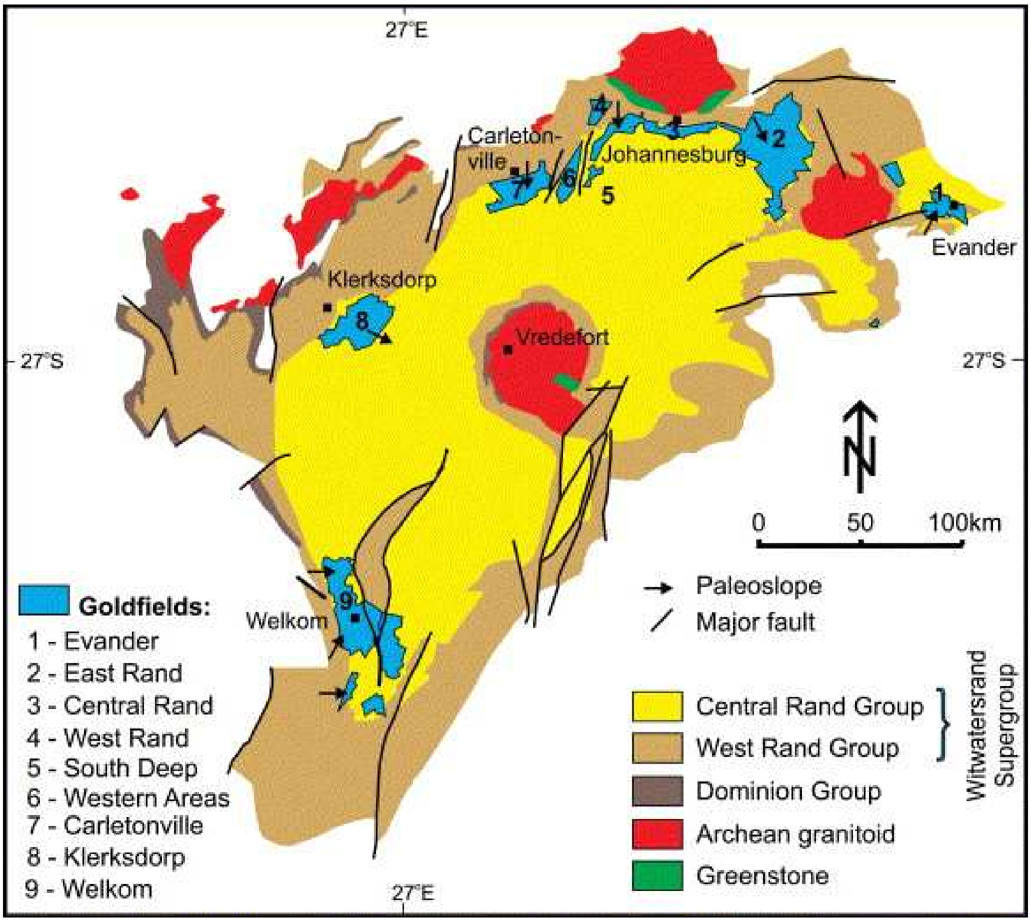


*Fig. 2.51. Simplified surface and subsurface geological map of the Witwatersrand Basin, also showing the distribution of Archaean granitoid domes, the location of the gold fields, major faults and paleocurrent directions of reefs in the Central Rand Group.*

One hundred years ago, gold was found in conglomerates on the farm Langlaagte. This find turned out to be fabulously rich, payable ore was present over a strike length of 80 kilometres, the reefs persisted in depth and so the Witwatersrand Goldfield prospered and grew and mining has continued to this day. The reefs occur from outcrop to very large depths (estimated to over 6 km). The deepest mine in the World, *Tau Tona* (4 km), it situated at the Rand, near Carletonville. In the South African Kaapvaal Craton, the geological temperature gradient is 10° C/km. as opposed to 30°C/km in the Netherlands. Therefore mines can be extremely deep at the Rand. Carletonville is in the West Wits Line, one of the world's premier gold and uranium regions and has made vast contributions to South Africa's economy. It extends some 50 kilometres westwards from the Middelvlei inlier near Randfontein to the Mooi River and southwards from the Wonderfontein Spruit for about 20 kilometres to Fochville.

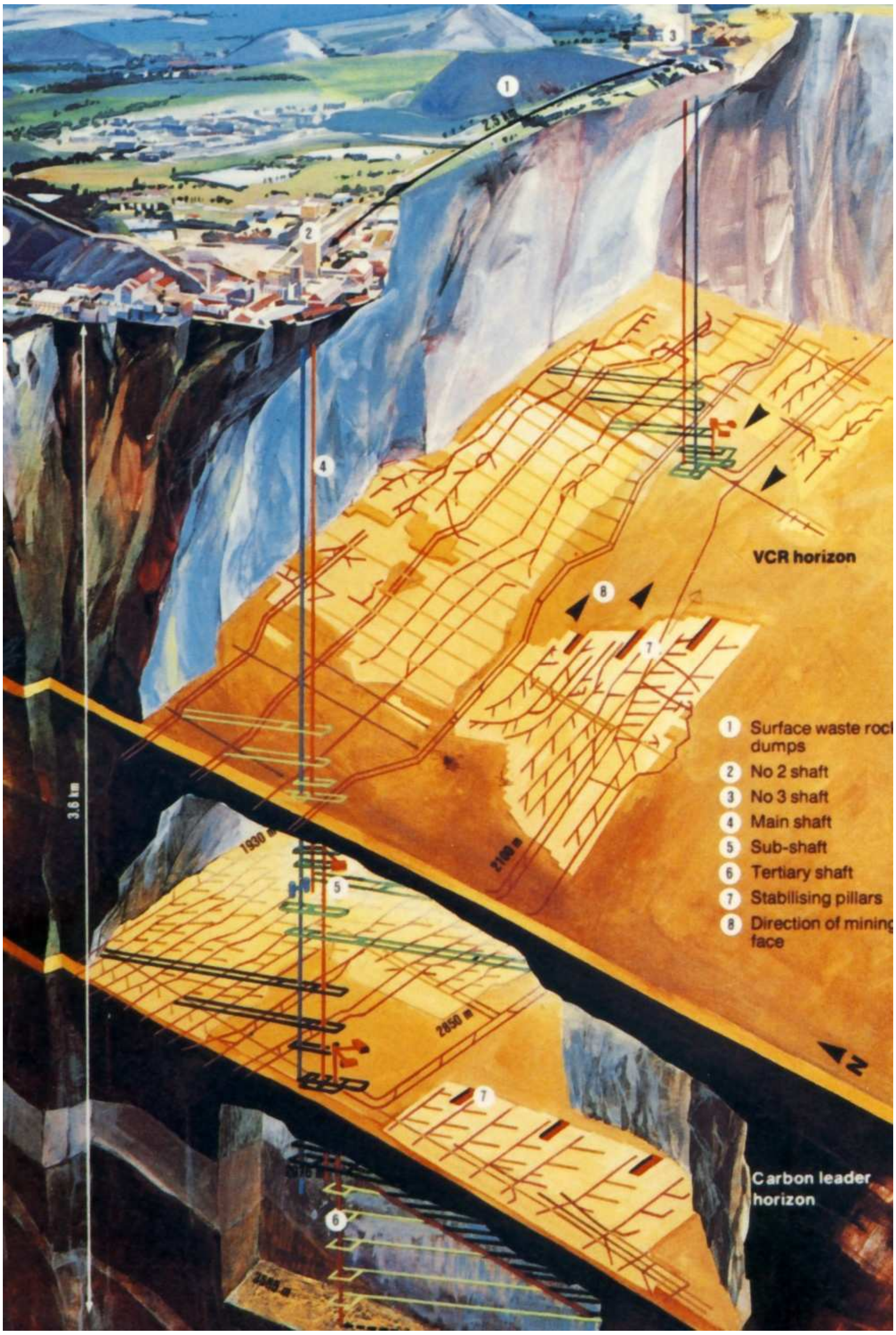


*Fig. 2.52. Image showing an idealized 3D model of the Western Deep Levels mine (Tau Tona) at Carletonville, Witwatersrand, South Africa. Vertical scale is 3.6 km.*

*Fig. 2.53. The Western Deep Levels Mine (Tau Tona) near Carletonville, Witwatersrand. Shaft No.2 is in the foreground (see Fig. 2.51).*

## II.7. References.

A.M. Evans, (1993) Ore Geology and Industrial Minerals, An Introduction. Blackwell Scientific Publishers, 390 pp.

M. Hale (1996, 1997) The Geology of Ore Deposits - Economic Geology. Unpublished lecture notes, Delft University of Technology, 149 pp.

# Chapter III. Industrial Minerals and Rocks

## III.1. Introduction

This chapter deals with Industrial Minerals, the less well known part of the raw materials mined from the Earth. Metallic ores and fossil fuels are the better known counter parts. The industrial minerals overlap sometimes with the ores, and an exact definition is hard to give. Broadly speaking, industrial minerals cover all materials man takes out of the Earth's crust except fuels, metallic ores, and gemstones. Notable overlaps are: diamonds, used not only for gemstones, but also as industrial material (for abrasive tools), evaporites (sulphates, salt, borates, phosphates), chromite, silica (used as a mineral as such in e.g. glass manufacturing, but also as ore for silicium), iron oxide (an ore for iron, but also used as a pigment), and bauxite.

The main source of information for this chapter is the book *"Industrial Minerals, A Global Geology"(1996) by Peter. W. Harben and Milos Kuzvart, Industrial Minerals Information Ltd, UK, 462 pp.*

Images are mainly taken from the internet, (often Wikipedia), some from a lecture series on Industrial Minerals by Dr. Peter W. Scott, Camborne School of Mines, University of Exeter, made for the International Mining Course EMC, and also from own stock.

Apart from industrial minerals, one can also speak of industrial rocks, such as limestone, or granite. The following classification can be made:

**Bates classification.**

| | **Industrial Rocks** | **Industrial Minerals** |
|---|---|---|
| Aspect | Large | Small |
| Unit Value | Low | High |
| Place Value | High | Low |
| Imports/Exports | Low | High |
| Distribution | Widespread | Restricted |
| Geology | Simple | Complex |
| Processing | Simple | Complex |
| | | |

Industrial Minerals can be classified on basis of market characteristics.
This classification is as follows:

1. **Bulk minerals**
   Limestone and clay for cement, gypsum for plaster, clay for bricks, building stone. Crushed rock and sand and gravel aggregates.
2. **National or regional commodities**
   Silica sand, limestone for chemicals and glass, kaolin clay for paper and ceramics, salt, potash, phosphates.

3. **Internationally traded commodities**
   magnesite, talc, graphite, nepheline syenite, olivine, andalusite, zeolites, zircon, wollastonite, fluorite, barites, diatomite, perlite.
4. **Dual-purpose metal ores**
   iron oxide pigments, titanium minerals, manganese ores, chromite.
5. **Very high value minerals**
   ultrahigh purity quartz, diamonds, gemstones: REE.

In the following, the most important industrial minerals and industrial rocks will be treated in brief, in an alphabetic order. The minerals and rocks listed below are treated in the previous chapter on ores, and will therefore not be discussed here, although they may also be seen as an industrial mineral/rock:

- bauxite
- beryllium minerals
- borates
- chromite
- diamond
- gypsum
- lithium minerals
- manganese minerals
- salt
- sodium (bi)carbonate and sodium sulphate
- sulphur

Asbestos was once regarded as a valuable industrial mineral. Because of its danger to human health, it is used less and less. Asbestos will not be treated here.

The main source of information for this chapter is:

*"Industrial Minerals, A Global Geology"(1996) by Peter. W. Harben and Milos Kuzvart, Industrial Minerals Information Ltd, UK, 462 pp.*

Images are mainly taken from the internet, (often Wikipedia), some from a lecture series on Industrial Minerals by Dr. Peter W. Scott, Camborne School of Mines, University of Exeter, made for the International Mining Course EMC, and also from own stock.

## *III.2. Aggregates, Armourstone, Decorative Stones*

### III.2.1. Aggregates

Aggregates are subdivided into:

- Crushed rock
- Sand and Gravel
- Secondary aggregates

Crushed rock may be granite, dolerite, basalt, greywacke (a type of sedimentary rock), quartzite, limestone, dolomite. They have various uses, mostly in construction. Water absorption should be low. They should contain no organic matter, and have a high (chemical) durability (no soluble salts, resistant to attack). They are also free of silt or clay. Sizes are e.g. 40, 25, 20, 14, 10, 6, 4mm, or combinations. There are various standards for strength (impact value, crushing value, polishing value, abrasion value). Porphyry (a textural name for granite with large feldspar crystals), is often used for aggregate, railroad beds or for road construction.

| | | |
|---|---|---|
|  |  |  |
| *Fig. 3.1a. Motorway. The A4 at Rijswijk. Aggregate is used in the bed of the motorway* | *Fig.3.1b. Gravel and aggregate in asphalt* | *Figure 3.1c. Railroad with a bed of aggregate.* |
|  |  |  |
| *Figure 3.1d. Railroad bed of aggregate.* | *Figure 3.1e. Granite porphyry, used for road pavements (cobble stone)* [15] | *Fig. 3.1f. Road pavement of cobble stone* |

Sand and gravel are treated in a separate paragraph (III.25.1). Secondary aggregates are: mine and quarry wastes, slags (ferrous and others), and demolition waste (concrete, bricks etc.). Slags from metallurgical furnaces (e.g. blast furnaces) are regularly used as aggregates in road construction. Demolition waste also may be used in such ways. For specific construction uses, there are restrictions on the material, and not every material is suited for every application. In areas where volcanic material is found, this also may be used in road construction (see at paragraph III.21, Pumice and Scoria).

## III.2.2. Armourstone.

Armourstone, used for protection at waterworks or sea defences must meet several requirements, which are: the size of blocks attainable, the dimensions of blocks

---

[15] Such stones are known in Dutch as “”kinderkopjes””, in Belgium as “kasseien”. They are often found in road pavements in more rural regions of Netherlands, Great Britain, Belgium and France.

(cuboid shapes preferred), the density, and the soundness (i.e. no cracks, no porosity). Armourstones may be granite, gneiss, basalt, dolerite[16], and quartzite.

*Figure 3.2a. Basalt used as armourstone at the beach head at Scheveningen.*

*Figure 3.2b. Armourstone of gneiss, Cromarty, Scotland*

*Fig.3.2c. Bazalt as protection against the wave action on a Dutch dike*

*Fig.3.2d. Basalt on a Dutch dike (left and middle part of the picture). Concrete replacements are piled on the top of the dike.*

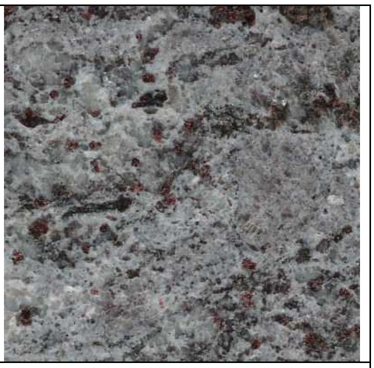
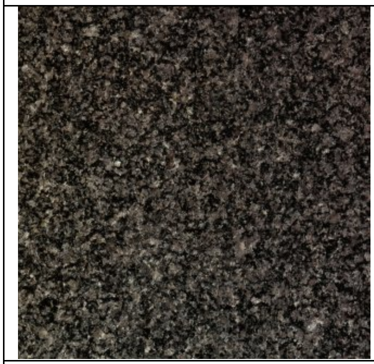
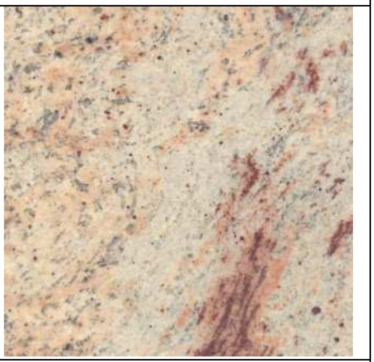
## III.2.3. Decorative Stone

Many natural rocks are used as decorative stones. Important types are granite, gabbro, gneiss, mica-schist, marble. Although some are widely used for aggregate and pavement stone, these rocks also often used in a decorative way. Examples are floor tiles and wall tiles in houses, offices and shops, tombstones, monuments and sculpture. Marble and limestone are treated in a separate paragraph. Figure 3.3. gives some eamples of the use of decorative stones. Figure 3.4. shows some some decorative types of granite, geneiss and gabbro.

---

[16] Basalt is a basic volcanic rock. Dolerite is a chemically similar rock, but forms dikes and sills. Diabase is often used as a synonym for dolerite. Gneiss is a common and widely distributed type of rock formed by high-grade regional metamorphic processes from preexisting formations that were originally either igneous or sedimentary rocks. Gneissic rocks are usually medium to coarse foliated and largely recrystallized, but do not contain large amounts of platy minerals.

| | | |
|---|---|---|
|  |  |  |
| *Fig. 3.3a. Making a tombstone* | *Fig.3.3b Decorative stone in the bathroom* | *Fig.3.3c. Decorative floor tiles* |

| | | |
|---|---|---|
|  |  |  |
| *Fig.3.4a Decorative Granite "Azul Noce"* | *Fig.3.4b Decorative Granite "Gran Violet"* | *Fig.3.4c Decorative Granite "Lavanda Blue"* |
|  |  |  |
| *Fig 3.4d. Decorative Gabbro* | *Figure 3.4e. Decorative Gneiss* | *Figure 3.4f. Decorative Gneiss* |

Granite is an igneous rock, which has as dominant minerals quartz, plagioclase, K-feldspar, biotite or muscovite. Gabbro is also an igneous rock, but with a different composition. It contains minerals like pyroxene[17], amphibole, biotite, plagioclase, olivine. Gabbro has no free quartz.

Gneiss is a medium to high grade metamorphic rock with a banded appearance. The original rocks may have been sandstone or granite.

## *III.3. Barium minerals*

---

[17] Pyroxenes are single-chain silicates, amphiboles are double-chain silicates.

These are barium sulphate (*barite*[18]) and barium carbonate (*whiterite*). The most important mineral is *barite* $BaSO_4$. it contains 65.7 % Ba. Barite occurs in all three main geological environments: magmatic, metamorphic and sedimentary. Whiterite is generally a secondary mineral, formed after barite.

Barite is a very heavy mineral, (s.g.4.5), which is chemically inert, rather soft, and relatively cheap. It has various uses, like weighting agent in drilling mud, feedstock for the chemical industry, and as a filler. Barium sulphate containing fluids, which have a large X-ray absorption and are non-toxic[19], are used as a contrasting fluid for medical X-ray investigations of the digestive organs.

The major categories of barite deposits are:

1. Vein and cavity fillings (metasomatic deposits)
2. Residual (eluvial) deposits
3. Bedded barite deposits

## III.3.1. Vein and Cavity Fillings

Barite carried by hydrothermal fluids or deep-seated brines is often deposited in faults, joints, cracks, bedding planes, breccia zones, solution channels, and sink structures.

*Figure 3.5. Barite, $BaSO_4$.*

Host rocks vary from igneous to sedimentary. Veins may be up to several hundreds of meters long, and from a few meters to a few decimetres in thickness. At depth barite mineralization may pass into barren quartz, calcite or siderite. Barite is often accompanied by fluorite ($CaF_2$), pyrite, galena, sphalerite, chalcopyrite, REE minerals. Barite veins form under low temperature epithermal conditions. The sulphate may be derived from near surface oxidation of sulfides. Barite is insoluble, and vein deposits may be the starting point for residual deposits.

---

[18] Barite is sometimes called barytes. The name barite is also sometimes spelled as *baryte.* The name barite is from Greek *baryos*, meaning heavy.

[19] N.B.: Most barium salt are however strongly toxic! Barium carbonate is for instance applied as rat-poison…

### II.3.2. Residual deposits

Barite is stable in the weathering regime, causing weathered vein and cavity deposits to change into residual barite deposits.

### II.3.3. Bedded deposits

Barite can occur as part of bedded bodies in layered sequences of rock, either as a primary constituent or a cementing agent, or associated with stratiform massive sulfide deposits. The typical sedimentary setting includes chert and siliceous shale. Several theories are presented for their genesis.

Important producers are USA, Irish Republic, UK, Italy, Germany, Slovakia, France, former USSR, Thailand, India, and Morocco.

## *III.4. Carbonate Rocks*

Calcium carbonate is one of the most widely used minerals. Application examples are construction material, air cleaning agents, sewage treatment, refined sugar, toothpaste, glass, steel, plastics.  Carbonate rocks are widespread. Genetic types are:

- Sedimentary (limestone, chalk, marl[20], dolomite, shells, aragonite sand, travertine)
- Metasomatic replacement (dolomite)
- Igneous (carbonatite)
- Metamorphic (marble)

Limestone is a sedimentary rocks consisting of  > 50% *calcite* and *dolomite*, with calcite predominating. Chalk is a fine-grained white variety with 97.5  - 98.5 % calcium carbonate. Dolomite (or *dolostone*, to distinguish it from the mineral) is a similar rock, but dolomite predominates. Limestones are biologically derived from seawater, and accumulate in a variety of marine environments. Common impurities are clay minerals, silica as chert or quartz and organic matter.

*Figure 3.6a. Limestone quarry.*

*Fig.3.6b. Part of the limestone quarry of ENCI, Maastricht.*

---

[20] Marl is in Dutch: mergel

Marble is the second largest and second important category of limestone. It consists of calcite (in the higher grades > 99 % calcium carbonate), with impurities like quartz, mica, chlorite, tremolite, graphite hematite limonite. Marble is generally formed by regional metamorphic processes, and it is generally found in mountainous regions. Fossils of sedimentary features are deformed or are gone completely.

Travertine is calcium carbonate formed by rapid chemical precipitation in freshwater around the opening or vent of natural warm or cold calcium charged springs. These springs are invariably associated to a local fault system, acting as a conduit and limestone as a source rock. *Travertine* is deposited in compact fibrous or concentric layers, producing a banded appearance and colours that range from white to shades of red and pink to yellow and gold.

Calcite is a common constituent of veins, either as the host for sulfides, or associated with quartz, barite and /or fluorite.

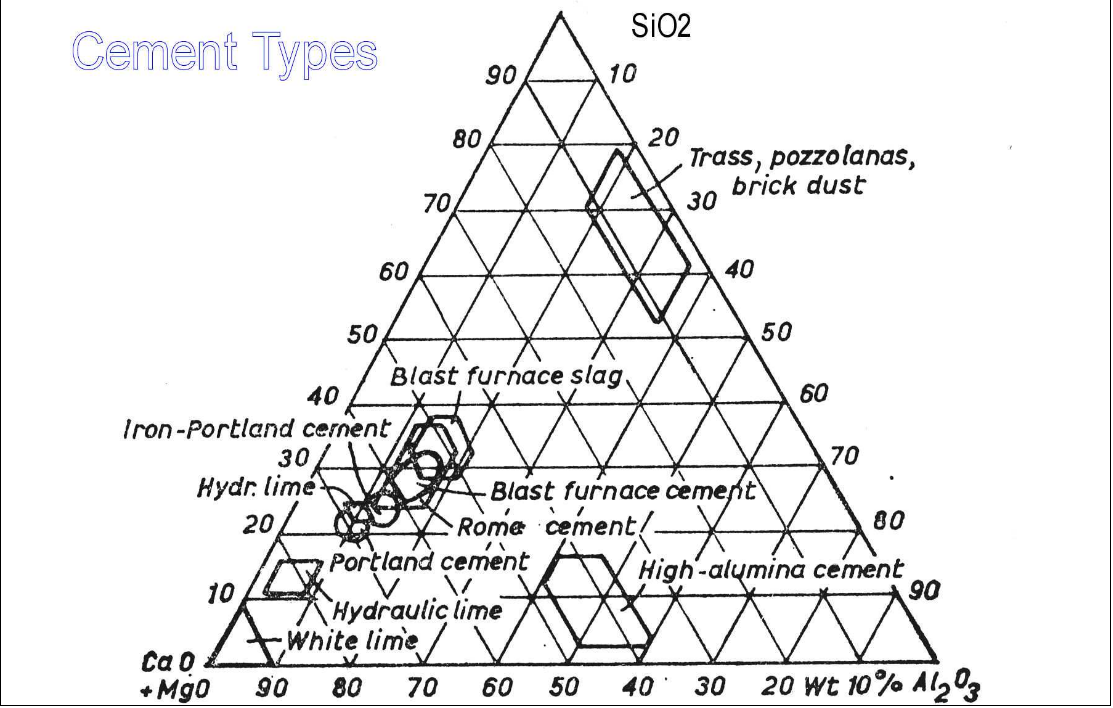


*Figure 3.7. Cement types with respect to composition and raw materials*

Limestone is the most versatile of all industrial rocks and minerals. It is used as crushed stone (aggregate, ballast, filler stone), or for cement manufacture. It is used for lime manufacture, or as ground calcium carbonate for agriculture and chemical uses, as filler, in glass and paper manufacture, in steelmaking and metallurgy etc. Limestone is also used as dimension stone (construction). Marble is used in construction and sculpture.

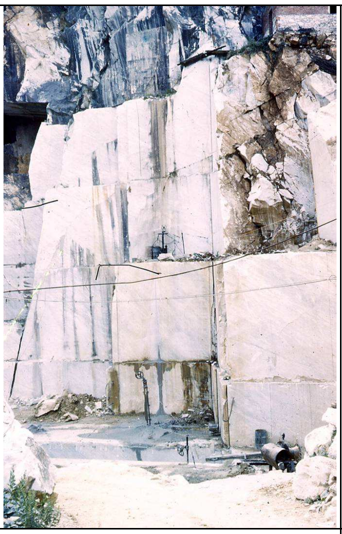
| | | |
|---|---|---|
|  |  |  |
| *Figure 3.8a. Cement, for bricklaying.* | *Figure 3.8b. Carrara Marble Quarry, Italy* | *Figure 3.8c.White marble: Venus de Milo, detail.* |

*Figure 3.9. Cement kiln.*

## *III.4. Celestite*

Celestite comes from Latin *celestis*, in allusion to the blue colour of the mineral. Although initially used mainly in fire-works (red colour), later applications such as the glass plate of colour TV's and computer monitors (now increasingly replaced by "flat screens" with liquid crystal technology), optical glass and glass tubings have made the once rarely used mineral to one of the most important industrial minerals.

Another important use is as Sr-ferrite, a ceramic permanent magnet. There are many other minor applications.

*Figure 3.10. Celestite,* $SrSO_4$

Significant concentration of strontium only occurs in the sedimentary environment. Celestite and strontianite[21] are the most common Sr-minerals, and of these only celestite $SrSO_4$, is mined. Strontiananite, barite and celestite all three occur in similar geological environments: veins and fissures, sedimentary bedded deposits, in the cap rock of salt domes.

Hydrothermal celestite deposits often contain fluorite, barite, calcite and lead and zinc sulfides. Celestite is often a by-product of the mining of (one of) the other minerals. Infiltration celestite deposits form geodes in limestone, celestite veins in clays and carbonate rocks, or metasomatic bodies in carbonate and sulphate rocks. Sedimentary deposits are generated in lakes and lagoons. Celestite accompanies gypsum, carbonates and other rocks in the form of concretions, seams or impregnations. Volcano sedimentary deposits are formed in lakes, associated with rhyolites, andesites, basalts and their tuffs.

Important producers are Mexico, Turkey, and China.

## *III.5. Clays*

Clay minerals are typically formed over long periods of time by the gradual chemical weathering of rocks (usually silicate-bearing) by low concentrations of carbonic acid and other diluted solvents. These solvents (usually acidic) migrate through the weathering rock after leaching through upper weathered layers. In addition to the weathering process, some clay minerals are formed by hydrothermal activity. Clay deposits may be formed in place as residual deposits, but thick deposits usually are formed as the result of a secondary sedimentary deposition process after they have been eroded and transported from their original location of formation. Clay deposits are typically associated with very low energy depositional environments such as large lake and marine deposits.

---

[21] Strontianite and the element Strontium (Sr) are named for the Scottish town *Strontian*

There are several important clay-types. There are many clay minerals. The most important clays are kaolinite-bearing clays, bentonite and hectorite clays, attapulgite and sepiolite clays, and a miscellaneous group, called common clay (and shale). These groups will be discussed in short, and the important clay minerals will also be treated with them.

### III.5.1. Kaolinite bearing clays

The mineral kaolinite has as a synonym *"china clay"*. The name originates from the clay of which the famous Chinese pottery and tableware was made. "China" is even used as a synonym for fine tableware and pottery made of this clay type. An ultimate example of "China" is given in figure 3.9.

*Figure 3.11. Chinese Ming-dynasty plate*

Kaolinite as a name comes form the Chinese *Kau-ling*, meaning the "high ridge", probably one of the first kaolinite quarries in history. Kaolin is white soft plastic clay composed of well ordered kaolinite with low iron content. Kaolinite is a phyllosilicate with composition $Al_2Si_2O_5(OH)_4$ . Kaolin is a very fine-grained material, with submicron size particles.

*Figure 3.12. Kaolin*

Ball clay contains up to 70 % kaolinite, but also illite[22], quartz, montmorillonite and chlorite. Ball clay is highly plastic, and its green strength[23] is higher than that of kaolin. Calcined, or fired ball clay is termed *chamotte*. Chamotte is used as a refractory (brick)stone, used as lining in kilns and furnaces, and can be used up to 1300°C.

*Figure 3.13. Refractory bricks, for lining in kilns and furnaces.*

Refractory and flint clay consists mainly of kaolinite. Another clay mineral found often in these clays is halloysite, $Al_2Si_2O_5(OH)_4$. Halloysite thus has the same chemical formula as kaolinite, but it has a different crystal structure.

Kaolinite bearing clays are formed in general by weathering of feldspar-rich rocks, such as granite, gneiss, syenite, arkose, feldspar-rich volcanic ash. Kaolin is found on many places in the world. Important producers are the China, USA, Great Britain, France, Spain, Germany, Czech Republic, former USSR, Israel, Japan, Australia and New Zealand.

## III.5.2.Bentonite and hectorite clays

*Bentonite* clays are composed largely of the mineral *montmorillonite* ($(Na,Ca)_{0,3}(Al,Mg)_2S_{i4}O_{10}(OH)_2\cdot n(H_2O)$,). This is a clay mineral from the *smectite[24] group.* The smectites may or may not exhibit swelling properties, when submersed in water. Na-montmorillonite is called swelling bentonite, whereas Ca-montmorillonite is a non-swelling bentonite. Ca-montmorillonite is called *fuller's earth* in the UK, but this term means something else in the USA. The name Bentonite is after the Benton shale formation (Montana, USA). Montmorillonite is named after the town

---

[22] Elite: $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)$
Montmorillonite: $(Na,Ca)_{0,3}(Al,Mg)_2S_{i4}O_{10}(OH)_2\cdot n(H_2O)$, synonym = bentonite
Chlorite: a mineral group, consisting of several complicated Mg-Fe-rich phyllosilicates. Most notable members are clinochlore $(Mg_5Al)(AlSi_3)O_{10}(OH)_8$ and chamosite $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$.

[23] Green strength = strength before firing, (sintering, baking, calcining)

[24] Smectite group: members of the smectite group include the dioctahedral minerals montmorillonite, beidellite, and nontronite, and the trioctahedral minerals hectorite (Li-rich), saponite (Mg-rich), and sauconite (Zn-rich).

Montmorillone in France. Hectorite is a clay mineral from altered volcanic tuff ash with a high silica content related to hot spring activity, with the formula: $Na_{0,3}(Mg,Li)_3Si_4O_{10}(OH)_2$. The name is for the locality (Hector, California).

*Figure 3.14. Bentonite*

Bentonite can be used in cement, adhesives, ceramic bodies, cosmetics and cat litter. Bentonite is also used as a *binding agent* in the manufacture of pellets as used in the iron and steelmaking industry. Fuller's earth, an ancient dry cleaning substance, is finely ground bentonite, typically used for purifying transformer oil. Bentonite, in small percentages, is used as an ingredient in commercially designed clay bodies and ceramic glazes. Its unique rheological properties make it also very useful in drilling and geotechnical engineering.

Bentonites originate through weathering of siliceous effusive rocks, or of mafic minerals such as biotite. Large economic bentonite deposits are formed invariably from effusive rocks rich in volcanic glass. Bentonite layers formed from pyroclastic may be very extensive.  Bentonite deposits occur world-wide.

Important producers are the USA, Canada, Greece, Cyprus, Turkey, Italy, Germany, Great Britain, former USSR, Japan, China, India, and South Africa.

## III.5.3.Attapulgite and Sepiolite

*Attapulgite* $(Mg,Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$ is also known as palygorskite. *Sepiolite*, $Mg_4Si_6O_{15}(OH)_2\cdot 6(H_2O)$, is also known as “Sea Foam”. Both are Mg-aluminiumsilicates with elongated crystals. The minerals are closely associated with bentonite, and have approximately the same uses.

## III.5.4.Common Clay and Shale

Common clays, of miscellaneous types, together with shales, and other fine-grained rocks are widely distributed, easily located, and used in products that lack rigid specifications and elaborate processing. They are found world-wide, and are used for e.g. bricks, flowerpots, floor and wall tiles, etc.

## III.6. Corundum

Corundum, $Al_2O_3$, and emery (a material consisting mainly of corundum, mixed with sometimes magnetite, $FeFe_2O_4$, rutile, $TiO_2$, or hercynite, $FeAl_2O_4$), are mainly used for abrasives. Corundum is the natural stable form of $Al_2O_3$, with hardness up to 9, and a specific gravity of 3.9 – 4.1. Corundum forms a magmatic segregation in quartz free igneous rocks, such as nepheline syenite, or more commonly in dike rocks by the desilication of an acid igneous rock in contact with a more basic one. It also occurs in aluminium-rich hornfels[25], and through metamorphosis of bauxite deposits. Corundum, due to its hardness, is not easily destroyed by mechanical transport, and may be found in placers.

*Figure 3.15a. Corundum*

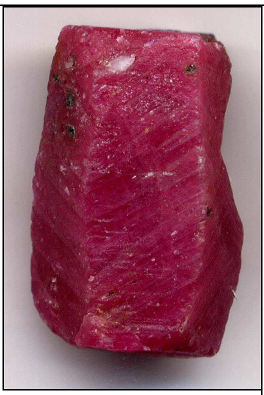


*Figure 3.15b. Ruby*

*Figure 3.15c. Sapphire*

Well formed corundum crystals coloured by impurities may also be *precious stones*, such as *sapphire* (blue, greenish yellow, reddish, from iron and titanium substitutions), or *ruby* (red, by chromium substitution). Sapphires and ruby have also many industrial uses, and may be synthesized quite easily. Corundum (and its precious varieties) is found in Turkey, Greece, USA, Zimbabwe, South Africa, and India.

## III.7. Diatomite

Diatomite is composed of the siliceous skeletons of microscopic unicellular floating aquatic algae called diatoms. Diatoms enclose themselves in a silica-shell. Diatomite is used as constructive material (building material) and destructive material, as it forms the stabilizing agent for nitro-glycerine, forming *dynamite*. Diatomite is also known under its German name *Kieselguhr*. In modern applications, it is used as a filler material in plastics, as a strengthening agent in rubber, or in toothpaste.

---

[25] Hornfels (from the German, meaning "hornstone") is the group designation for a series of contact metamorphic rocks that have been baked and indurated by the heat of intrusive igneous masses and have been rendered massive, hard, splintery, and in some cases exceedingly tough and durable. The original rocks may be clays, or impure limestones. The mineral composition of hornfels is variable.

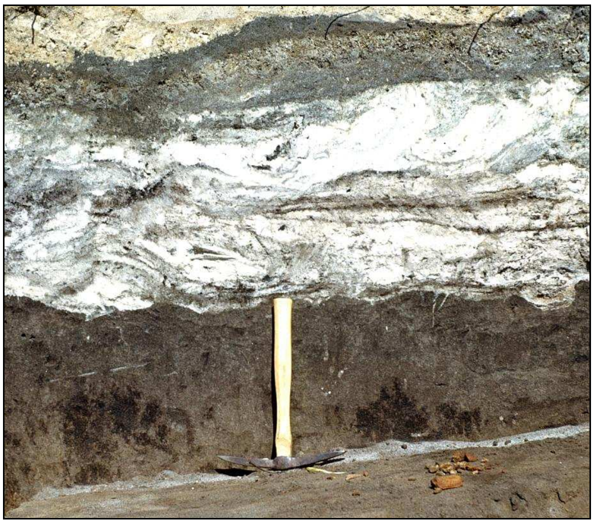
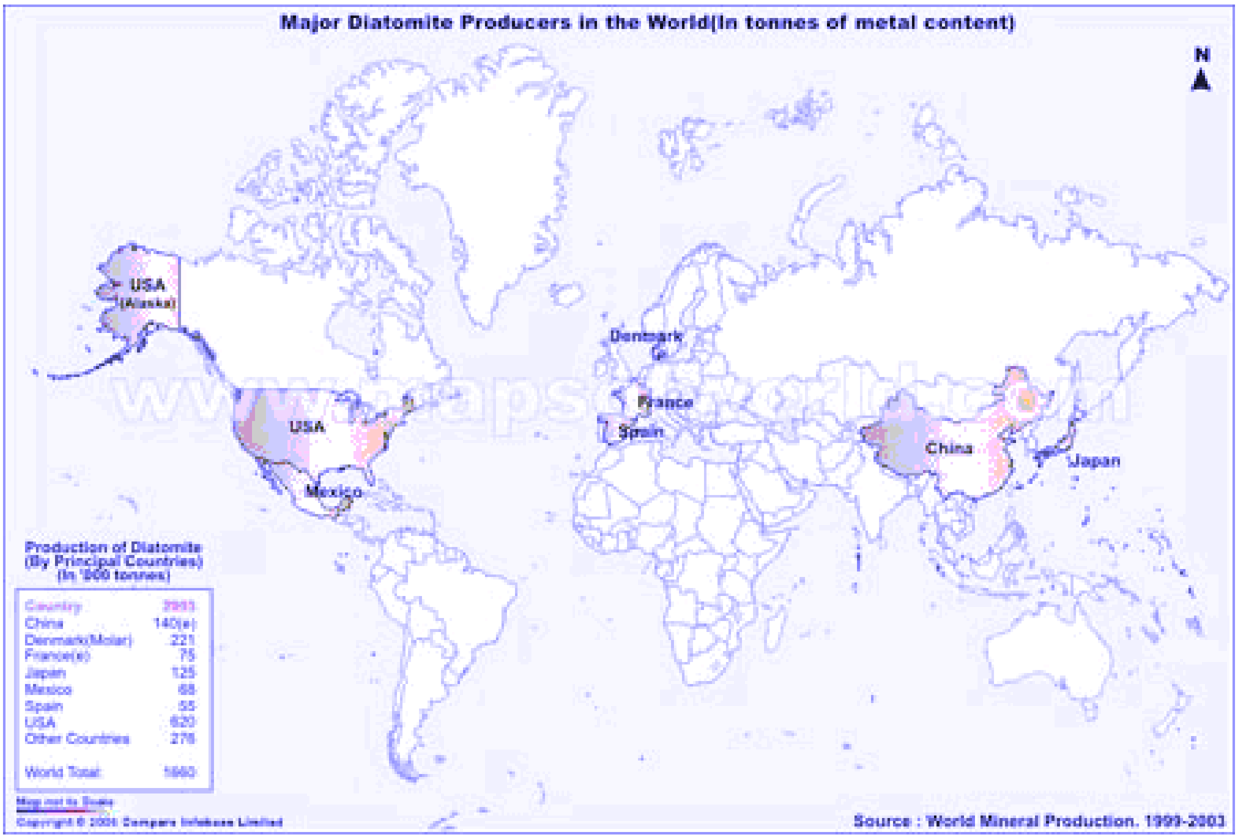


*Figure 3.16. Banded diatomite deposit (white material) in Texas, USA.*

Diatomite deposits are of Tertiary or Quaternary age. Different species of diatoms thrive in fresh, brackish or marine waters. Some can live even in moist soils and on the surface of rocks and vegetation. Silica must be available in large quantities to provide a thriving diatom population. Often diatomites are associated with volcanic ash, which was probably the source of the silica. Diatomite deposits generally contain impurities, such as clay, volcanic ash, chert, silt, gypsum, salt etc. Deposits range in thickness from a few centimetres to many tenths of meters. The bedding may be finely laminated or massive. Diatomites occur in the USA, Canada, Mexico, China, Japan, France, Spain, Denmark, and Romania.



Production of Diatomite
(By Principal Countries)
(In '000 tonnes)

| Country | 2003 |
|---|---|
| China | 140(e) |
| Denmark(Molar) | 221 |
| France(e) | 75 |
| Japan | 125 |
| Mexico | 68 |
| Spain | 55 |
| USA | 620 |
| Other Countries | 276 |
| World Total | 1960 |

*Figure 3.17. Major Diatomite producers in the World.*

## III.8. Feldspar

It is estimated that about 60 % of the Earth's Crust is composed of feldspar. It certainly is one of the most widespread minerals. However, localities where feldspar can be produced in large quantities with a consistently high grade are not so common. There is even a fairly active international trade in this common commodity. The feldspars are divided into the Alkali-feldspars (K-feldspar – Na-feldspar), and the plagioclases (Na-feldspar - Ca-feldspar). Most of the feldspar (60%) is used in glass manufacture, where the Na-Ca-feldspars are used widely. Next (35%) comes the ceramics industry, which uses the feldspar mainly as a fluxing agent. It is a common constituent of soft porcelains, tableware, sanitary ware, electrical porcelain, white ware, pottery, and tile.

*Figure 3.18. Nepheline syenite from Sweden.*

Rocks exploited for their feldspar content are (granite) pegmatite, granitoid to alkaline silica under saturated intrusive rocks: leucocratic granites, albitites, alaskite[26], aplite (fine-grained intrusive rock in which quartz and feldspar are the dominant minerals), and *nepheline syenite* (a plutonic rock that consists largely of nepheline, $(Na,K)AlSiO_4$ and alkali feldspar).

Feldspar is produced in the USA, Mexico, Germany France, Scandinavia, Finland, Russia, Portugal, Spain, Italy, and South Africa.

## III.9. Fluorspar

Fluorspar is another name for the mineral *fluorite*, $CaF_2$. It is the only commercial exploited mineral used for the extraction of fluorine (F). In the past, *cryolite* ($Na_3AlF_6$) was also used. Fluorspar is produced in three grades: acid, ceramic, metallurgical. Acid grade fluorspar (minimum 87 % $CaF_2$) is used to produce HF, by reacting $CaF_2$ in a kiln at high temperature with sulphuric acid to produce $CaSO_4$ and HF. HF is the starting chemical for the production of organic and inorganic fluoride chemicals, elemental fluorine and synthetic cryolite. HF is also used in the aluminium industry.

---

[26] In the United States, a commonly used term for a granitic rock containing few, if any, dark minerals. The term is used to designate granitoid rocks of the composition alkali granite.

Ceramic grade fluorspar ((80 – 95 % $CaF_2$), is mainly used in the glass industry as an additive to make glass white, or opalescent), and in the ceramic industry for the production of enamels[27].

Metallurgical grade fluorspar must contain a minimum of 60 % $CaF_2$. It is used in steelmaking, due to its low melting point. It is added to the slag to reduce the slag's melting point and surface tension. It leads to the formation of an eutectic mixture, with a low melting temperature, in which the impurities in the iron ore are bound.

Large cubic crystals of fluorite are desired by mineral collectors. Fluorite is generally dark violet to pink, orange-red or sometimes green.

*Figure 3.19. Fluorite (violet/pink cubes) and galena*

Fluorine is a relatively widespread element in nature. A strong affinity exists between fluorine and elements like beryllium, calcium, lithium, manganese, niobium, tin, tungsten, uranium, lead, zinc. It also frequently substitutes for hydroxyl in hydroxyl bearing minerals. In apatite, fluorine dominates generally over OH. Fluorspar is found in a wide variety of ore deposits, being of hydrothermal, mesothermal, epithermal, origin, pegmatitic, or sedimentary.

Fluorite is produced in Mexico, USA, South Africa, Kenya, Namibia, China, Mongolia, France, Spain, Italy, the UK, Czech Republic, and Russia.

## *III.10. Garnet*

The garnet group is a silicate group with the general formula $\mathbf{X_3Y_2(SiO_4)_3}$, with **X** being possibly Ca, Mg, $Fe^{2+}$, $Mn^{2+}$, and **Y** possibly Al, $Fe^{3+}$, $Cr^{3+}$, , or in part Ti or $Mn^{3+}$. The garnet group is generally considered to comprise 6 varieties (table 3.1) with somewhat similar physical characteristics.

---

[27] Enamel: In Dutch this is *glazuur, emaille*

*Figure 3.20. Almandite garnet.*

| **Mineral** | **Formula** | **SG (average)** | **H** | **Occurrences** |
|---|---|---|---|---|
| Almandite[28] | $Fe^{2+}{}_3Al_2(SiO_4)_3$ | 4.2 | 7 - 8 | Schist, gneiss, metamorphic rocks, contact zones, some igneous rocks, detrital mineral in sediments |
| Andradite | $Ca_3Fe^{3+}(SiO_4)_3$ | 3.9 | 6.5 - 7 | Chlorite schist, serpentinite, alkaline igneous rocks, metamorphosed limestone |
| Grossularite[10] | $Ca_3Al_2(SiO_4)_3$ | 3.6 | 6.5 – 7.5 | Metamorphosed impure calcareous rocks, especially in contact zones |
| Pyrope | $Mg_3Al_2(SiO_4)_3$ | 3.7 | 7.5 | Peridotite and associated serpentinites, sands and gravels derived from them, eclogite, anorthosites, diamond bearing peridotite |
| Spessartite[10] | $Mn^{2+}{}_3Al_2(SiO_4)_3$ | 4.2 | 6.5 – 7.5 | Granite pegmatites, gneiss, quartzite, schist, rhyolite, skarn deposits |
| Uvarovite | $Ca_3Cr_2(SiO_4)_3$ | 3.6 | 6.5 - 7 | Associated with chromite in serpentinite, skarn, metamorphosed lime stone |

*Table 3.1. The garnet group.*

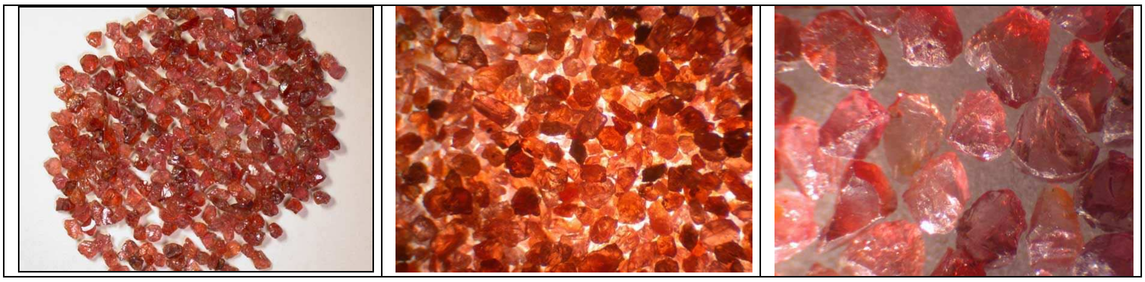


*Figure 3.21. Almandite garnets for abrasives, Crystals are a few mm’s across*

The most usual application of garnet is as an abrasive, used in sandblasting, lapping, polishing, or in water jets (cutting). It may also be used in toothpaste. Garnet is also used in water filtration where it is applied as a non-corrosive heavy material to retain the filtration bed during backwashing (cleaning). Some varieties are used as a semi-precious stone (almandite, grossularite, pyrope, spessartite).

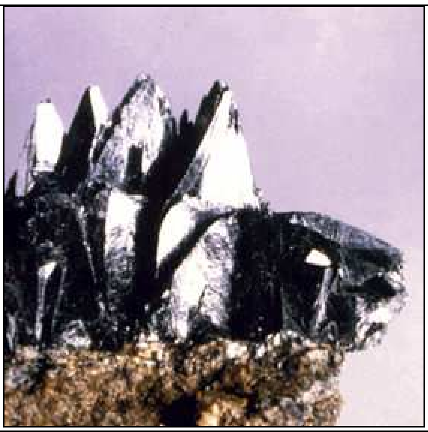
Major producers are the USA, Canada, Australia, China, India, and Pakistan. Garnets are also produced synthetically.

---

[28] The names of these garnets are sometimes spelled as *almandine, grossular, spessartine*

## *III.11. Graphite*

Graphite has been used in the past to manufacture pencils, but most modern applications are in refractories, batteries, atomic reactors, and in electrodes in electric arc furnaces. Graphite is one of the two natural solid forms of carbon. The other is diamond. Natural graphite is subdivided into three forms: flake, high crystalline, amorphous. Graphite is also made synthetically.

|  |  |
|---|---|
| *Figure 3.22a. Massive graphite* | *Figure 3.22b.Graphite flakes from Baffin Island,Canada* |

### III.11.1. Flake graphite

Flake graphite is a naturally occurring form of graphite that is typically found as discrete flakes ranging in size from 50-800 micrometers in diameter and 1-150 micrometers thick. This form of graphite has a high degree of crystallinity, which equates to near theoretical true density, high thermal and electric conductivity, and low springback (excellent molding characteristics). This commercial term (flake graphite) denotes flat plate like grains, disseminated through layers of originally carbonaceous sedimentary rocks that have been metamorphosed to a high grade. The major host rocks are quartz mica schist, feldspathic or micaeous quartzite, gneiss, and marble. Depending on the carbon content of the parent rocks, the graphite content of the metamorphic rock may range from proportions sufficient to colour the rock to amounts as much as 90% of the rock. Impurities (quartz, feldspars, mica, amphibole, garnet) are easily separated, but grinding is difficult, because of the platy nature of the grains.

Flake graphite is used in many applications including but not limited to powder metallurgy, fuel cell bi-polar plates, coatings, thermal materials, friction moderators, electrically conductive materials, refractories, general lubricant applications, pencils, gaskets, rubber compounds, and other advanced polymer systems. Commercial grades are available in purities ranging from 80-99.9% carbon, and sizes from 2-800 microns.

Flake deposits occur in Madagascar, Austria, Norway, former USSR, China, USA.

### III.11.2. High crystalline graphite

This type of graphite is also known as vein-type graphite or lump graphite. It occurs in veins constituting 75 – 100 % graphitic carbon. These deposits occur mainly in igneous or metamorphic rocks, commonly Precambrian in age. Veins range from thin films to 3 m thick layers, stretching over a thousand meters. Graphite occurs in coarse platy or needle like crystals. Impurities include quartz, feldspar, pyrite, pyroxene, apatite, and calcite. This relatively rare type of graphite is found mainly in Sri Lanka.

### III.11.3. Amorphous graphite

The term "amorphous graphite" is a contradiction in terms. All graphite is crystalline by definition, therefore it is impossible for graphite to be amorphous.  It refers to any massive graphite, whose crystallinity is only discernable under the microscope, i.e. it is microcrystalline or cryptocrystalline. It has a soft earthy lustre, different from the metallic lustre of the other two varieties. To the untrained eye a piece of amorphous graphite simply looks amorphous", like a lump of anthracite coal. However, it is much denser than anthracite, 2.2g/cc vs. 1.7g/cc, and is soft and lubricious. It is mainly derived from thermally metamorphosed beds of coal or carbonaceous rocks.  The minimum economic graphite content is considered to be 80 %.  Amorphous graphite is extracted using conventional coal-

*Figure 3.23. Amorphous Graphite*

Amorphous graphite is used in many lubricant products especially greases, forging lubricants, etc. Most of the current supply of amorphous graphite available in the United States is imported from Mexico and China. Previously other sources included Korea, Italy, and Rhode Island USA.

### III.11.4. Synthetic graphite

Primary synthetic graphite is produced from petroleum coke, a processed residue of petroleum distillation containing 95 % carbon. The coke, together with a coal tar binder and a small quantity of petroleum based oil is heated and extruded. This is a "green bar" or "green stock", usually in the shape of the final product. This is fired at a temperature of 800 - 1000°C to covert the binder to coke, and allow for shrinkage.

The resulting material is impregnated with coal tar or petroleum pitch to reduce the porosity. Graphitization is achieved in an electrical furnace at temperatures of 2500 - 3000°C (!). Secondary synthetic graphite is produced from heat treating calcined petroleum

*Figure 3.24. Synthetic Graphite Rounds*

## III.12. Gypsum

Gypsum is by many considered to be an industrial mineral, but in this course, it is treated in Chapter II among the ore minerals (evaporites).

## III.13. Iodine

Iodine was discovered by Bernard Courtois in 1811. Although it is rare in the solar system and Earth's crust, the iodides are very soluble in water, and the element is concentrated in seawater, although it is also found in some minerals and soils. The element may be prepared in an ultra pure form through the reaction of potassium iodide with copper(II) sulphate. There are also a few other methods of isolating this element in the laboratory. Although the element is actually quite rare, kelp and certain plants and algae have some ability to concentrate iodine, which helps introduce the element into the food chain.

Iodine under standard conditions is a dark-purple/dark-brown solid with the formula $I_2$. It can be seen apparently subliming at standard temperatures into a violet-pink gas that has an irritating odour. This halogen forms compounds with many elements, but is less reactive than the other members of its Group VII (halogens) and has some metallic light reflectance.

*Figure 3.25. Iodine crystals*

The most important sources for iodine are

- Dried seaweed
- Iodine minerals (lautarite $CaI_2$, dietzeite $Ca_2(IO_3)_2(CrO_4)$), found in very dry regions on the Earth (nitrate deposits in the Atacama desert).
- Subterranean brines, including oil and gas field examples.

Most important producers of iodine are Japan and Chile. Iodine is used in pharmaceuticals, antiseptics (providone-iodine, tincture of iodine), medicine, food supplements, dyes, catalysts, light bulbs (tungsten-iodide addition to the filament), halogen lights, photography (K-Iodide), and water purification.

| | |
|---|---|
|  |  |
| *Figure 3.26a. The well known iodine containing table salt (mainly NaCl with some KI) from JOZO®.* | *Fig. 3.26b. Betadine®, an antiseptic aqueous solution of an organic compound containing Iodine (Providon-iodine)* |

## *III.14. Iron Oxide*

Besides being the most used ore for the production of iron, iron oxide is mainly used as a **pigment**. The same iron oxide that can devastate a car, can also decorate and draw. Its use as a pigment is already thousands of years old. The cave paintings of France and northern Spain belong to the oldest examples. Iron oxide comes in a variety of colours, and the range can be extended through blending. Hematite[29] ($Fe_2O_3$) contributes a red colour, limonite[30],c.q. goethite[31] (FeOOH) gives yellow, and magnetite ($Fe_3O_4$)[32] contributes brown to black colours.

| | |
|---|---|
|  |  |
| *Figure 3.27a. Hematite (kidney ore) Michigan, USA* | *Figure 3.27b.Goethite from Minas Gerais, Brazil.* |

In nature manganese is often associated with these minerals, and the manganese content influences the colour. Commercially there is a gradation of shades from the red and yellow iron-rich and manganese-poor *ochre* through the brown and orange of *raw sienna*[33] and *burnt sienna* and the dark brown of *umber*.

| | | | |
|---|---|---|---|
|  |  |  |  |
| *Figure 3.28a. Ochre* | *Figure 3.28b. Raw sienna* | *Figure 3.28.c. Burnt sienna* | *Figure 3.28d. Raw umber* |

For the genesis of iron oxide deposits, see chapter II. The iron oxide pigments are also produced synthetically, for instance from the thermal decomposition of iron salts such as Fe-sulphate. Synthetic pigment production is considerably larger than the natural pigment production. Significant natural iron oxide pigment producers are India, Cyprus, USA, France, the UK, Italy Austria, and South Africa.

---

[29] From the Greek, αιμία, *haima*, blood, in allusion to vivid red color of the powder

[30] *Limonite* is actually a mixture of hydroxylized hematite (hydrohematite $Fe_2O_{3-x}$ $(OH)_{2x}$ )and more or less well crystallized goethite FeOOH. Limonite is not an official mineral, but the name often used as a synonym for goethite.

[31] Named after the German poet, *J. W. von Goethe* (1749-1832).

[32] More correct would be the formula $FeFe_2O_4$, which shows the mineral to belong to the *spinel group* with the general formula $AB_2O_4$. Named for Magnes, a Geek shepherd, who discovered the mineral on Mt, Ida, He noted that the nails of his shoe and the iron ferrule of his staff clung to a rock. Synonyms are lodestone or magnetic iron ore.

[33] After the Italian *"terra di Sienna"*

## *III.15. Magnesite and Magnesia*

Magnesia (MgO) is basic to modern society. In industry, its inertness and high melting point allow magnesia to be used as a refractory in steel furnaces, nonferrous metal processing units, cement kilns and the like. More than 4/5 of the total production of magnesia goes into refractories. The remainder is used in a number of products, including animal feedstuffs, fertilizers, special cements, and a variety of chemicals.

Raw magnesite ($MgCO_3$) has a limited market for pasture improvement and as a fertilizer, batch raw material for the glass and ceramics industries, and as a feedstock for the production of magnesium metal.  Raw magnesite is white, relatively soft and chemically inert, and it can be used as a filler in paint, paper, plastics, rubber, as a carrier for pesticides, as an anticaking agent, and several others.

Most of the magnesite is however sold as a grade of dead-burned magnesia and caustic calcined magnesia, formed when magnesite is calcined (burnt) to remove the $CO_2$. Dead-burned magnesia (DBM), MgO, is produced by heating crystalline magnesite or magnesium hydroxide at over 1450°C. During calcination the admixtures in magnesite give rise to a range of new minerals, such as periclase, forsterite, spinels, monticellite[34]. The higher the periclase content, the higher the quality of the product. This material is hard, dense and chemically inert. It is used together with spinel ($MgAl_2O_4$) (magnesia-spinel bricks) and also together with carbon in refractory bricks (magnesia-carbon bricks). Outside the refractory industry, a chemically reactive MgO is desired, which is the so-called caustic (light burned) magnesia: that is MgO with a little $CO_2$ still present. This produced by calcining magnesite or another magnesia feed at temperatures of 800 - 1000°C. Uses include stack gas scrubbing, water and sewage treatment, pharmaceuticals and medicine, acid neutralization, animal feed supplement and fertilizer. It has hydraulic properties, and together with $MgCl_2.6H_2O$[35] it is used in special cements for specialty flooring materials which are resistant to acids and oils (oxycloride cements). Chemical grade MgO is a feedstock for a variety of chemicals.

---

[34] *Periclase,* MgO, from the Greek peri - "around" and klao - "to cut.";  *forsterite*, $Mg_2SiO_4$, a member of the olivine series, named after German naturalist Johann Forster; *monticellit*e, $CaMgSiO_4$,  also an olivine-like mineral, for the Italian mineralogist Teodoro Monticelli

[35] *Bischofite,* $MgCl_2.6H_2O$, is named for For Karl Gustav Bischof (1792-1870), German geologist and mineral chemist.

| | | | |
|---|---|---|---|
|  |  |  |  |
| *Figure 3.29a. Dead Burned Magnesia (DBM). Nedmag Industries, Veendam* | *Figure 3.29b. Caustic Magnesia. Nedmag Industries, Veendam* | *Figure 3.29c. $MgCl_2.6H_2O$-pellets, Nedmag Industries, Veendam. Used for de-icing of roads during winter maintenance* | *Figure 3.29d. $MgCl_2.6H_2O$-flakes. Nedmag Industries, Veendam. Used for oxychloride cement, and for de-icing of roads during winter maintenance* |

Fused MgO, produced at 3000°C finds use as an electric insulator, and as a specialty refractory. Brucite ($MgOH_2$)[36] is a soft white mineral, which is used as a fire retardant and smoke suppressor. It is also used as a filler material in plastics, paint and as a high MgO feedstock. As a metal, this element's principal use is as an alloying additive to aluminium. Magnesium metal and alloys are highly flammable in their pure form when molten, as a powder, or in ribbon form. Burning or molten magnesium metal reacts violently with water. Magnesium powder is an explosive hazard.

*Figure 3.30. Vapour deposited crystal of magnesium (Mg)*

For completeness, it may be noted that the material used in gymnastics to have a better grip, is often termed *chalk*, or (also incorrectly) "*magnesium powder*". This is not MgO, but basic magnesium carbonate: $Mg(OH)_2.4MgCO_3.4H_2O$.

---

[36] *Brucite*, ($Mg(OH)_2$ is named after A. Bruce (1777-1818), an American mineralogist.

*Figure 3.31. A ladle charging a steel converter. The refractory lining of the ladle is partly made of magnesia-containing bricks*

Magnesium, one of the most abundant elements in the Earth's crust, is concentrated in seawater and various subterranean brines, a variety of rock types, including dolomite and serpentinite[37], and more than 60 minerals including magnesite and brucite. Magnesite, with the more general formula $(Mg,Fe)CO_3$, is by far the most important commercial mineral.

*Figure 3.32a. Magnesite crystals*

*Figure 3.32b Magnesite*

As the ions of $Fe^{2+}$and $Mg^{2+}$ differ only slightly in size, in comparison with the $Ca^{2+}$ ion, and there is an isomorphous substitution possible for Fe and Mg. Ca and Mg do not substitute isomorphically because the ionic radii differ to much. Therefore Calcite and dolomite occur in magnesite deposits always as mechanical admixtures, where Fe is firmly bound within the magnesite lattice. Pure magnesite ($MgCO_3$) as rarely found

---

[37] *Dolomite,* $CaMgCO_3$ named after the French mineralogist D. de Dolomieu. The name is also used for a carbonate rock with dolomite as a main mineral. Dolostone is sometimes used for the rocktype to avoid confusion.
*Serpentinite* is composed of one or more minerals of the serpentine group. This is a group of common rock-forming hydrous magnesium iron phyllosilicate $(Mg, Fe)_3Si_2O_5(OH)_4$

in nature. The natural mineral is almost always part of one or the other isomorphous series. It occurs as an alteration product of magnesium rich rocks, in sedimentary deposits, as a gangue mineral in hydrothermal ore veins, and as a primary mineral in igneous rocks. There are two physical forms of magnesia: cryptocrystalline (or “amorphous” magnesia), and (macro) crystalline magnesite (“bone” magnesite).

The distribution and concentration of magnesium may be summarized as follows:

Crystalline magnesite: derived from carbonate rocks through hydrothermal processes
    Examples: Veitsch, Styria, Austria, Slovakia, Navarra, Spain, Satka, Russia, British Columbia, Canada, Nevada, USA, Saudi-Arabia
Cryptocrystalline magnesite:
    Derived from serpentinite via hydrothermal processes. Examples occur in: Former Yugoslavia, Austria, Greece, Turkey, India, California, USA, Quebec, Canada.
    Sedimentary processes. Examples occur in: Liaoning province, China (marine), former Yugoslavia, Macedonia, Nevada and California, USA, Queensland, Australia (lacustrine).
    From serpentine via weathering and infiltration. Urals, Russia, Germany, Poland, former Yugoslavia
Brucite (Mg(OH)2) originates along granite dolomite contacts. Examples occur in Russia, Texas, USA
Bischoffite ($MgCl_2$). Salt lakes, subterranean brines (Groningen)
Magnesia from seawater. Occurs worldwide
Magnesia from brines. Subterranean brines: examples are found in Groningen, The Netherlands[38], Michigan, USA. Salt Lakes and Seas: Utah, USA, Dead Sea, Israel, Jordan

## *III.16. Mica*

Mica is not one single mineral, but a mineral group with a number of common physical properties. They are hydrous phyllosilicates, with the general formula $X_2Y_{4-6}Z_8O_{20}(OH, F)_4$ , with *X* is mainly K, Na, Ca, *Y*, mainly Al, Fe, Mg, *Z* is mainly Al or Si. The most common varieties found in nature are *biotite,* $K(Mg, Fe^{2+})_3Si_3AlO_{10}(OH)_2$, and *muscovite,* $KAl_2Si_3AlO_{10}(OH)_2$, also called white mica, *phlogopite,* $KMg_3SiAlO_{10}(OH)_2$, *lepidolite,* $K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$ and *zinnwa*ldite, $KLiFe^{2+}Al(AlSi_3)O_{10}(F,OH)_2$. All the micas crystallize in the monoclinic system and have perfect basal cleavage, which allows them to split into very thin sheets. These sheets are both flexible and elastic. The colour of mica varies from colourless to a range of colours to dark brown and black. Hardness between 2 and 3, good electrical insulating properties. Micas have a wide range of uses, ranging from the sparkle on greeting cards, to lost circulation material in drilling muds. Less then halve a century ago, a well known application was as windows in stoves and furnaces. Only muscovite and phlogopite can be considered of commercial importance. The main geological environments may be summarized as follows:

---

[38] Near Veendam, where Nedmag “mines” $MgCl_2$

Muscovite: acid igneous rocks, granites, pegmatites. Examples are Appalachian Mountains, Colorado Plateau, USA, Scandinavia, Kola Peninsula, Russia, Minas Gerais, Brazil, Andra Pradesh, India, and Zimbabwe
Phlogopite: Hydrothermal deposits, Russia, Madagascar
Alkaline ultrabasic rocks and associated carbonatites. Examples: Kovdor deposit, Kola Peninsula, Russia, Suzor, Quebec Canada

*Fig. 3.33. Muscovite booklet in feldspar. Mount Palmer, Australia*

## III.17. Nitrates

Nitrates are still produced naturally in Chile (Atacama Desert), but most of the nitrates used in industry and agriculture are produced synthetically. Direct synthesis of ammonia from atmospheric nitrogen by the Haber-Bosch[39] process, solved the bottleneck in ammonia production, which before the invention of this process was made out of the coking of bituminous coal. Nitrates were also produced in the past from guano deposits (bird and bat droppings)

## III.18. Olivine

Olivine is an olive-green coloured mineral, which is an isomorphous solid solution between *forsterite*, $Mg_2SiO_4$, and *fayalite*, $Fe_2SiO_4$. The mineral is used as slag conditioner in the iron making industry (its major use), and further in the manufacture of refractory bricks and foundry sand, The desired composition of olivine is 85 % forsterite or higher, as the melting temperature drops considerably with increasing iron content (see Fig. 3.33). Olivine is also regarded as a semiprecious stone. Gem quality olivine is called *peridote.*

Olivine is a very common mineral in the Earth's Crust. It occurs in basic igneous and metamorphic rocks, and in ultrabasic igneous rocks. Rock containing > 90 % forsterite is called *dunite*. Olivine weathers easily, and commercial producers of dunite are limited: Norway, USA, and Austria. The largest olivine deposit in the world is in the Fjordane complex in West-Norway.

---

[39] Heating of nitrogen and hydrogen under HT and HP in presence of a catalyst forms $NH_3$. Patented in 1910 by F. Haber and C. Bosch.

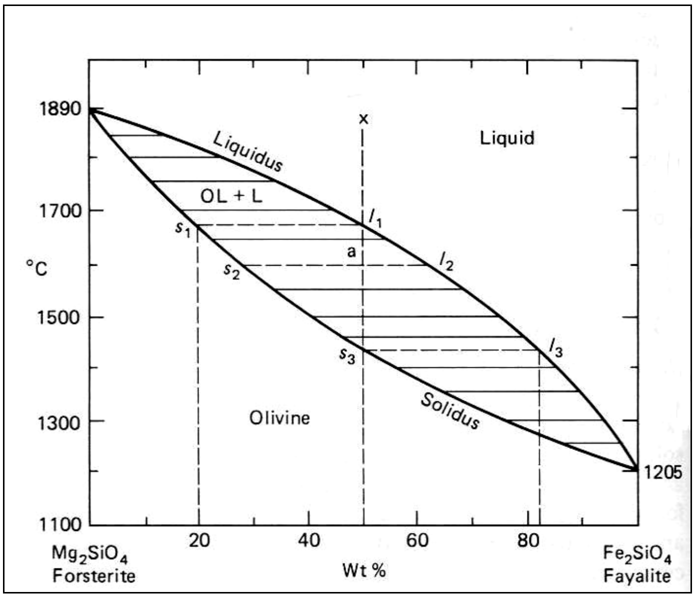


*Fig. 3.34. The olivine solid solution. Note the temperature difference over the liquidus going from Mg-rich to Fe-rich: 1890 – 1205°C*

| | |
|---|---|
|  |  |
| *Figure 3.35a. Dunite, N-Carolina.* | *Fig. 3.35b. Olivine, gem quality (peridote)* |

## III.19. Perlite

Perlite is an altered rhyolitic glass[40], containing 2 – 5 % water in the glass structure. When heated quickly to the fusion temperature, the contained water is released as steam, creating pressure on the heat-softened wall, which leads to cellular fluffy particles. It is used as a building material. Commercial perlite deposits are restricted to Tertiary and Quaternary volcanic rocks. Perlites are produced in the western USA, Iceland, Northern Ireland, Massif Central, France, Germany, Greece, Turkey, along the circumpacific volcanic belt, and in Armenia. The USA is the largest producer.

---

[40] Rhyolite is an igneous, volcanic (extrusive) rock, of felsic (silicon-rich) composition (typically >69% $SiO_2$. It can be considered as the extrusive equivalent to the plutonic rock type granite. It is often glassy, due to its high silica content.

## *III.20. Phosphate rock and Potassium Minerals*

Phosphates (apatite, monazite) are very often considered to be industrial minerals, but are treated in this course as an ore. Potassium-bearing minerals are treated in this course under *evaporites.* Therefore see Chapter II.

## *III.21. Pumice and Scoria*

Pumice and scoria are products of explosive volcanism. Pumice is a light coloured highly vesicular volcanic glass. Pumice is very Si-rich material. Common colours are white, gray, yellow, pink or brown. The rigid bubbles are small, spherically or elliptically shaped and separated by thin walls. The cells are not connected, so the material is not permeable, or in just a slight amount. The specific gravity of pumice is <1, and it floats on water. Although the glass itself is quite hard, the cell walls break easily, and pumice can be readily worked with no great effort. Scoria or cinder is the basic counterpart of pumice. It is rusty red to black pyroclastic material that accumulates in cinder cones. The vesicules of scoria tend to be coarser and more variable than those of pumice. Scoria is also heavier and has a higher crushing strength. The rocks are mainly used in the building construction industry, and for road construction. The rocks may originate from air-fall deposits (ash, lapilli), pyroclastic flows, epiclastic deposits (erosion, transportation and redeposition of pumice and scoria deposits). These materials are of course found in volcanic areas, of recent to subrecent times.

Numerous examples are found in the Eifel Mountains of Germany, where late Tertiary to Quaternary deposits of scoria and ash are quarried for utilization in the (road) construction industry.

*Fig. 3.36. Lapilli and ash quarry in the Eifel Mountains, Germany. (Herchenberg volcano, at Burgbrohl).*

## *III.22. Pyrophyllite and Talc*

Pyrophyllite is the aluminium counterpart of talc. The respective chemical formulas are:

- Pyrophyllite: $Al_2Si_4O_{10}(OH)_2$
- Talc: $Mg_3Si_4O_{10}(OH)_2$

They are often confused, as their physical properties are very similar. However, pyrophyllite is, contrary to talc, highly refractory, as its name indicates[41].

### III.22.1. Pyrophyllite

Pyrophyllite is mainly used as a refractory, up to 1200°C. At that temperature the minerals decomposes into corundum cristobalite and water. It has low values for thermal conductivity, coefficient of expansion, hot load deformation, bulk density. It has excellent heat stability and resists corrosion from molten metals and slags, and has a low heating shrinkage. It finds use in alumina silica monolithic refractories, used in many applications ranging from insulating firebricks to ladle linings. In refractories pyrophyllite is commonly combined with zircon[42].

*Figure 3.37. A ladle charging a steel converter. The ladle lining is partly made of pyrophyllite-containing bricks*

Pure pyrophyllite is rarely found in nature. It occurs in two more or less distinct varieties, namely, as crystalline folia and as compact masses. Commercial utilization

---

[41] Pyrophyllite, from *pyros = fire* and *phyllithos=cleavable stone*

[42] Zircon = $ZrSiO_4$

of pyrophyllite is usually based on pyrophyllite plus one or more other minerals (e.g. muscovite, diaspore, kyanite, quartz, chloritoid, epidote, rutile) producing a natural blend. The deposits are classified into 5 types:

1. Hydrothermal deposits in metasomatic rocks in continental or island arc volcanic zones
2. Metamorphosed metasomatic rocks in Paleozoic submarine volcanic zones
3. hydrothermal deposits in the wall rock of hydrothermal quartz veins along Paleozoic and Archaean granitoids and in metamorphosed clastic rock suites
4. Stratiform deposits in Paleozoic clastic clay suites containing pyroclastic material and coal seams.
5. Deposits in clay formed by weathering.

Japan is the bulk producer of pyrophyllite, followed by Korea. Minor producers are the USA, Canada, Brazil and Australia.

## III.22.2. Talc

Talc[43] is a versatile mineral, used as a filler in paint, plastics, paper, rubber, in adhesives, stucco, and in pharmaceuticals. The most well known application is as pharmaceutical/cosmetical talc powder. Shortly after birth, most of us are quite intimate talc users (Fig 3.38b).

| | |
|---|---|
|  | <br> |
| *Fig 3.38a. A block of white talc* | *Fig 3.38b. Talc used as baby powder.* |

Talc occurs generally as large masses of macroscopically indistinguishable crystals. The colour of talc is actually quite variable, due to the presence of various trace elements. Nevertheless, even dark shades grind to a more or less white and often bright powder. Talc is chemically inert, with a high oil absorption, a very low hydroscopicity, a high fusion point with low shrinkage when fired. It also has low electrical and thermal conductivity. There are various grades of talc, and applications vary with the grade. Talc used for refractories is less suited for pharmaceutical applications. Talc used in pharmaceuticals is again less suited as a filler in plastics etc.

---

[43] From the Arabic *Talq*. *Steatite* (from Greek steatos = fat) and *soapstone* are synonyms for massive talc. Talc has a greasy, soaplike feeling, when crushed between the fingers.

Ceramics is the largest consumer of talc in the USA. In Europe the use as a filler in the paper industry is the largest. High quality talc is used in the cosmetics and pharmaceutical industries, as talc powder, face powder, as a lubricant or glidant in tablet or capsule manufacture, as a filler in tablets. Specifications for pharmaceuticals talc are understandably extremely rigid and strict, and are laid down by (semi-)governmental organizations. Regulations exist for loss on ignition (LOI)[44], acid soluble substances, microbial content, chloride, arsenic and heavy metal content etc. The chemical industry uses talc as a material with a large surface area in catalysis. In the rubber industry, talc finds application as in the production of electric cable insulation.

In commercial applications, not all material called talc is really talc. Other minerals present may be tremolite, $Ca_2Mg_5(Si_8O_{22})(OH)_2$, anthophyllite, $Mg_7Si_8O_{22}(OH)_2$, serpentine, e.g. $Mg_3S_{i2}O_5(OH)_4$, quartz, dolomite, calcite, magnesite. The most common accompanying mineral is tremolite. It has been demonstrated that talc form at temperatures between 500°C and 700°C, whereas below 500°C serpentine forms. Above 700°C, minerals without an OH-group form, such as enstatite ($MgSiO_3$), quartz and forsterite ($Mg_2SiO_4$). In nature talc originates from Mg-rich rocks react with hydrothermal silica in the final phase of regional or contact metamorphism (greenschist to amphibolite facies). Four main types of deposits are recognized:

1. From ultramafic rocks (peridotite[45]) Vermont, Pennsylvania, Georgia, California, Texas, Arkansas, USA, Ontario, Quebec, Canada, Southern Spain, Finland, Russia, Egypt.
2. From mafic rocks (gabbro[46]) Virginia, USA, Egypt
3. From Mg-carbonate rocks (dolostone[47]) Alabama, Texas, California, USA, Australia, Korea, China, Russia, Northern Spain
4. Metamorphic (dolostone). N-Carolina, California, USA, New York, Georgia, Madoc , Ontario, Canada, Italy, Russia, Germany, Leoben, Austria, Slovakia, Finland, France, Spain, Brazil.

The production of talc takes place in approximately 40 courtiers, with China as the main producer, followed by the USA, Brazil, Finland and France. Some countries have gained a reputation in one or more industries. Chinese, French, and Australian talc are used in cosmetics, talc from New York mainly in ceramics, etc.

---

[44] Loss On Ignition or LOI: the weight loss measured when a material is fired to certain high temperatures. This is due to the loss of volatilizing parts of the material, such as water, chloride, fluoride, organic material, etc.

[45] Peridotite: a dense, coarse-grained igneous rock, consisting mostly of the minerals olivine and pyroxene. It is derived from the upper mantle, has < 45 % silica, and is rich in Mg.

[46] Gabbro: a mafic igneous plutonic rock, the equivalent of basalt

[47] Dolostone: Dolostone is a sedimentary carbonate rock that contains a high percentage of the mineral dolomite. It is usually referred to as dolomite rock.. Formerly it was termed magnesian limestone.

## *III.23. Rare-Earth Minerals*

Rare Earth Minerals are also considered to be ore minerals and/or industrial mineral. Although they are also mentioned in Chapter II, something more will be told of them here. Rare Earth is a famous misnomer: rare earths are rather metals than earth-metals, and are as matter of fact, not rare, but rather common. The Rare Earth Elements (or Lanthanides) are the elements La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu[48]. Often Sc and Y are considered Rare Earth Elements (REE). With the exception of the highly-unstable promethium (Pm), the rare earth elements (REE) are found in relatively high concentrations in the earth's crust with Cerium (Ce) being the 25th most abundant element in the earth's crust.

Rare earth elements are incorporated into many modern technological devices, including superconductors, miniaturized magnets, electronic polishers, refining catalysts and hybrid car components. Rare earth ions are used as the active ions in luminescent materials used in optoelectronics applications, most notably the Nd:YAG laser. *Phosphors* with rare earth dopants are also widely used in cathode ray tube technology such as television sets.

Up until 1948, most of the world's Rare Earths were sourced from placer sand deposits in India and Brazil. Through the 50's, South Africa then took the status as the world's Rare Earth source, after large Rare Earth bearing veins were discovered. The discovery of the large Mountain Pass deposit in California, USA , triggered more research for applications for REE's. However, China now produces over 95% of the world's Rare Earth supply. The most famous deposit is at *Bayan Obo* (also spelled Baiyun Ebo), Inner Mongolia.

---

[48] Named: *Lantanum, Cerium, Praeseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, Lutetium.*

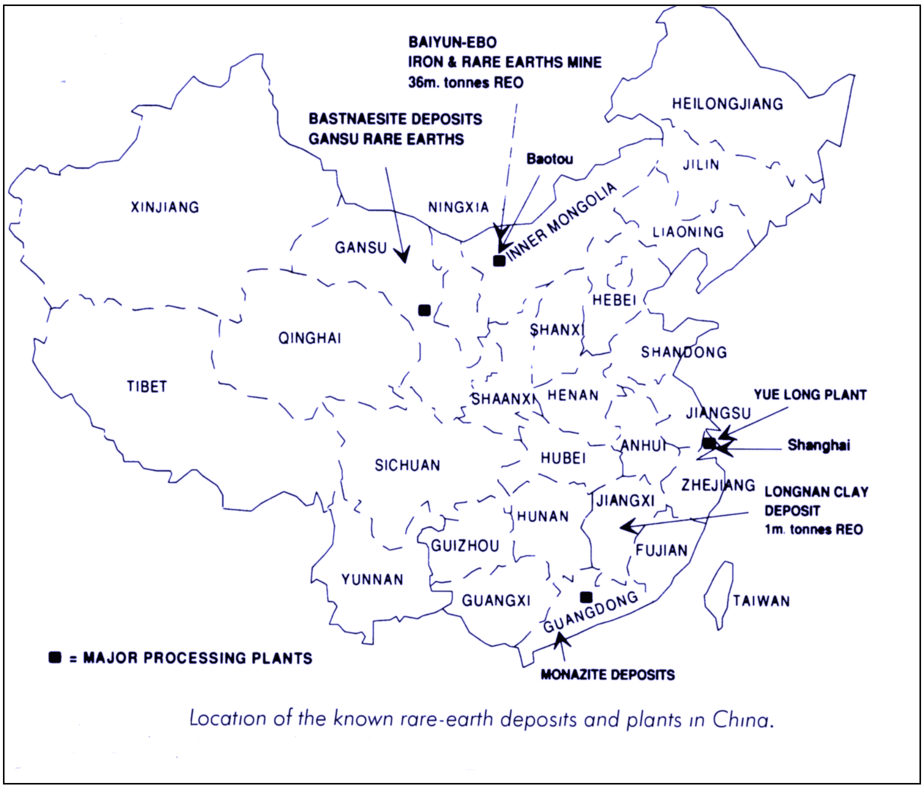


*Fig. 3.39. Location of Rare Earth deposits and processing plants in China. Modified after Harben and Kuzvart, 1996*

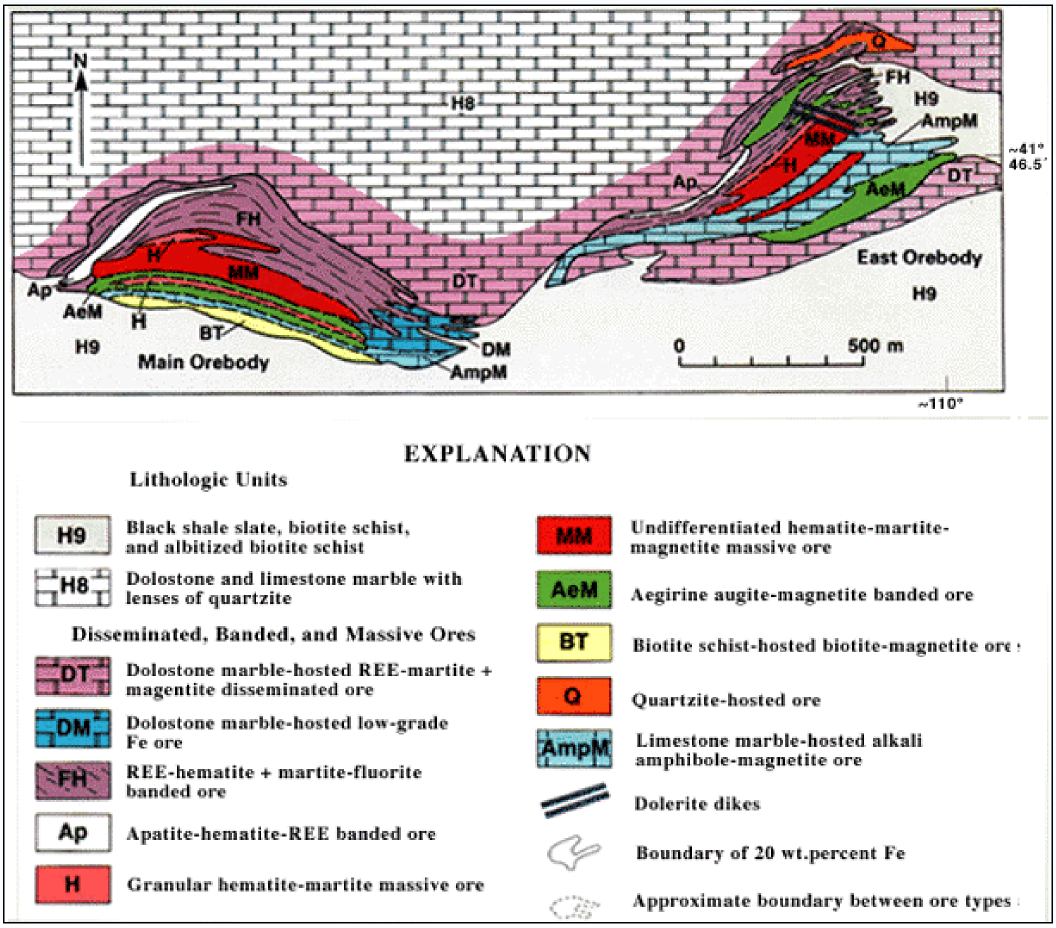


*Figure 3.40. Sketch map of the Bayan Obo ore bodies.*

REE deposits are in carbonatites, or in placers (see chapter II). The most important REE-minerals are monazite and bastnaesite.

Monazite is subdivided into several types, depending on the prevailing REE:

- monazite-Ce (Ce, La, Pr, Nd, Th, Y)$PO_4$
- monazite-La (La, Ce, Nd, Pr)$PO_4$
- monazite-Nd (Nd, La, Ce, Pr)$PO_4$
- monazite-Pr (Pr, Nd, Ce, La)$PO_4$

Monazite[49] is also often a leading ore for Thorium (Th). *Monazite powder thus is generally radio-active, and must be handled with care!*

☢

Bastnaesite[50], (REE)$CO_3F$, is also subdivided depending on the prevailing REE, but the Ce-, La, and Nd-varieties are the most common. Bastnaesite contains in general the Light REE (LREE) (La – Sm). Another important REE-mineral is *xenotime*[51] principally $YPO_4$. It contains rather the Heavy REE (HREE), i.e. Eu – Lu. With respect to radio-active elements, Uranium is found regularly in xenotime in low amounts..

| | |
|---|---|
|  |  |
| *Figure 3.41a. Monazite powder.*<br>☢ | *Fig. 3.41b. Crystal of Ce-bastnaesite from Pakistan.* |

## III.24. Salt

(Rock)salt or NaCl, is the most common salt used. Others are KCl, and $MgCl_2$. Salts are dealt with under evaporites (Chapter II). For $MgCl_2$ see also paragraph III.14. The uses of salt are well known.

---

[49] Monazite from Greek *monazein* = to be alone, in allusion to its isolated crystals

[50] Bastnaesite from *Bastnäs*, Sweden, where it was first discovered.

[51] Xenotime from the Greek words *xenos*, "foreign", and *time*, "honour".

## *III.25. Silica*

Silica ($SiO_2$) occurs in nature mainly as *quartz*, cryptocrystalline *chalcedony*, and amorphous *opal*. Silica varieties such as *cristobalite* and *tridymite* are in nature relatively rare, and are, if necessary, produced synthetically. Quartz is the most (some say the second most) abundant mineral in the Earth's Crust, (competing with feldspar), the most common *gangue*[52] mineral in ore deposits, the major proportion of the world's sands,  and it has widespread distribution in sedimentary, metamorphic and igneous rocks. Commercial examples however are relatively rare, being confined to deposits with specific and sometimes unusual characteristics. The name *quartz is* possibly derived from:

- West Slavic *kwardy*, meaning hard (*(c.f. Dutch:  kwarts)*
- Saxon *querklufterz*, meaning cross-vein ore, which may have been simplified to q*uererz*

Quartz is a very versatile mineral, its applications ranging from road building to computer chips, from glass-windows to abrasive. Silica bearing products include the following:

- Sand and gravel
- Sandstone,
- Quartzite
- Vein quartz and crystal quartz
- Flint, tripoli, novaculite
- Diatomite

Diatomite is discussed in paragraph III.6, and will not be mentioned here further.

### III.25.1. Quartz, Sand, Gravel, Sandstone

These materials are put to use in several ways. This may be as construction material, as compound to produce another material, or as a filler material.

**Quartz, sandstone, gravel and silica as construction material, or as aggregate**

Sandstone was, and is also used as a construction material as such. In the Netherlands, many old buildings are for instance constructed with the famous *Bentheimer Sandstone*, a rather pure, well cemented but still porous sandstone, with a very regular structure, quarried in the county Bentheim, NW-Germany. Historical records of use as a construction material go back to the 13th century. Many monuments in Germany, The Netherlands and abroad are made with *Bentheimer Sandstone*. Below are a few examples.

---

[52] the commercially worthless mineral matter associated with economically valuable metallic minerals in a deposit

| | | |
|---|---|---|
|  |  |  |
| *Fig. 3.42a. The Royal Palace, Amsterdam.* | *Fig 3.42b. Bentheim Castle, Bad Bentheim.* | *Figure 3.42c. Nieuwe Kerk Delft* |

Sand and gravel are very important for construction and road building, as aggregates in concrete, and as fill. Other uses are plaster sand, snow and ice control, railroad ballast, roofing granules, filtration material.

*Fig. 3.43. Base layer of asphalt concrete in a road under construction. Gravel is an important constituent.*

For aggregate that goes into concrete, there are stringent requirements. Especially soundness, resistance to freezing and thawing, sorption sensivity, resistance to wetting and drying, resistance to abrasion. Also very important is the **alkali-silica reactivity (ASR),** as fine-grained or opaline material is used: these materials react with alkalies liberated by the cement, forming a gel that absorbs water from the cement base, and swells, causing the concrete to crack or blister.

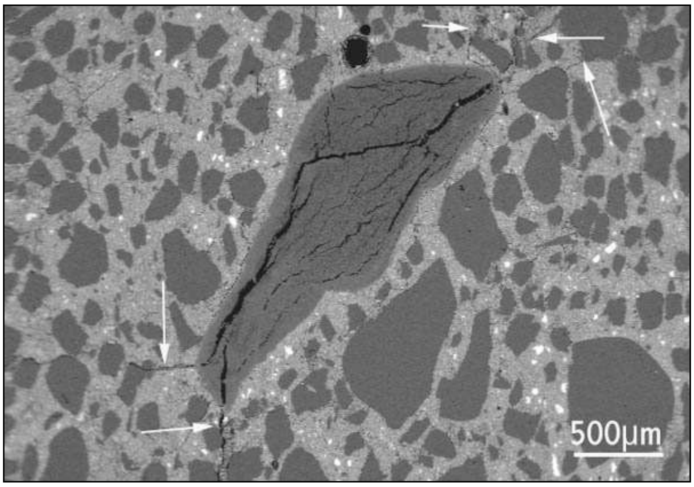


*Figure 3.44. ASR: polished section of concrete, viewed with a scanning electron microscope, showing a chert aggregate particle with extensive internal cracks due to alkali-silica reaction. The cracks extend from the aggregate into the nearby concrete (arrowed).*

**Glass Manufacture**

Silica sand is ubiquitous in all the main types of commercial glass. Smaller quantities are used in fiberglass formulations. The sand must be > 98.5 % quartz, sometimes even > 99% quartz, and there are strict regulations for the amounts of $Fe_2O_3$ (gives a brown colour to the glass), $Al_2O_3$, MgO, CaO, $Na_2O$, $K_2O$, $TiO_2$, $ZrO_2$, and $Cr_2O_3$ (renders a green colour).

Typical packaging glass compositions[53] are:

| **Element** | **Wt%** | **Wt%** | **Wt%** |
|---|---|---|---|
| $SiO_2$ | *73.0* | *73.0* | *72.0* |
| $Al_2O_3$ | *1.45* | *1.55* | *1.08* |
| $Fe_2O_3$ | *0.024* | *0.33* | *0.103* |
| CaO | *10.8* | *11.7* | *8.6* |
| MgO | *0.31* | *0.26* | *3.78* |
| $Na_2O$ | *13.8* | *12.4* | *13.4* |
| $K_2O$ | *0.36* | *0.44* | *0.59* |
| $SO_3$ | *0.19* | *0.17* | *0.24* |
| **Total** | *99.3* | *98.9* | *98.9* |

These compositions are called soda-lime glass. They are common for white transparent glass: glass containers (bottles and jars) for beverages, food, and some commodity items. Brown glass (e.g. for beer bottles) would contain much more $Fe_2O_3$. Green glass for e.g. wine bottles would contain more $Cr_2O_3$. Typical window pane glass (float glass[54]) has as a slightly different composition:

---

[53] Compositions from analytical glass standards provided by BSN Glasspack, Leerdam

[54] Float glass is a sheet of glass made by floating molten glass on a bed of molten tin. This method gives the sheet uniform thickness and very flat surfaces. Modern windows are made from float glass.

| **Element** | **Wt %** |
|---|---|
| $SiO_2$ | *73.0* |
| $Al_2O_3$ | *0.15* |
| $Fe_2O_3$ | *0.1* |
| CaO | *9.0* |
| MgO | *4.0* |
| $Na_2O$ | *14.0* |
| $K_2O$ | *0.03* |
| $TiO_2$ | *0.02* |
| **Total** | *100.28* |

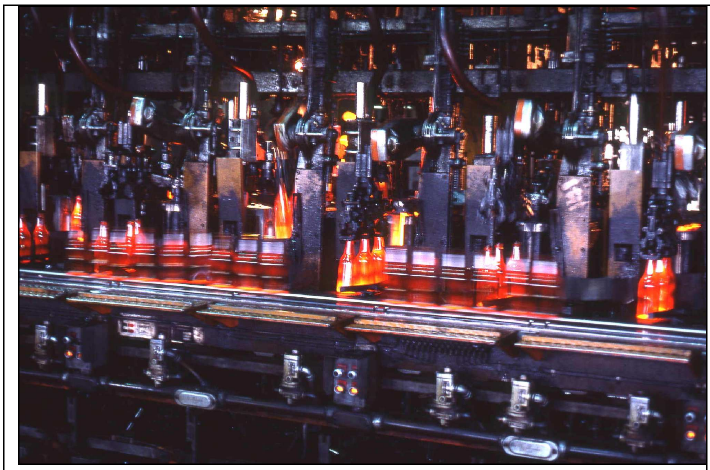


*Fig. 3.45a. Manufacturing of packaging glass*

*Fig. 3.45b Reusable soda-lime glass bottles.*

## Ceramics

In ceramics, silica can constitute as much as 40% of whiteware body. Its functions include adding whiteness to the body, making it easier to dry, and providing compatibility between body and glaze. In addition to regular silica sand, flint is also used. It has the advantage of good thermal behaviour and resistance to crazing (=forming of microcracks). Quartz is also used very much in refractories, where it is often converted to cristobalite. The conversion takes place at 1470°C, and cristobalite stable to 1700°C. Quartz is there fore suited to be used in refractories for the production of silica bricks. Quartz is also used as an additive in other types of refractory bricks (alumino-silicate), in order to shift the elastic behaviour of the composite material to the right value of stiffness.

## Metallurgy

In metallurgy, foundry sands are often made of high silica sand, either bonded with naturally contained clay, or admixed with a sodium silicate or a synthetic resin. Other sands, notably chromite, zircon and olivine are also used, but quartz is much cheaper. Another use for quartz in metallurgy is as a flux in smelting[55] base metal ores, where

---

[55] **N.B.:** Melting and smelting are very similar words, but they mean not the same.
*Melting*: change a solid material from solid to liquid state by applying heat.
*Smelting*: Chemical reduction of a metal compound to produce the pure metal, usually by applying heat. Examples: to transfer scrap metal from solid state to liquid state in a furnace is *melting*, but to

iron and basic oxides are to be separated from the base metal by being slagged as a silicate. The silica is used to balance the lime-silica ratio of the blast furnace.

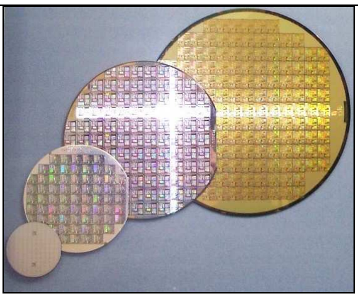
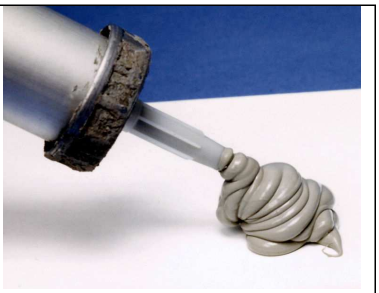
### Silicon Carbide

Silicon Carbide (SiC), is a versatile *abrasive* and refractory, and is made by heating a mixture of crushed quartz (silica sand) and petroleum coke, and a reducing agent like wood chips. They are built in an electric furnace around a core of granular carbon. Passing an electrical current through the core generates a temperature of about 2400°C, and silicon carbide is formed. Requirements for the quartz are 99.7 % silica, maximum0.05 % $Fe_2O_3$ and $Al_2O_3$, 0.01 % CaO and 5 % moisture. As an abrasive it is known under the name *carborundum*[56]. Pure SiC is colourless, but generally it is coloured blue or black due to impurities (nitrogen or aluminium).

*Fig. 3.46. SiC.*

### Silicon (Si metal) production

Lumps of quartz, quartzite, or very pure silica sand (“zilverzand”) are used to produce silicon (Si). Requirements are even more severe than for SiC. For the production of Si suited for semiconductors, the amount of Fe must be as low as possible. This leads also to severe limits in the Fe-content of the coke used for reduction. For the formation of ferrosilicon the requirements are slightly less rigorous. Silicon is also used for alloy production and for the production of silicone.

| | | |
|---|---|---|
|  |  |  |
| *Fig. 3.47a. Ingot of pure Silicon* | *Fig 3.47b Siliconwafers, 2 inch, 4 inch, 6 inch, and 8 inch.* | *Fig. 3.47c. Silicone-adhesive* |

---

reduce copper sulfide to molten copper and $SO_3$ in a furnace is *smelting*. In this process the copper also melts

[56] Carborundum is a trademark of Saint-Gobain Abrasives

### Other Applications

There are many other applications for quartz, such as “proppant sand”, used in the fracturing or opening of reservoir rocks of oil and gas wells, in the form of fine-grained (milled) quartz flour as a filler in plastics, rubber, paint, adhesives, etc. Silica sand treated with caustic soda produces sodium silicate (waterglass), an important chemical used in detergents, catalysts, pigments, adhesives, papermaking, ore treatment, and as feedstock in the manufacture of aluminiumsilicate, calciumsilicate and zeolite.

### Quartz and Sandstone Deposits, Pure Quartz Deposits

Quartz and sandstone deposits are widespread throughout the world, but very *pure* quartz is somewhat rare. Very pure quartz sand is found sometimes in fossil shoreline dunes. Dutch examples are the Miocene silica sands found in the vicinity of Heerlen and Brunssum, Limburg. The sands are produced in 5 quarries where they occur in layers ranging from 5 to 50 meters thick. The sands occur in various qualities, but a part is suited for silicon production. Lesser qualities are used for glass production (BSN Glasspack), for use in ceramics (MOSA), or as filler sands. The pure white sands are called *zilverzand*. Yearly production is approximately 0.8 M tonnes. Similar deposits are found in Belgium (near Maasmechelen, and in the area Dessel-Mol-Lommel).

| | |
|---|---|
|  |  |
| *Figure 3.48a. The quartz sand quarry of Sigrano*[57] *near Heerlen.* | *Fig 3.48b Sigrano quarry.* |

## III. 25.2. Quartz and Quartz Crystal

High purity quartz crystals may appear in many forms. Coloured crystalline quartz including amethyst (purple) citrine (yellow), rose quartz (pink, rose red) have been valued for centuries as a semi-precious stone. Other forms include agate, jasper, onyx, flint.

---

[57] Sigrano is a Dutch subsidiary company of the Belgian Industrial Minerals company Sibelco.

| | |
|---|---|
|  |  |
| *Fig. 3.49a. Quartz crystal* | *Fig. 3.49b. Quartz crystals from Arkansas* |

Clear colourless quartz has been used in the production of wedges, lenses in microscopes, and other optical instruments. Today the major consumer is the electronics industry, which utilizes two important physical properties of the quartz crystal. First quartz is dielectric, which means that it does not conduct electricity, but permits the electric fields to exist and act across it. Second, quartz possesses piëzo-electricity, which means that if a pressure is applied in a proper direction on the crystal, a one of its surfaces gets positively charged, another negatively. Conversely, if a potential difference is applied to the surfaces, the crystal deforms. Thin wafers of quartz may be brought in an electronic circuit by coating their surfaces with metal and attaching flexible wires.  In 1921, it was discovered that a thin quartz crystal plate could be used to control the frequency of radio oscillator circuits. Using this discovery, it became possible to tune a radio to a precise wavelength without wandering or drifting. Other applications of this discovery are the well known quartz-clocks.

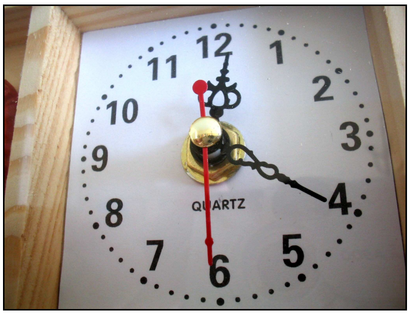


*Fig. 3.50. Quartz-clock*

However, natural crystals are rarely suitable for these exacting applications. Twinning, so-called “ghost crystals[58]”, bubbles vacuoles etc. render a crystal unusable for such applications.  Piëzo-electric grade quartz is now in general made synthetically by hydrothermal growth in an autoclave. The process requires however a feedstock of very pure quartz, without crystal faces. Again, pure quartz sand (“zilverzand)”is well suited as a feed.

Crystal and massive quartz are common in hydrothermal veins and pegmatites, plus placer deposits, whenever the material has been eroded, transported and (re)deposited.

---

[58] In a ghost crystal, or phantom crystal, the outline(s) of an earlier growth stage or earlier existing crystal(s) is visible.

Sedimentary deposits

- Crystal quartz placers. Examples: Brazil, China, Madagascar
- Fossil shoreline deposits: Examples: Belgium, The Netherlands.

Igneous deposits

- Cavity rich pegmatite veins. Examples: Brazil, Madagascar, Ukraine, Russia, Kazakhstan, Urals, China, Mongolia, France
- Hydrothermal quartz veins. Examples: France, Switzerland, Russia, Brail, Arkansas, USA
- Veins dikes, plugs in various rocks
- Quartz-pegmatites

### III. 25.3 Tripoli, Novaculite, Flint

The name *tripoli* (tripolite) was first used for diatomaceous material found near the port of Tripoli on the North African coast. Later it was used for deposits of fine-grained siliceous materials that appeared to be similar, but was actually a residuum of from the weathering of siliceous limestone. . Definitions are therefore far from exact, but in general tripoli is regarded as a residual material that is highly siliceous, microcrystalline, soft, friable, and porous. The silica content averages 98 – 99 %, the remainder being alumina, titania, iron oxide. The iron content influences the rock's colour, which ranges from white to yellow to brown and red. Tripoli is also known as "rotten stone".

*Novaculite* describes a fine-quality whetstone[59], or abrasive. Geologically speaking, it is a homogeneous mostly white or light coloured rock, translucent on thin edges, with a dull to waxy lustre. It is comprised entirely of microcrystalline quartz.

*Flint* has been used for a while as a source for fine high-purity silica. Also it may be used as an iron-free grinding medium.

The principal uses of tripoli, novaculite and flint are as abrasive. Tripoli grains lack sharp edges, and may be used in toothpaste and industrial soaps, as a buffing or polishing compound. It is also used as a filler material in paint, plastics and various enamels.

## *III.26. Sillimanite, Andalusite, Kyanite, Mullite*

*Sillimanite, andalusite and kyanite* are all three $Al_2SiO_5$. As anhydrous refractory aluminosilicates, they are all three used in refractories. The three are commonly referred to as the sillimanite minerals. The main use is in bricks, shapes, refractory cements, mortars, plastics. They are used in the metallurgical industry in the linings for electrical furnaces, for copper-smelting, in zinc-smelting and in gold refining. They are also used in the glass industry, in the superstructure of glass batch tanks. The refractoriness of the sillimanite minerals rests in the fact that when calcined at 1200 – 1250°C, they produce a mixture of silica and *mullite*[60], a mineral similar to sillimanite, which is stable to 1800°C

---

[59] Whetstone=slijpsteen

[60] Actually, the mullite formula is defined as $Al_{(4+2x)}Si_{(2-2x)}O_{(10-x)}$ where x =0.17 to 0.59

$Al_2SiO_5$ + heat = $Al_6Si_2O_{13}$ + $SiO_2$.

The $SiO_2$ is in the cristobalite form.  Mullite is extremely refractory, and has almost no volume change on heating or cooling (small coefficient of expansion). And can withstand abrasion and slag erosion. Its conductivity is medium and, has a high compressive strength. . It is also resistant to corrosion. Mullite is the material sought by the ceramic industry, and the sillimanite minerals serve mainly as "mullite-ore". Natural mullite is found, where metamorphism has provided calcination of kaolin and/or sillimanite minerals, as on the island of Mull, after which mullite is named. Natural mullite deposits are however rare, and mullite is in nature never found in commercial quantities. Mullite can be produced synthetically from sintering or fusing bauxite and kaolin, or alumina and silica. The synthetic material has a high cost, and is used where the natural material does not meet stringent requirements.

Outside the refractory industry, the sillimanite minerals may be used as abrasives, grinding pebbles, in welding rod fluxes, and nozzles, as a constituent in glass, in spark plugs, in non-slipping floors.

In nature the minerals are formed in aluminous metamorphic rocks, and their weathered derivatives. They are mainly formed in contact metamorphism of aluminous rocks, during high grade regional metamorphism of alumina rich rocks, and in desilicified (metasomatically altered pegmatites), and in alluvial deposits. Kyanite forms under conditions of regional high pressure metamorphism.
The sillimanite minerals are produced by just a handful of countries, including South Africa, The USA, Brazil, Russia, Europe, India (one of the oldest producers), China, and Australia.

*Fig. 3.51. Mullite, white, formed after kaolinite as a result of baking by an underground coal fire, Mnt Wingen, Australia*

## III.27. Slate

Slate[61] is a name for a rock derived from argillaceous sediments or fine grained volcanic ashes by metamorphism, and characterized by cleavage planes independent of the original bedding.   The slaty cleavage, which facilitates the rock to be split into

---

[61] Dutch: leisteen

tile-like pieces, is the most characteristical feature. Slate is already used for many centuries as a building material. Slate consists of a complex network of shreds, scales and fibres consisting of mica, chiefly illite and sericite. Through them are distributed needle shaped rods of quartz and other minerals. Such minerals may be calcite, rutile, dolomite, plagioclase, pyrite (which stains the slate), or carbonaceous matter.

Slate is found where thick sections of shale have undergone intense folding and mild dynamic metamorphism. Slate is found in many countries. Important producers are the UK (Wales), Spain, France, Italy, The USA (Pennsylvania, New York, Vermont).

|  |  |
|---|---|
| *Fig. 3.52a. Slate* | *Fig 3.52b. Slate roof* |

## *III.28.Titanium Minerals*

Titanium (Ti) has the name of being an exotic metal, used in for example fighter aircraft and other high tech applications. However, titanium is a widespread element, and is of more daily use than expected. Ti is concentrated mainly in the form of ilmenite ($FeTiO_3$), rutile and anatase (both $TiO_2$). On weathering ilmenite[62] may loose iron, and be altered to ***leucoxene***. Leucoxene is a fine granular alteration product of titanium minerals. It varies in colour from yellow to brown. It is not a valid mineral species and consists mainly of rutile or anatase. Rutile is a common accessory mineral in high-temperature and high-pressure metamorphic rocks and in igneous rocks. Rutile is the preferred polymorph of $TiO_2$ in such environments because it has the lowest molecular volume of the three polymorphs; it is thus the primary titanium bearing phase in most high pressure metamorphic rocks. Brookite and anatase are typical polymorphs of rutile formed by retrogression of metamorphic rutile. Within the igneous environment, rutile is a common accessory mineral in plutonic igneous rocks, although it is also found occasionally in extrusive igneous rocks. Rutile is a very resistant against mechanical and chemical weathering, and can easily be mechanically concentrated. It is a common mineral in placers. (See also chapter II: §II.6. Allochtoneous ore deposits - Placer deposits). Anatase and brookite are found in the igneous environment particularly as products of autogenic alteration during the cooling of plutonic rocks; most anatase is from alteration of ilmenite. The main producer of rutile from placer deposits is Australia, followed by India, the USA (also primary ilmenite deposits), Sri Lanka, South Africa, Brazil, Sierra Leone, Canada and

---

[62] Ilmenite is named after it's type locality*: Ilmen* Mountains, southern Urals.  Ilmenite is opaque, looking in hand specimen brownish black with a bluish luster, resembling magnetite, but being weakly to non-magnetic.

the former USSR. Canada, Brazil and the former USSR produce titanium minerals from secondary and primary deposits. The main primary ilmenite deposit in Europe is the Tellness ilmenite deposit in Norway (see chapter II). It is the largest ilmenite mine in the world.

*Ilmenite* is most easily converted into titanium dioxide via a sulphate process. Sulphate process plants must utilize low-vanadium ilmenite, as vanadium is a penalty element. The sulphate process is as follows:

$FeTiO_3 + 5\ H_2O + 2H_2SO_4 = TiOSO_4 + FeSO_4.7H_2O$
This reaction proceeds at 150 – 180°C. In the next step, titanylsulphate is then hydrolyzed.

$TiOSO_4 + 2H_2O = TiO(OH)_2 + H_2SO_4$

The $Ti(OH)_2$ is calcined at 90°C to produce $TiO_2$ . The iron sulphate waste product is a major disadvantage of this process. Ilmenite can also be used for production of $TiO_2$ by a chlorination process.

Rutile is the most important of the trio of $TiO_2$ polymorphs: *rutile*, *anatase* and *brookite*[63]. It is the principal commercial mineral. The main market for titanium is not the metal market, but the market for $TiO_2$-production. $TiO_2$, perhaps not expected, is made from titania-ores by chemical processes in order to get an as pure product as possible. The modern $TiO_2$ production is via a chloride route: $TiO_2$ (rutile or anatase) feedstock is chlorinated at 925 - 1010°C in the presence of petroleum coke to produce $TiCl_4$ (also termed “tickle”, after the chemical formula). This is distilled and then oxidized in oxygen at 985°C to produce $TiO_2$ and chlorine ($Cl_2$). The $TiO_2$ is calcined at high temperatures to remove hydrochloric acid and chlorine, leaving a high purity titanium dioxide.

| | |
|---|---|
|  |  |
| *Fig. 3.53a $TiO_2$-powder.* | *Fig. 3.53b. White paint, with $TiO_2$ as a pigment.* |

---

[63] Rutile: from the Latin, rutilus - "reddish." Rutile crystals appear reddish under a polarizing microscope.
Anatase: from the Greek, anatasis - "elongation”. A synonym is octahedrite. It is a rather rare mineral.
Brookite: named after the English mineralogist, Henry James Brooke (1771-1857), a London mineralogist and wool trader. Brookite is the rarest of the titanium-oxides.

$TiO_2$ is unrivalled in terms of whiteness, opacity, refractive index and light scattering properties. High purity $TiO_2$ is used as a white pigment in paint, rubber, plastics, paper, or as food colouring agent (having E number E171). It is also used in medicine (pills and tablets), and in most toothpastes. This pigment is used extensively in plastics and other applications for its UV resistant properties where it acts as a UV absorber, efficiently transforming destructive UV light energy into heat. In ceramic glazes titanium dioxide acts as an opacifier and seeds crystal formation.
As $TiO_2$ has strong UV-absorption, it is commonly used in sunscreens (=”sun tanning lotion, sun milk”). In almost every sunscreen with a physical blocker, titanium dioxide is found because of its high refractive index, its strong UV light absorbing capabilities and its resistance to discolouration under ultraviolet light.

*Fig. 3.54. Nivea Sun® contains $TiO_2$ as a physical sun blocker*

This advantage enhances its stability and ability to protect the skin from ultraviolet light. Sunscreens designed for infants or people with sensitive skin are often based on titanium dioxide.
Titanium metal, because it is non-toxic to living tissue, can be used in the manufacture of artificial bones, heart valves and pacemakers, in microsurgery, and in food additives. The shiny white metal is even used for spectacle frames, watches and tie clips.

## III.29. Vermiculite

Vermiculite is a versatile material, that is widely used. Physically and structurally *vermiculite*[64] resembles the micas. It splits into thin flexible but inelastic bronze to yellowish brown or black flakes with a bright to pearly lustre. Its chemical formula $(Mg,Fe^{2+},Al)_3(Al,Si)_4O_{10}(OH)_2\cdot 4(H_2O)$ contains 4 molecules of water, which give vermiculite some rather unusual properties. Vermiculite clays are weathered micas in which the $K^+$ ions between the molecular sheets are replaced by $Mg^{2+}$ and $Fe^{2+}$ cations

---

[64] From the Latin vermiculus, "little worm”

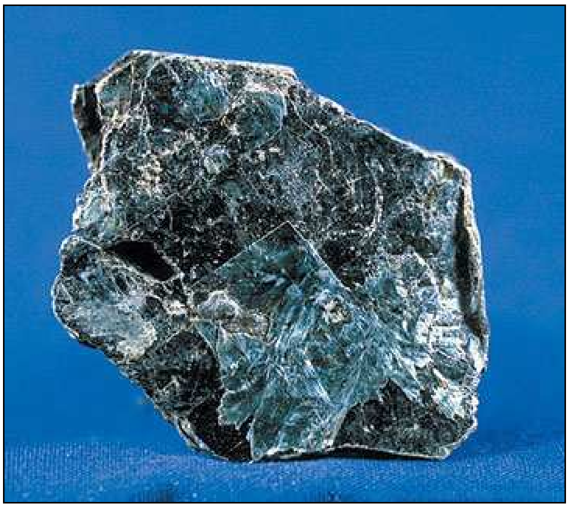


*Fig 3.55. Vermiculite*

On rapid heating above 870°C, vermiculite releases water as steam forcing the layers of the crystal structure apart at right angles to the cleavage in an accordion-like expansion. In theory, pure vermiculite can expand to 30 - 40 times its original volume. In practice, material as mined reaches expansions of 8 – 12 times. The bulk density of vermiculite is lowered from 640 -960 kg/m$^3$ to 56 – 192 kg/m$^3$ upon expansion. The exfoliation produces a product consisting of 90% trapped air.

Thermally exfoliated vermiculite is lightweight, has good thermal and acoustic insulation, is chemically inert, relatively refractory, fire resistant, rot proof, odourless, and non-irritating. These properties are desirable in a variety of building products, such as lightweight aggregate, lightweight wallboard, and loose fill insulation.

Exfoliated vermiculite mixed with cement is used for insulation of steam pipes, boilers, and furnaces. It is used in all sorts of fire proof boards and materials.  It is also used in refractories.  It is one of the main replacements of asbestos, which was used for many years for these applications, but is rarely used nowadays because of the severe health risks.

Vermiculite can absorb relatively large volumes of fluids, which makes it possible to use it in horticulture, admixed with peat and plant nutrients as a soilless plant medium. It can also be used as anti-caking agent.

Unexfoliated vermiculite is used in fire rated wall board. To reduce slag build-up in coal fired boiler tubes, and in drilling muds. Vermiculite has a high cation exchange capacity. The cation potential and the layer silicate structure of vermiculite is used in coating applications and inorganic films.

Vermiculite may be produced by weathering from biotite, phlogopite, diopside, hornblende or serpentinite along fault zones, by hydrothermal alteration of pyroxenites, peridotites, dunites, carbonatites and amphibole schists.

Vermiculite occurs in ultrabasic and alkaline rock complexes, in altered carbonate rock complexes, in reaction zones of pegmatites, talc deposits, and the like, micaceous gneisses and other metamorphic rocks.

South Africa and the USA account for almost ¾ of the world production of vermiculite. The former USSR, China and Brazil are other producers.

## *III.30. Wollastonite*

Wollastonite[65], $CaSiO_3$, was merely a mineralogical curiosum, until applications were found in the 1950's. Wollastonite forms coarsely bladed masses, that break down into acicular[66] crystal-fragments.

*Figure 3.56. Wollastonite mass.*

Furthermore, it is hard, and white coloured and chemically inert.  These properties make it useful as filler in paint rubber plastics, adhesives and ceramic bonded abrasives. In paint for example, the acicular wollastonite particles act as a flattening agent, and allow paint after application to settle out and dry in a film of uniform thickness. The interlocking needle shaped particles also improve toughness and durability, as well as scrub and weather resistance. Its high brightness reduces pigment load, and its low oil absorption reduces binder requirements and therefore reduces pigment costs. In plastics and boards and panels, the needle shaped structure increases impact tensile and flexural strength.  In addition, boards and panels are fire proof with good sound deadening properties.

## *III.31. Zeolites*

The zeolites are a very diverse family of minerals, discovered in the 18th century. The term was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed, upon rapidly heating a natural mineral, that the stones began to dance about as the water evaporated. Using the Greek words zein, and lithos, which mean “boiling stone”. he called this material zeolite.

The zeolites comprise a series of  hydrated aluminosilicates of alkaline or alkaline earth elements.  Structurally they are made up of infinitely extending 3-dimensional networks of $(Si,Al)O_4$-tetrahedra, with alkali-or alkali-earth elements outside it for

---

[65] Named after the English mineralogist W.H. Wollaston (1766-1826)
[66] Acicular = needlelike

charge balance. The second building block consists of single rings of 4,5,6,8,10, or 12 tetrahedra, of double rings of 4, 6, 8 tetrahedra, or larger symmetrical polyhedra. These building blocks form the most important property of the zeolites: *connected micropores.*

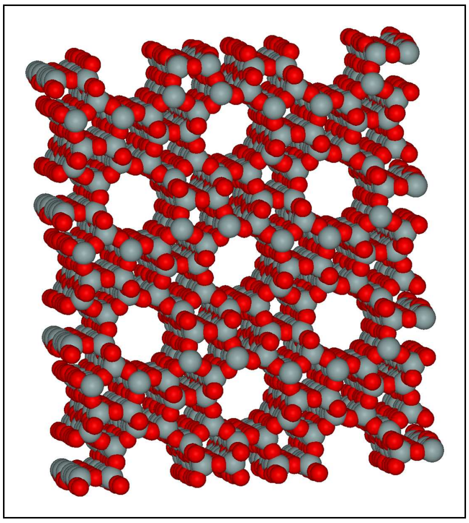


*Fig. 3.57. A zeolite structure, showing the micropores*

Zeolites are microporous solids known as "*molecular sieves*". The term *molecular sieve* refers to a particular property of these materials, i.e. the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. These are conventionally defined by the ring size of the aperture.. These rings are not always perfectly flat and symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pore openings for all rings of one size are not identical.

Zeolites occur in three basic structures:

1. Chainlike structures, whose minerals form acicular to needle shape crystals (e.g. natrolite)
2. Sheetlike structures, producing flattened crystals (e.g. heulandite)
3. Frameworks structures with more or less equidimensional crystals (e.g. chabazite)

The desirable characteristics are in brief:

- *High degree of hydration*
- *Low density and large void volume when dehydrated*
- *Stability of the crystal structure also when dehydrated*
- *Cation-exchange properties*
- *Uniform molecular size tunnels in the dehydrated crystals*
- *Various physical properties such as electric conductivity*
- *Adsorption of gases and vapours*
- *Catalytic properties*

Zeolites can thus selectively adsorb molecules, when dehydrated. Also they can be used for separation, and for instance can be used for the separation of pentane and octane from branch hydrocarbons, the latter which cannot pass through the zeolite's micropores. Zeolites are extensively used in water purification, in the petrochemical industry, in the nuclear industry, as a catalyst, in agriculture.

*Fig 3.58. Natural zeolites.*

The natural zeolites are about 50 in total, the most common being *analcime*[67], *heulandite, chabazite, clinoptilolite, erionite, faujasite, ferrierite, laumontite, mordenite, natrolite, offretite and philippsite*. Only mordenite, clinoptilolite, chabazite, erionite, philippsite and analcime are found in natural state pure enough to be used in industry.

Zeolites are formed where pore water reacts with materials like volcanic glass, poorly crystalline clay, plagioclase, silica. Zeolite formation is usually favoured by a high ratio of $Mg^{2+}$ and $H^+$, to $Na^+$, $K^+$, and $Ca^{2+}$. The specific type formed depends on the composition of the original rock, P,T, partial pressure of $H_2O$, activities of certain ions. Occurrences are in deep sea sediments, weathering at Earth's surface, alkaline saline lakes, groundwater percolation zones in acidic tephra[68], low, moderate, high temperature hydrothermal regimes, diagenesis, or primary magmatic. The type of zeolite varies with the environment.

Zeolites were long considered to somewhat of a rarity, but in the first half of the last century, application were discovered, and zeolites were made synthetically. Nowadays, natural zeolites are actually the challenger of the synthetic counterparts, which are *chemically engineered in a meticulous way, to meet industrial demands*.

---

[67] Analcime from Greek analkis = without strength, due to ist weak electric properties when heated; Chabazite from Greek Chabasios, an ancient stone ascribed to Orpheus, Clinoptilolite, from Greek klinein , to bend or slope (monoclinic) and ptilo (feather) ; Erionite from Greek erion (wool); Faujasite after B. Faujas de St Fond (1741 – 1819), Ferrierite, after W.F. Ferier (1865 – 1950), Laumontite after L. de Laumont( 1747 – 1837), Mordenite, after Morden, Nova Scotia, Natrolite, after natrium, Offretite, after A.J.J Offre; Philipssite, after W. Philiips (1775 – 1829).

[68] Tephra is air-fall material produced by a volcanic eruption regardless of composition or fragment size

## ***III.32. Zirconium minerals***

Zirconium is, just like titanium considered to be an exotic element. Just like titanium, is not rare at all: it is the twentieth among the elements in the ranks of abundance, and more common than copper, tin, lead and zinc. Zirconium concentration is limited to a mere 20 minerals, but just *zircon*[69] ($ZrSiO_4$) and the less important *baddeleyite*[70] ($ZrO_2$) are the commercially interesting minerals. Common impurities in zircon and baddeleyite include Hafnium (Hf), Uranium (U), and Thorium (Th), as well as REE, Y, Ca, Mg and Fe. U and Th may substitute for Zr in the lattice. Radio-active emanations result in internal alterations, called *metamictisation*. Zircon concentrates may be regarded hazardous because of radio-activity. The amounts of Th and U are, however, generally much lower than in monazite. In general zircon does not pose a health hazard.

Zircon is used mainly for the manufacture of refractories, as foundry sand and in ceramics. Zircon's melting point (> 2430°C) plus its low coefficient of expansion, low wettability by molten metal, excellent thermal diffusivity, and its high chemical stability make it an ideal refractory, used in ladle linings, continuous steel casting nozzles, refractory bricks for glass melting furnaces, and refractory cement. These properties plus its high thermal conductivity and density, thermal stability at elevated temperatures, the rounded shape of its particles that readily accept binders, and its neutral or slightly acid pH make it also ideal as foundry sand used in steelmaking, foundry flour used as mold paint, investment casting[71], as well as super alloy and titanium casting. In ceramics, zircon is found in speciality products, glazes, frits[72], and enamels. Wet ground zircon flour acts as an opacifier for porcelain glazes and enamels, because of the high refractive index of zircon, which gives the same effect as when using titania in paint. Other specific examples include sanitary ware, wall tile, dinnerware, glazed brick and industrial tile. Zirconia ($ZrO_2$) may be used in ceramic pigments.

In similar fashion to titanium, zirconium metal is produced by a chlorination process, converting zircon to zirconium tetrachloride, which is refined with aluminium or magnesium into raw zirconium which is re-melted to 99.99% pure zirconium metal.

Zirconia ($ZrO_2$) is produced from reacting zircon at high temperatures with dolomite. The melting point of zirconia is 200°C higher than that of zircon, and it is of course used as a refractory material. Zirconia is also used in speciality glasses, electronic catalyst, and in the production of cubic zirconia gemstones: diamond substitute, "imitation diamonds", CZ or cubic zirconia, and (incorrectly of course), "zircon".

---

[69] The name either derives from the Arabic word *zarqun*, meaning vermilion, or from the Persian *zargun*, meaning golden-colored.

[70] For Joseph Baddeley, who first called attention to the Sri Lankan material

[71] Also known as "lost wax casting"

[72] A frit (sometimes spelled fritt) is a ground glass or glaze used in pottery.

*Fig. 3.59. A zirconia  brilliant*

Zirconia stabilized with yttrium yields hard and tough engineering ceramics (YSZ), which may be used in extrusion dyes, engine parts and the like.

Hafnium (Hf) has similar properties as zirconium, and is  produced mainly from zircon. Its uses are as a neutron absorber in nuclear reactor control rods, in electronics, in diverse alloys, and as electrode in plasma cutting.

Zircon deposits are similar to those of rutile: they occur in primary igneous rocks, but are mainly produced form placers. See also chapter II.

## *III.33. References*

P.W. Harben, M. Kuzvart (1996) Industrial Minerals, A Global Geology.  Industrial Minerals Information Ltd, UK, 462 pp.

P.W. Scott (2008) Powerpoint presentations for European Mining Course EMC, Camborne School of Mines, University of Exeter.

# Chapter IV. Crystal Chemical and Crystallographical Aspects of Sulfides, Oxides and Hydroxides.

## *IV.I. Introduction*

In this chapter, some crystal chemical and crystallographical aspects of sulfides 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 crystallographical 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.

## *IV.2. Sulfides*[73]

### IV.2.1. Properties of sulfides (and arsenides)

When a sulfide is compared with “normal” rock forming minerals, it soon appears that sulfides 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 sulfides. Not every sulfide needs to poses 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 phenomenons, without going to much in depth in solid state chemistry or solid state physics.

<u>High Density</u>

This is caused by two things.

1. The first (and most simple) is the often high atomic number of the elements in the sulfides/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.)

---

[73] Arsenides, selenides, tellurides and complex sulphur compounds (sulfo-antimonides, sulfo-arsenides) are usually treated together with sulfides.

2. Short interatomic distances in sulfides and arsenides. This is because more then one valence electron participates in the chemical bond, which makes short atomic distances possible (hybridization and overlap of orbitals).

### *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 sulfides 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 sulfides 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 an 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 sulfide. Compositional differences in sulfides thus may influence the reflection behaviour.

### *Electrical Conductivity*

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

### *Magnetical properties*

Magnetic properties of sulfides have their origin in unpaired electrons of the metal atoms, similar to the magnetism of some spinels (magnetite). Magnetism of sulfides (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 sulfide has its effect on the netto 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 extensive for this course.

### *High ductility*

This can be explained by the covalent or metal character of the chemical bonds.

### *Surface reactivity and tarnishing*

Tarnishing: By means of bonding of oxygen to the surface the character of the bonds of the sulfide 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: sulfides 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.

## IV.2.2. Classification and structure of common sulfides and arsenides

### IV.2.2.1. Introduction

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

- *Glanze.* Properties like galena, thus metallic lustre, lead grey colour, low hardness, perfect cleavage. Often this are sulfides of Cu, Pb, and Ag, like galena, chacocite).
- *Kiese.* The properties of pyrite serve as a model for the Kiese. Usually these are Ni, Fe, Co and Pt-sulfides (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.

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

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

1. **Monosulfides (MS) and derived structures.**
    a. *Sphalerite (ZnS) structure* with derivatives like the chalcopyrite structure, the tennantite-tetrahedrite series, the sulphosalt luzonite[74].
    b. *Wurtzite structure* (ZnS), with as derived structures those of the

---

[74] N.B.: a ***sulphosalt*** 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 ($3Ag_2S.Sb_2S_3$), geocronite ($Pb_{14}(As,Sb)_6S_{23}$). Sulfides and sulphosalts are generally treated together in mineralogical handbooks.

sulphosalt enargite.

c. *Nickeline structure* (NiAs), with derivatives Troilite (FeS) and pyrrhotite ($Fe_{1-x}S$)
d. *Millerite structure* (NiS)
e. *Pentlandite structure* $(Ni,Fe)_9S_8$
f. *Galena structure* (PbS) with as derivatives silversulphosalts and cinnaber (HgS).
g. *Covellite structure* (CuS)

2. **Disulfides ($MS_2$) and derived structures**
    a. *Molybdenite structure ($MoS_2$)*
    b. *Pyrite structure ($FeS_2$)* and the cobaltite group (cobaltite, CoAsS, gersdorffite, NiAsS, and similar minerals, e.g. ullmannite, NiSbS)
    c. *Marcasite structure ($FeS_2$)* and arsenopyrite (FeAsS)[75]

3. **Other stoichiometries ($M_xS_y$)**
    *a. Chalcocite structure ($Cu_2S$)*
    *b. Stibnite structure ($Sb_2S_3$)* and related Bi, Pb- and As-Sb sulphosalts

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

### IV.2.2.2. Monosulfides (MS)

a) Sphalerite[76] structure and wurtzite structure

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 polytypes[77] which differ in the stacking of the tetrahedrons. In the case of sphalerite, it is a cubic symmetry (ccp)[78], 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.

---

[75] ***Pyrite and marcasite*** are both $FeS_2$, and are also dimorphs. Pyrite is cubic, marcasite orthorhombic. The name ***pyrite*** is derived from *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 recognised words in (proto)Indo-european.. Compare with the prefix *"pyr"* in pyrolysis, pyrometallurgy etc. The name ***marcasite*** is derived from Arabic or Moorish name for pyrites and similar material of uncertain origin.

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

[77] 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.

[78] ccp = cubic closest packing; hcp = hexagonal closest packing.

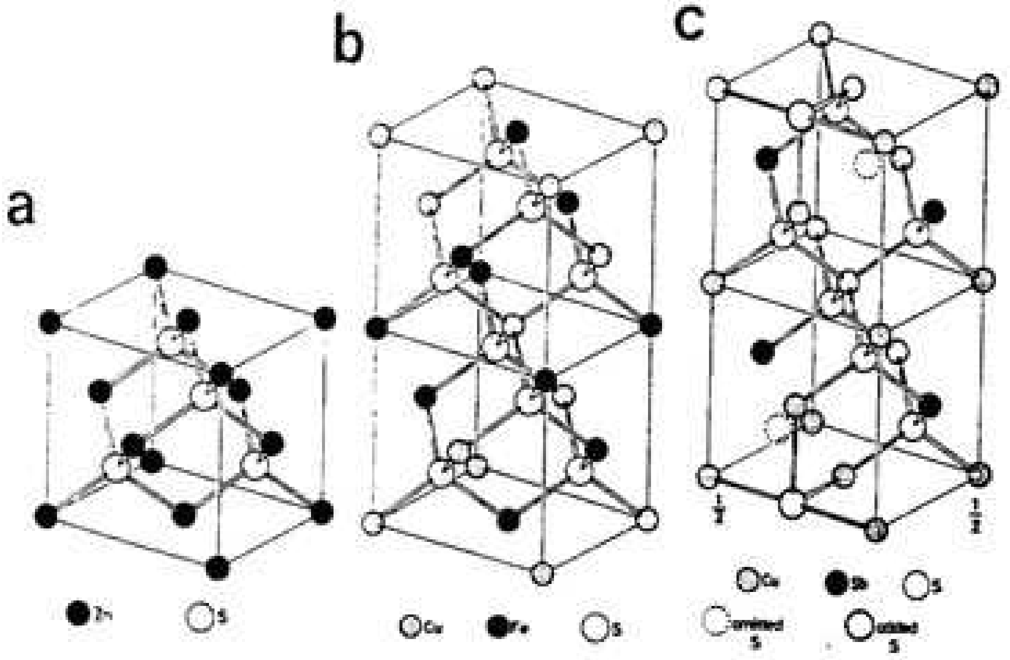


*Fig. 4.1. The sphalerite structure (a) with the derivative structures of chalcopyrite (b) and tetrahedrite (c)*

There are many derivatives of the sphalerite structure known. A very well know 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 ($Cu_2FeSnS_4$) has a similar structure, where layers of ordered Cu and Sn alternate with layers with Cu.

Luzonite[79] ($Cu_3(As,Sb)S_4$) is a tetragonal derivative of chalcopyrite. Enargite, a polymorph of luzonite is derived from the wurtzite structure (fig. 4.2.). Typical is a tetrahedral coordination of As or Sb by S. Many sulphosalts are derived from the sphalerite structure.

---

[79] ***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***: Mancayan, Luzon Island, Phillippines

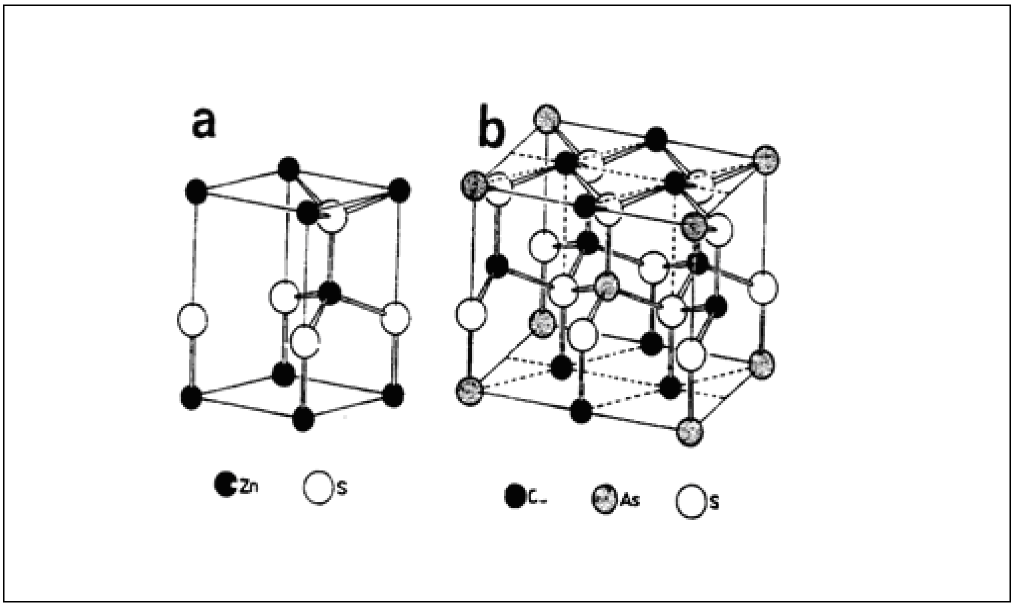


*Fig. 4.2 The wurtzite structure and the derived structure of enargite.*

Tennantite[80] ($Cu_{12}As_4S_{13}$) and tetrahedrite ($Cu_{12}Sb_4S_{13}$) 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/tennantite series is a complete solid solution, which also can take up other elements (Hg, Ag).

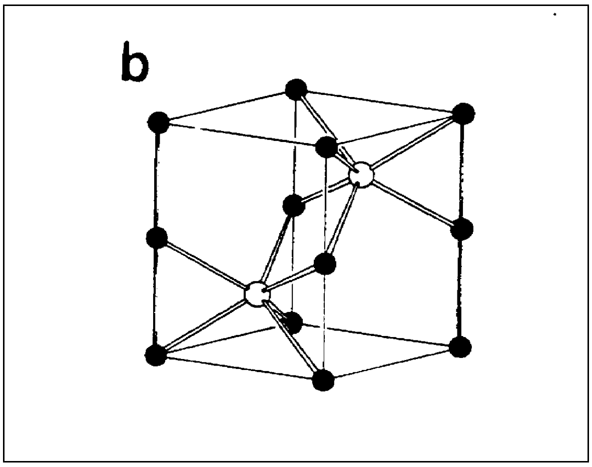


*Fig 4.3. The structure of Nickeline NiAs.*
*Closed spheres are Ni, open spheres are As.*

b) Nickeline Structure.

The nickeline[81] structure is hexagonal, with the more electronegative ions arranged in a hcp The remaining ions occupy the octahedral positions. Metal-metal bonds along

---

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

[81] ***Nickeline*** (synonym ***nicolite***): named after its composition.

the c-axis give the structure its stability. The nickeline structure is quite important and occurs a lot for sulfides of transition metals. A-stoichiometry is also frequently encountered. A complex derivative of the nickeline structure is the structure of pyrrhotite[82] ($Fe_{1-x}S$). 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. Troilite [83](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 ($T > 379\ ^0C$) has the NiAs-structure, and has also a-stoichiometry, like pyrrhotite. The LT-form (millerite[84]) is stoichiometric, and has a rhombohedric structure.

### d) De pentlandite structure $(Ni,Fe)_9S_8$.

Pentlandite[85] has a complicated fcc-structure[86]. 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) Galena[87] structure and its derivatives: sulphosalts and cinnaber.

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

---

[82] From the Greek, phyrrhotes, "redness," in allusion to the color.

[83] Named for Dominico Troili, who described, in 1766, a meteorite which fell in Albareto, near Modena, Italy.

84 Named after the English mineralogist, William Hallowes Miller (1801-1880).

[85] Named after the Irish natural historian, J. B. Pentland (1797-1873).

[86] fcc= face centered cubic, ccp = cubic closest packing.

[87] The Roman naturalist, Pliny, used the name ***galena*** to describe lead ore. The word is possible of Etruscan origin.

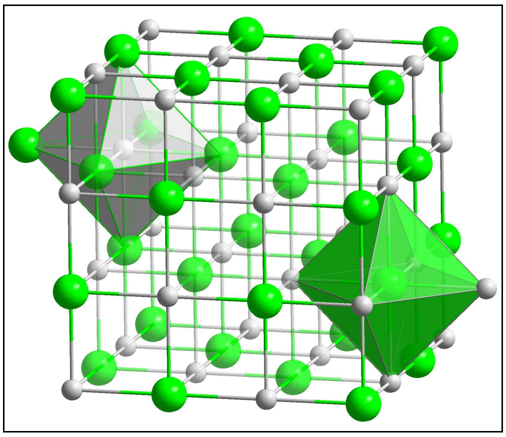


*Fig. 4.4a. The crystal structure of sodium chloride.*
*Each atom has six nearest neighbours, in octahedral geometry*

e) Covellite structure.

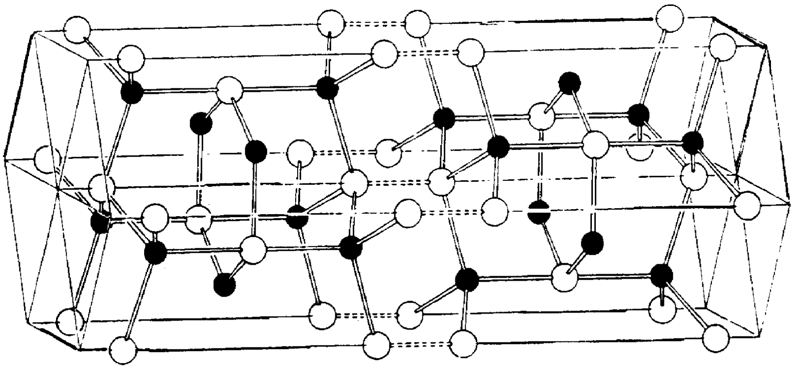


*Figure 4.5. The structure of covellite. Closed spheres are Cu, open spheres are S. Dashed lines indicate the covalent bonds which keep the layers together.*

The chemical formula of covellite[88], 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 hare 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 $CuFeS_2$, chalcopyrite, $Cu_5FeS_4$, bornite, and $Cu_2S$, 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.

---

[88] *Named after the Italian mineralogist, N. Covelli (1790-1829).*

### IV.2.2.3. Disulfides

a) Molybdenite structure ($MoS_2$)

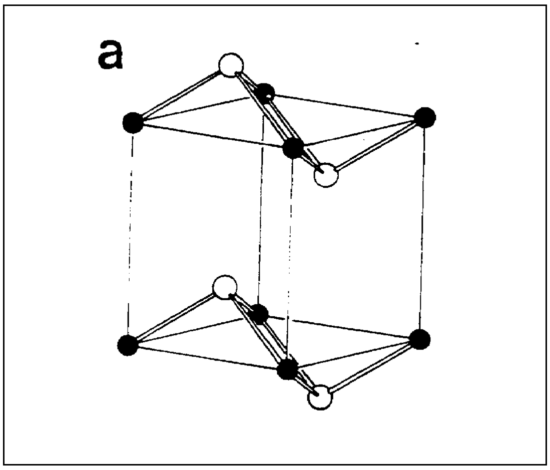


*Fig. 4.6. De structure van $CdI_2$. Molybdenite also crystallizes in this structure. Closed spheres are metal atoms.*

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

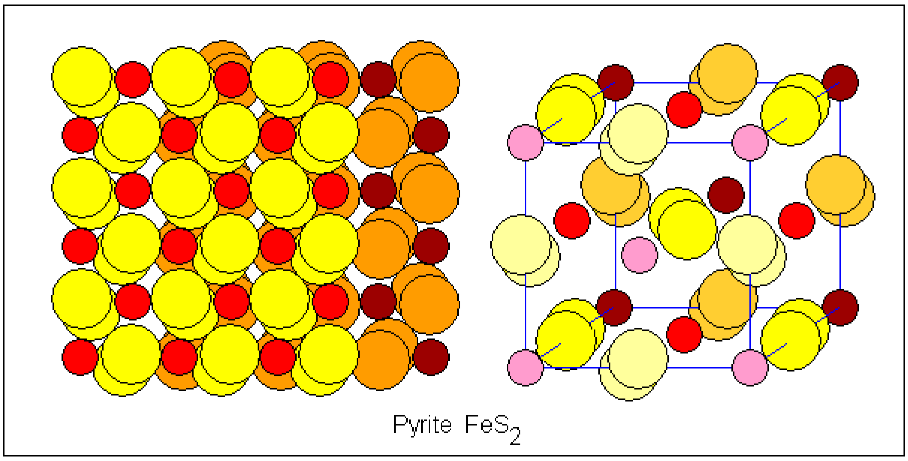


*Figure 4.7.Pyrite is often described as having a modified halite structure. However, iron atoms alternate with pairs of covalently-bonded sulphur atoms. The pairs of atoms are skewed in alternate directions, so pyrite has lower symmetry than halite. In this sketch, iron atoms are red and sulphur yellow. 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 $S_2$-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 $S_2$-pair. The pyrite group is quite numerous. Members include vaesite[89] ($NiS_2$), hauerite[90] $MnS_2$, sperrylite[91] ($PtAs_2$).

Members of the cobaltite-group (cobaltite[92],CoAsS, gersdorffite[93], NiAsS, and ullmanite[94] NiSbS) have structures which resemble the pyrite structure very much. The group –V metals (As, Sb) replace one S of the $S_2$-pair. See fig. 4.9 for a comparison of the pyrite and ullmannite group.

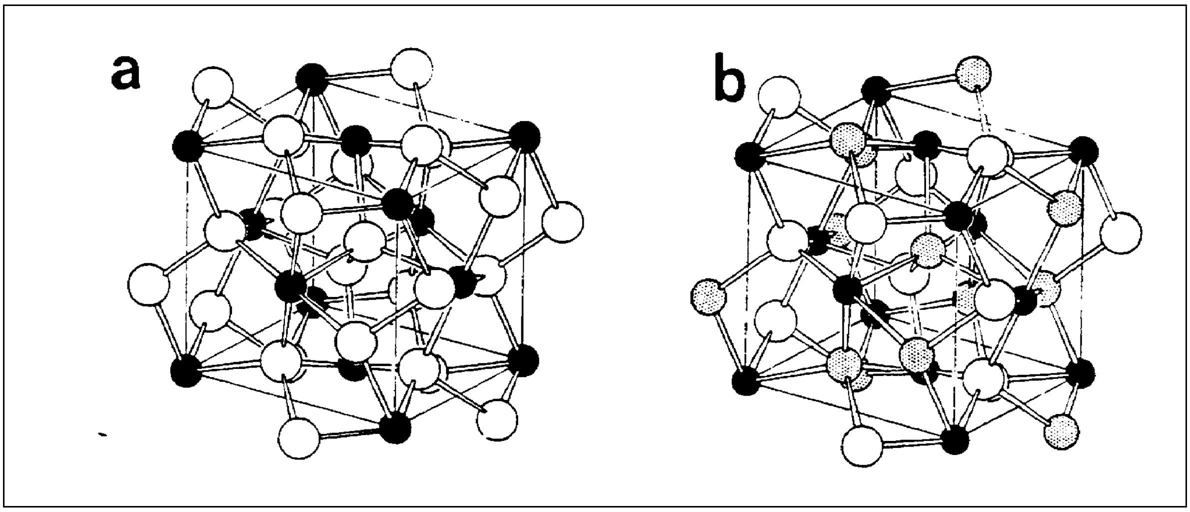


*Fig. 4.8. a) The structure of pyrite. Closed spheres are Fe. b) The structure of ullmannite NiSbS. Grey spheres are Sb.*

c) Marcasite structure and derivatives

Marcasite is an orthorhombic polymorph of pyrite. The structure is given in figure 4.9. Arsenopyrite[95] 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 tot 0.82. The structure of arsenopyrite is triclinic, but As-rich varieties can approach a monoclinic symmetry. Loellingite[96] (or Löllingite), $FeAs_2$, also crystallizes in the marcasite structure.

---

[89] *Named for Johannes Vaes, Belgian mineralogist for the Union Miniere du Haut Katanga.*

[90] *Named after the Austrian geologists, J. R. Hauer (1778-1863) and F. R. Hauer (1822-1899).*

[91] *Named after its discoverer, the American chemist, F. L. Sperry*

[92] *Name after mines in the Cobalt district, Ontario, Canada*

[93] *Named after Herr von Gersdorff, owner of Schladming Mine, Austria.*

[94] *Named after the German chemist and mineralogist, J. Ch. Ullmann (1771-1821).*

[95] *Named after the minerals chemical composition. Arsenopyrite crystal may resemble pyrite in handspecimen, but it are never real cubes, as arsenopyrite is triclinic.*

[96] *Named after Lölling, Hüttenberg, Carinthia, Austria*

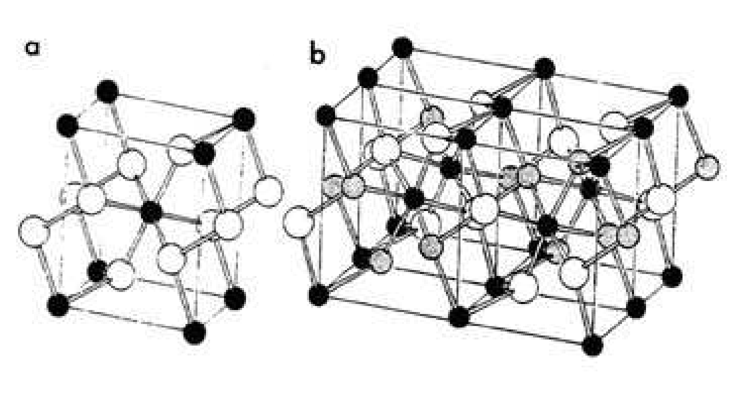


*Fig 4.9. (a) The structure of marcasite, , $FeS_2$ (closed spheres are Fe) (b) arsenopyrite, FeAsS. Grey spheres are As.*

### IV.2.2.4. Other stoichiometries ($M_xS_y$)

a) Chalcocite[97] structure and derivatives (digenite, djurleite).

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

At $104^0$ 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 $350^0$ C this hexagonal chalcocite changes into a cubic form with a variable stoichiometry ($Cu_{1.765}S$ - $Cu_{1.79}S$), 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* ($Cu_{1.96}S$). Optically, chalcocite and djurleite are difficult to separate. The difference in optical properties between chalcocite and digenite is considerable.

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

Digenite often contains a little Fe, which can be admitted into the structure at HT. Digenite is sometimes seen as a member of the Cu-Fe-S-group of sulfides, chemically related to chalcopyrite[25], cubanite, and *bornite*[98]

The tetragonal bornite ($Cu_5FeS_4$) is related to digenite. The structure of bornite, one of the most readily identified sulfides is based on a ccp stacking of S-atoms. Above

---

[97] ***Chalcocite*** *from the Greek, meaning chalkos, "copper".* ***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 S. Djurle, who first synthesized the compound later found in nature.*

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

$335^0$C there is complete solid solution between bornite and digenite. HT-bornite also has (limited) solid solution with chacopyrite. The disintegration of these compositions results in the often peculiar, but common exolution-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.

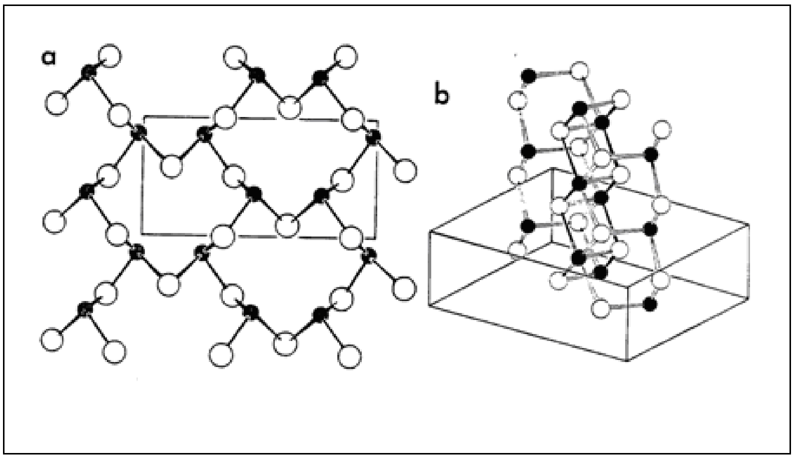


*Fig 4.10 The layer structure of orpiment ($As_2S_3$)* ***(a)****,*
*projected along the b-axis, and one of the fourfold chains in stibnite ($Sb_2S_3$)* ***(b)****. Open circles are sulphur.*

Examples are:

- *stibnite*[99] ($Sb_2S_3$) (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, aikinite, emplectite).

## IV.3. Oxides

### IV.3.1. Properties of Oxides

The mineralogy of oxides is different from that of sulfides because of the occurrence of ionic bonds. Oxides are because of these stronger bonds in general harder and more brittle than sulfides. Also they are often translucent. Magnetic properties are known from some minerals in the (inverse) spinel series (magnetite), ilmenite ($FeTiO_3$),

---

[99] ***Stibnite***: From the Greek, stimmi or stibi, "antimony," thence to the Latin, stibium. Antimonite: from the Greek anthemon, "flower" in allusion to the form of 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".

wüstite[100] ($Fe_{1-x}O$) 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 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.

## IV.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. Tetrahedrical cavities are empty in stoichiometric structures. Examples of minerals with this structure are periclase (MgO), manganosite (MnO) and wüstiet (FeO).

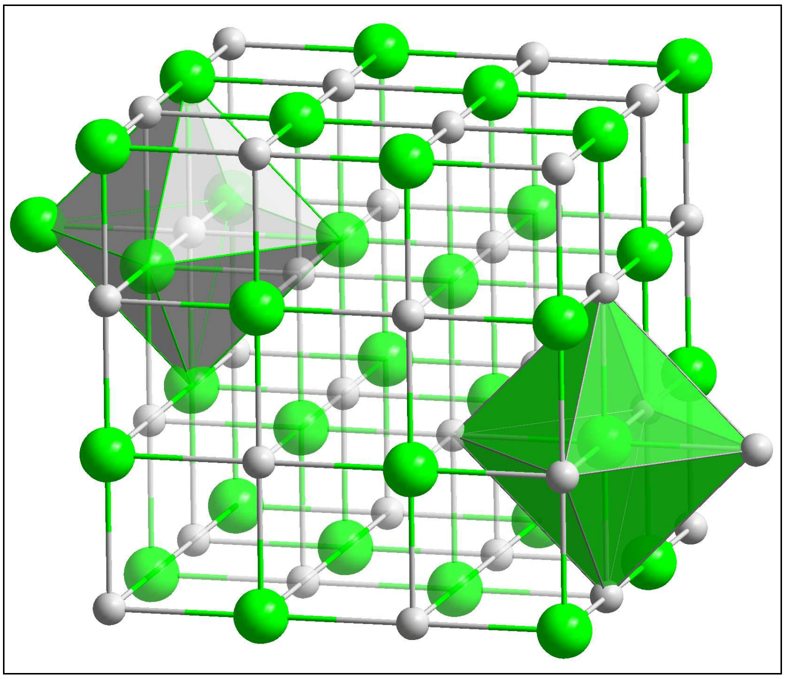


*Fig. 4.11. The NaCl-structure.*

---

[100] ***Wüstite*** (also wuestite): named after Ewald Wüst (1875-1934), who first synthesized it.

- **Perovskite structure ($ABO_3$)**

  In the perovskite[101] structure, also derived from the a ccp-stacking of oxygens, ¼ of the oxygen atoms is replaced by the large cation A, whereas ¼ 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 replces Ti. There are many synthetic varieties, for instance $BaTiO_3$.

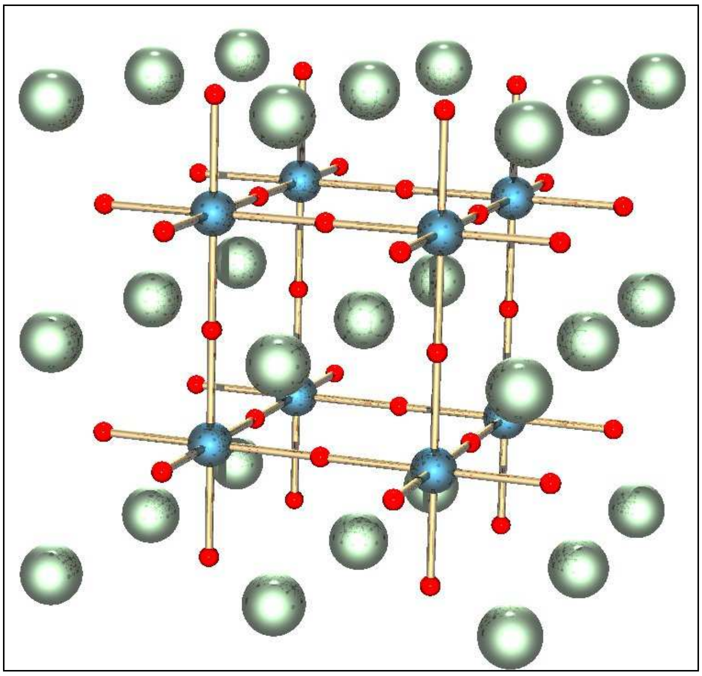


*Fig. 4.12. The perovskite-structure. Red = O, Blue= Ti, Greenish = Ca*

- **Fluorite structure ($AO_2$)**

  Oxides with the fluorite structure (fig. 4.13) have a structure also derived from a ccp-stacking of oxygens, 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* ($ThO_2$). Related is the structure of uraninite ($U_3O_8$)

---

[101] Named after the Russian mineralogist, L. A. Perovski (1792-1856).

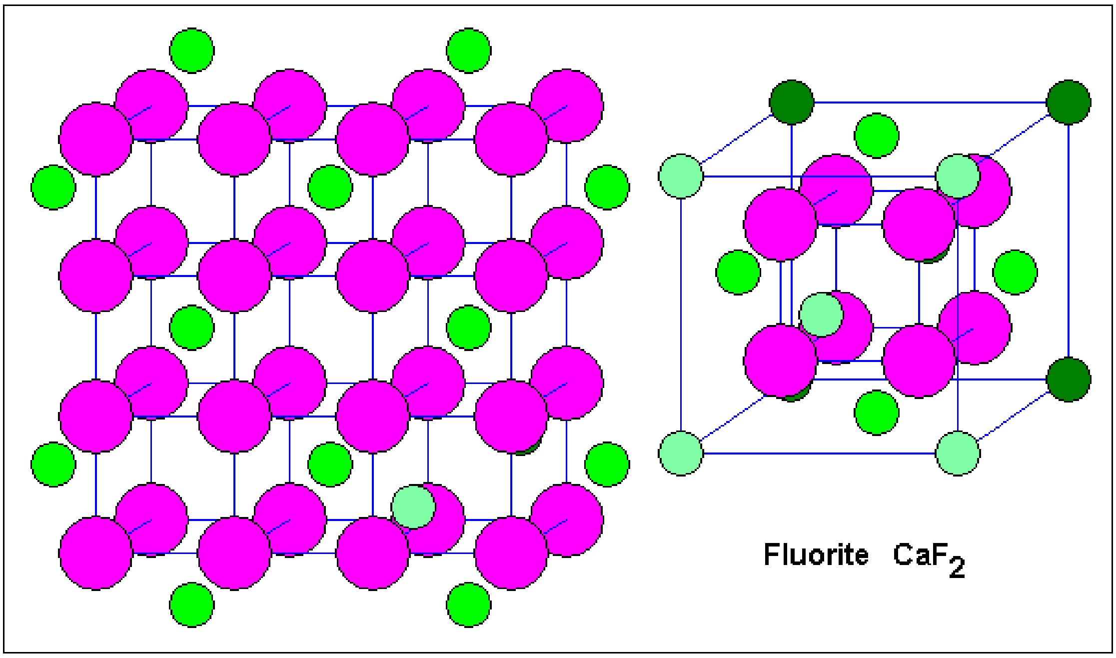


*Fig. 4.13. The fluorite structure. With derived oxides, oxygen takes the place of F and the cation takes the place of Ca.*

- **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.

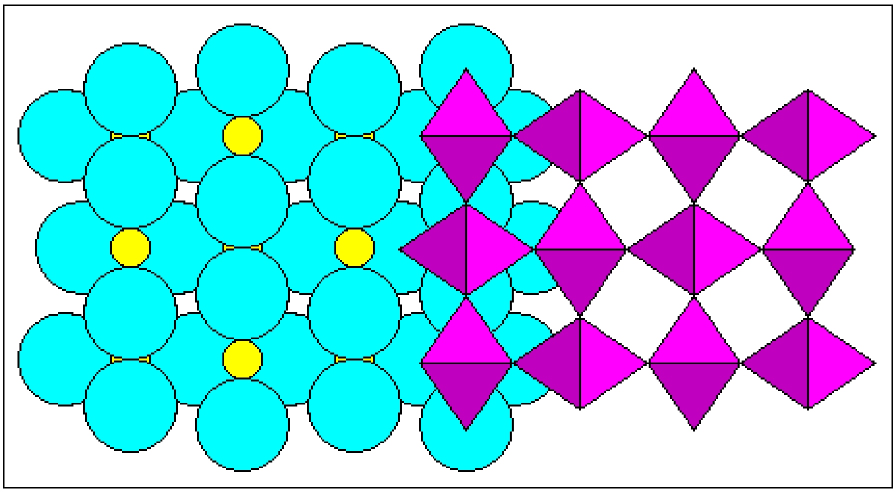


*Fig. 4.14 Viewed down the fourfold symmetry axis, the rutile-structure looks like this. Octahedra with Ti at their centres enclose square tunnels.*

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 axis*[102].
Examples of minerals with this structure are *rutile*[103] ($TiO_2$), *cassiterite* ($SnO_2$), *pyrolusite* ($MnO_2$). Cassiterite is the most important tin-ore mineral. Pyrolusite is the most important Mn-ore mineral.

- **Spinel[104] 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 inversee. When the most occurring cation is located in the octahedral position, the structure is called normal spinel. If the most occurring cation is dived over the two types of sites, the structure is called inverse spinel. The spinel structure is given in fig.4.18.

---

[103] 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.

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

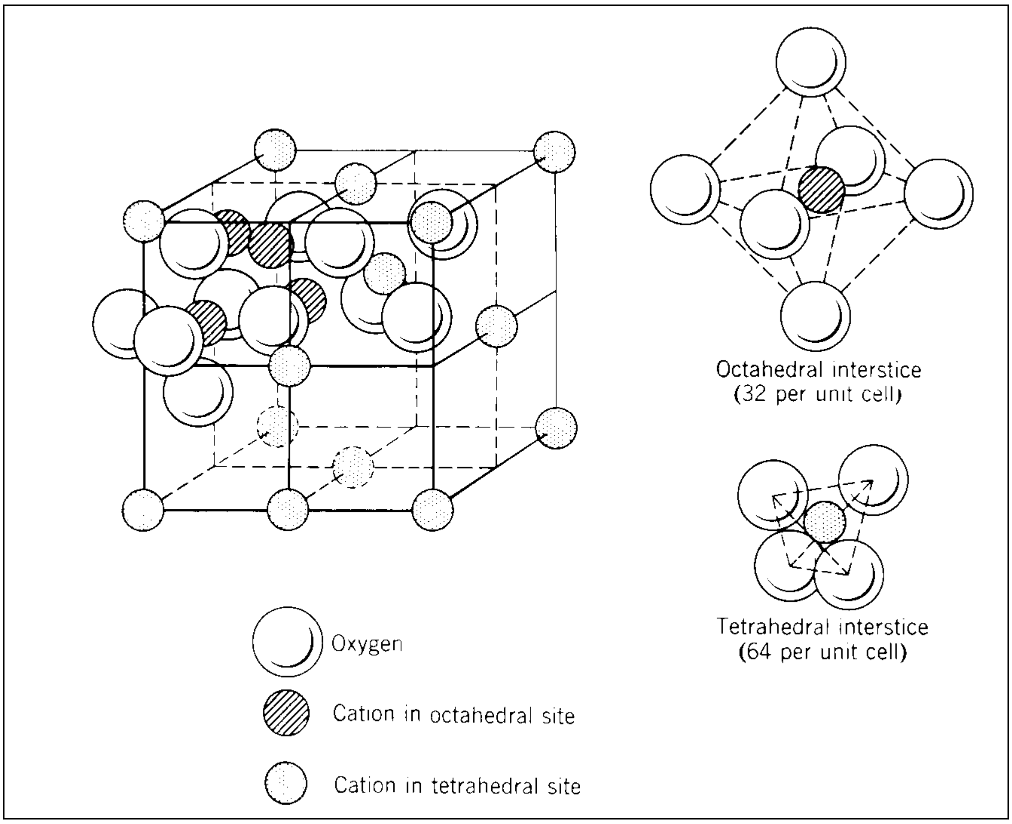


*Figure 4.15. The spinel structure*

Important examples are *spinel s.s.*($MgAl_2O_4$, normal spinel), *magnetite* ($FeFe_2O_4$, inverse spinel), *chromite* ($Fe^{2+}Cr^{3+}{}_2O_4$, normal), and *ulvöspinel*[105] ($Ti^{4+}Fe^{2+}{}_2O_4$). Magnetite forms solid solutions with many spinels, but the one with ulvöspinel is most likely the most important. This $Ti_xFe_{3-x}O_4$ series is called titanomagnetite. Exolution Ti-rich phases of titanomagnetites gives rise to exolved ilmenite ($FeTiO_3$)-lamellae in magnetite.

Spinels are also very important because some of them (that is: some inversee spinels) exhibit ***magnetic* *properties***. The archetypical example is *magnetite*. The type of magnetism displayed by magnetite is called ***ferrimagnetism***[106]. 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 this the 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 bases on the magnetite structure. Such material are called ferroxcubes (magnetite and its related *ferrites* are cubic).

---

[105] Name derived from Sodra Ulvön island, Angermanland, Sweden and the spinel group

[106] ***Ferri-magnetism*** is different from ***ferro-magnetism***. Above its Curie-point, both types become ***para-magnetic***. ***Antiferro-magnets*** are ferri-magnets where the magnetic moments of the electronspins cancel out.

- **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).

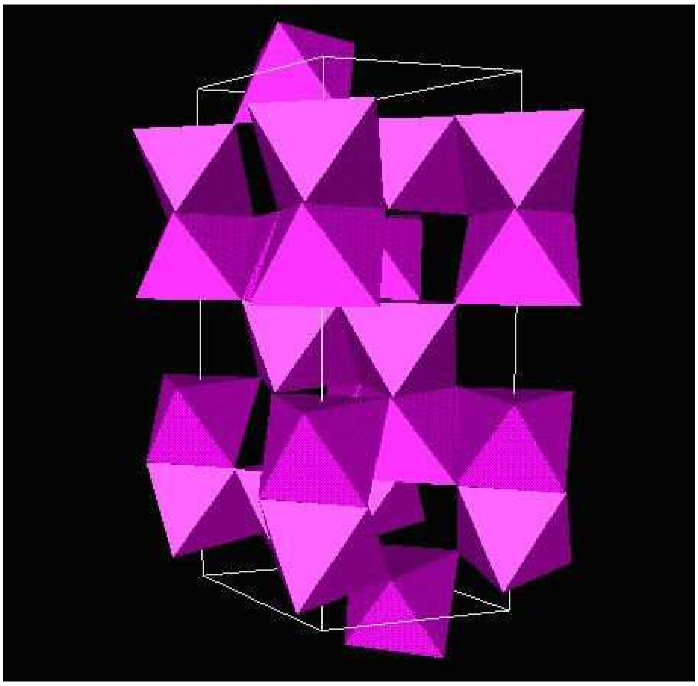


*Fig. 4.16. The corundum structure*

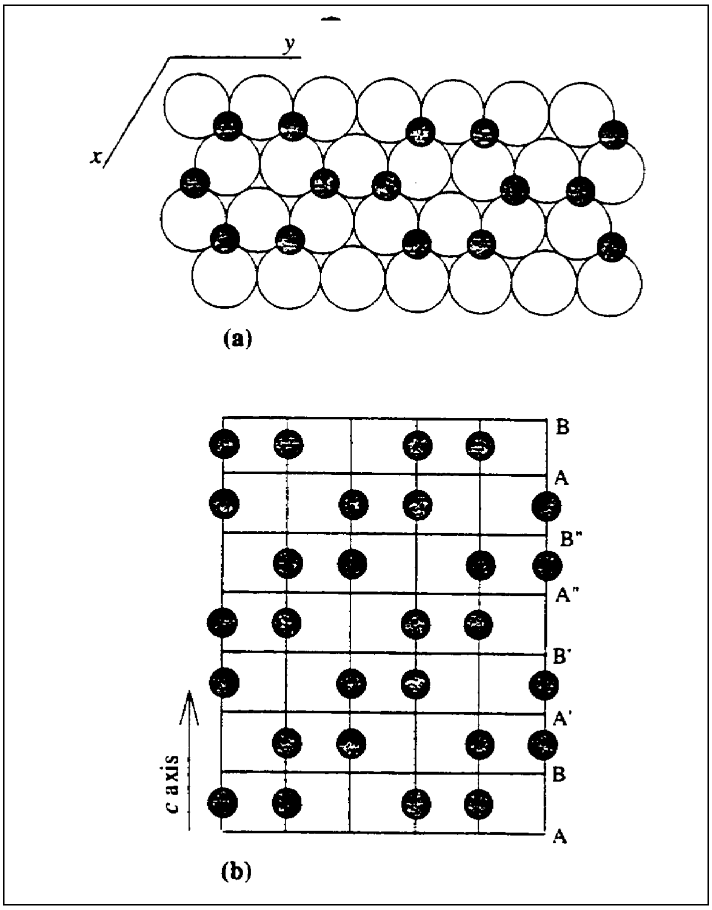


*Fig. 4.17. The corundum structure.*

## IV.4. HYDROXIDES (M-O-OH)

### IV.4.1. Fe- and Al-oxy-hydroxides

*Goethite* 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. $Fe^{3+}$-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. The 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* (α-AlOOH), Diaspore occurs in bauxites.

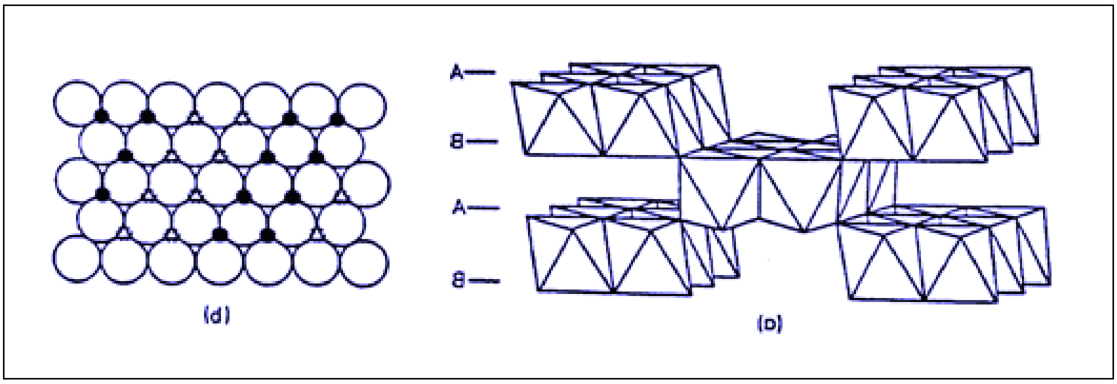


*Fig. 4.18. The goethite structure.*

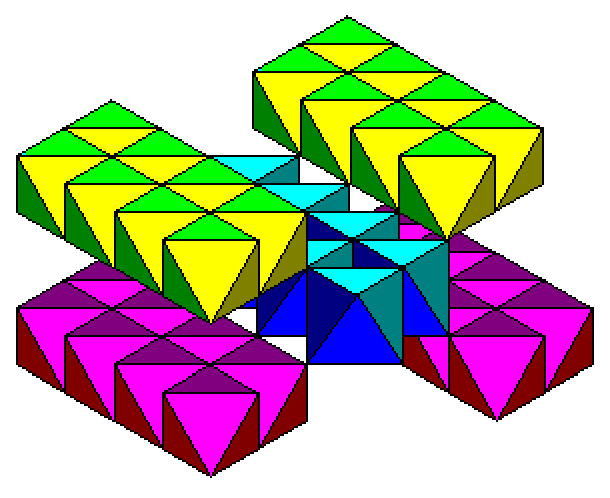


*Fig. 4.19. The goethite structure in an oblique view.*

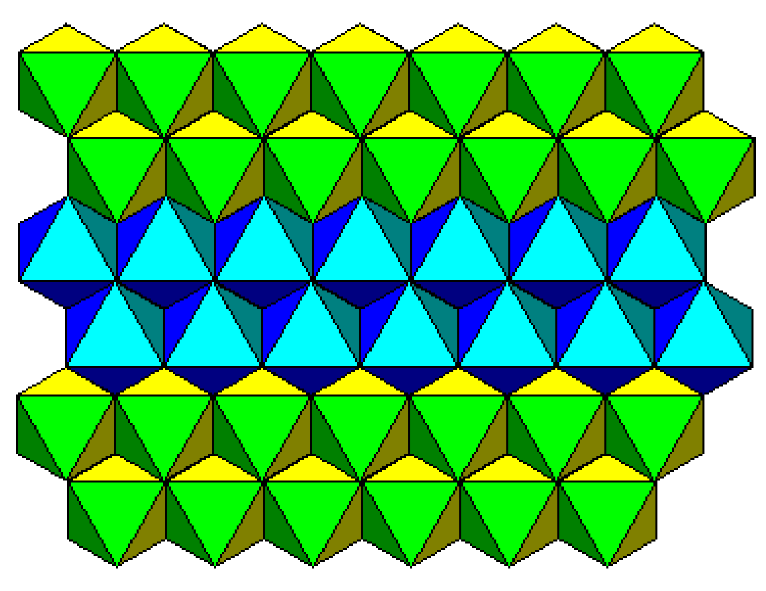


*Fig. 4.20. The goethite structure, top view*

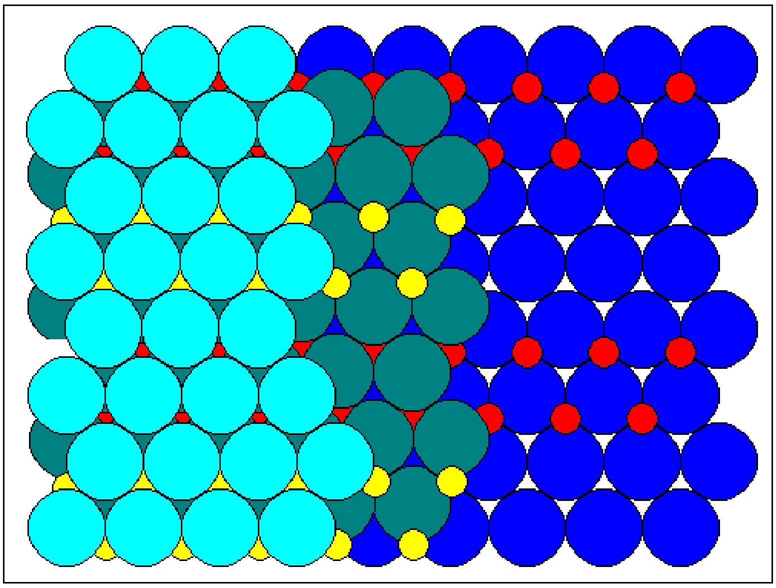


*Figure 4.21. Ball model of the goethite structure.*
*The octahedral layers are indicated in various shades of blue,*
*cations in red and yellow.*

A polymorph of goethite is the much more rare *lepidocrocite*[107] ($\gamma$-FeOOH). The analogous Al-oxyhydroxide is boehmite, 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 $Fe(O,OH)_2^-$ chains may occur.

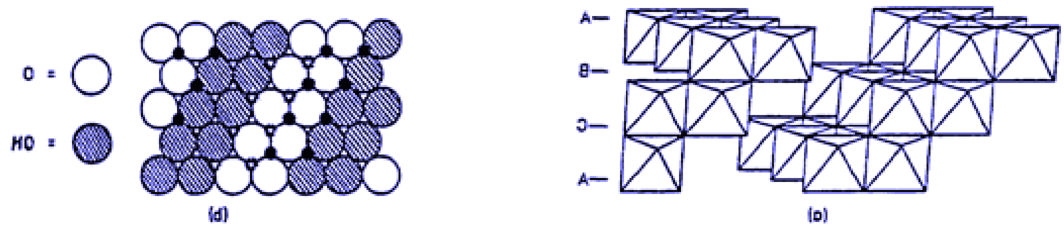


*Fig. 4.22. The structure of lepdicrocite. Modified after Craig and Vaughan,1993*

---

[107] Lepidocrocite: name from the Greek lipis - "scale" and krokis - "fibre." Boehmite: named after the German geologist and paleontologist, Johannes Böhm (1857-1938).

*Fig. 4.23. Goethite, Minas Gerais, Brazil.*

## IV.4.2. Mn-oxyhydroxides

Analogous to the Fe-oxyhydroxides and Al-oxyhydroxides, there are also Mn-oxyhydroxides. The number of Mn-oxides an hydroxides is vary 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 (ß-$MnO_2$) is at a closer look often rather $\gamma$-$MnO_2$ or $\delta$-$MnO_2$.

*Pyrolusite* has a rutile-structure but the other $MnO_2$-polymorphs have mixed structures. *Ramsdellite*[108] (Mn-O-OH.x$H_2O$) 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.

*Psilomelane*[109] 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 *romanechite*[110] 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.

---

[108] ***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: $Mn^{4+}_{0.85}O_{1.7}Mn^{2+}_{0.15}(OH)_{0.3}$

[109] Psilomelane: named in 1758, from the Greek psilos - "smooth" and melas - "black."

[110] ***Romanechite***: Romaneche, 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: $KMn^{4+}_6Mn^{2+}_2O_{16}$.

*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.

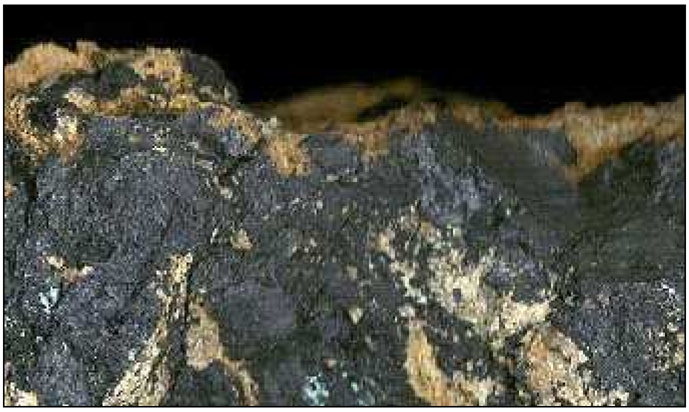


*Fig. 4.25. Psilomelane.*

## IV.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 |
|---|---|---|---|---|
| Sulfides | Monosulfides | 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, cinnaber | Galena is the only important Pb-ore |
| | | Covellite structure | covellite | Minor Cu-ore. Widespread alteration product of chalcopyrite. First discovered natural superconductor |
| | Disulfides | Molybdenite structure | molybdenite | |
| | | Pyrite structure | pyrite-subgroup, cobaltite-subgroup, gersdoffite-subgroup, ullmanite-subgroup | Very extensive group. Many sulfide 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., ulvospinel | |
| | | Inverse spinel | magnetite, chromite | Magnetite and chromite are important ore minerals for respectively Fe and Cr. Magnetite is the archetypical cubic *ferrimagnet* |
| | 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, diaspore | Important minerals in respectively iron oxides and bauxites. Boehmite has also many industrial applications. |
| | Mn-oxyhydroxides | | Cryptomelane, romanechite, “psilomelane” | Common in many Mn-ores |

## IV.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.

# Chapter V. Coal

**By Dr. K.H.A.A. Wolf**

## V.1. Preface

This chapter deals with all aspects of coal in general, i.e.:

- Environment of deposition,
- Coal Petrography
- Coalification,
- Technical analysis
- Coking
- Exploration and Exploitation
- Reserves
- Literature

This text is associated to a series of presentations on Blackboard. Both notes and ppt-files are supposed to be used for your exam.

## V.2. A General Introduction

Coal is a mineral which is classified as a biogene sedimentary rock in the group of sedimentary hydro-carbons. It is a combustible, black rock consisting mainly of carbon. It is created out of vegetation that accumulated in mostly swamp type environments over millions of years. In the nature coal is present in geological formations varying in age from Carboniferous till Miocene. In Northwestern Europe, productive coal seams are mostly of Carboniferous or Pensylvanian age (ca $300x10^6$ year). Brown coal or lignites are usually present in formations younger than the Cretaceous sub-era (< ca $65x10^6$ year). During the Carboniferous and other warm periods, the earth's climate was extremely favorable for plant growth, often situated in stagnant swamps. These were low in oxygen and as a result reduced decomposition, creating carbon accumulations. In due course, sea rise and/or subsidence submerged swamps at (ir)regular intervals and covered them with sand, clay and other debris. Over eons of burial history, the organic material was heated up and compacted under the weight of the overlying sediments, which slowly transformed it from peat, through brown coal, via bituminous coal to anthracite.

The quality of each coal deposit is determined by temperature and pressure and by the length of time in formation, which is referred to as its ‘organic maturity’. Initially the peat is converted into lignite or ‘brown coal’ – these are coal-types with low organic maturity. In comparison to other coals, lignite is quite soft and its color can range from dark black to various shades of brown. Over many more millions of years, the continuing effects of temperature and pressure produces further change in the lignite, progressively increasing its organic maturity and transforming it into the range known as ‘sub-bituminous’ coals. Further chemical and physical changes occur until these coals became harder and blacker, forming the ‘bituminous’ or ‘hard coals’. Under the right conditions, the progressive increase in the organic maturity can continue, finally forming anthracite.

## *V.3. Original environments of deposition of coal*

(This chapter consists for a major part of excerpts of L.Thomas, Coal Geology, 2005)

Coals are the result of the accumulation of vegetation debris in specific depositional environments. Buildup of these debris have been affected by synsedimentary and postsedimentary events first to create very carbon accumulations and later to produce coal seams of differing rank and degrees of structural complexity. Sedimentary successions of different era and geographical areas show comparable lithological structures. The origin of coal has been studied for over a century and a variety of models exist. They all try to classify the depositional environment. However, it is difficult to provide an acceptable clarification for the lateral continuity, cyclic nature and physical and chemical features of coal and coal sequences.

As mentioned before, peat is the source for coal. Fundamentals for the growth of thick peat deposits are (from Diessel, 1992):

- a slow continuous rise of the groundwater table which maintains a more or less constant relationship between the water table and the upper surface of the peat deposit, that is, effectively, subsidence;
- protection of the mire (by beaches, sand bars and the like) against major and prolonged flooding by the sea, and by natural levees against river flood-waters; and
- physiographic and other conditions affecting the supply of sediments which allow peat to form over prolonged periods without interruption by the deposition of fluviatile sediments.

If the groundwater table rises too quickly, either because of rapid subsidence or, in paralic settings, because of a combination of subsidence and eustatic sea-level rise, the mire will be drowned or limnic or marine sediments will be deposited. If subsidence is too slow, the plant material on the surface will rot and the peat which has already formed will be eroded. Seam formation thus depends on the relationships between paleogeography and tectonic movements within the sedimentary area.

Hence, peat formation depends on permanent present stagnant groundwater, above or close to the ground surface so that accumulated plant material will not decompose. These conditions occur most commonly in coastal flatlands where sea water dams up fresh water coming off the land. Therefore, most swamps are associated with sea coasts or the shores of large inland lakes. Depending on their geographical position at the time of deposition, coal deposits are referred to as paralic (close to the sea coast) or limnic (inland). It should be emphasized that it is rare for coals to be entirely paralic or entirely limnic in character, usually they are a mixture of transitional types.

Diessel (1992) lists some twenty coalproducing environments within the following groups:

- the braid plain
- the alluvial valley and upper delta plain the lower delta plain
- the barrier beach/strand plain system, and the estuary.

The coals formed in each of these systems tend to occur in seams of characteristic form and distribution, and to have properties related to their depositional environment. For example; many coal seams deposited in lower delta plains are characterized by large extent and thickness and by association with shales, whereas seams deposited in upper delta plains (within inter-channel areas) are discontinuous, of variable thickness and often associated with sandstones.

The recognition of depositional models to explain the origin of coal-bearing sequences and their relationship to surrounding sediments has been achieved by a comparison of the environments under which modern peats are formed and ancient sequences containing coals. The traditional depositional model was based on the “cyclothem”, a series of lithotypes occurring in repeated 'cycles'. This concept has been modified to a model that relates lateral and vertical sequential changes to depositional settings that have been recognized in modern fluvial, deltaic and coastal barrier systems.

Apart from rank, which is governed by burial and subsequent tectonic history, the remaining properties are determined by factors controlling the mire where the peat originally formed. These factors include type of mire, type(s) of vegetation, growth rate, degree of humification, base-level changes, and rate of clastic sediment input (McCabe and Parrish 1992). About 3% of the earth's surface is covered by peat, totaling 310 million hectares (World Energy Council 1998). This includes the tropical peats, (>1 m thick) of Southeast Asia which cover almost 200 000 km2.

Diessel (1992) divides peat-producing wetlands into ombrogenous peatlands or mires (owing their origin to rainfall) and topogenous peatlands, (owing their origin to a place and its surface/groundwater regime). A great variety of topogenous peats, form when waterlogging of vegetation is caused by groundwater, but ombrogenous pears are of greater extent but less varied in character. The inorganic content of mires is seen to increase in the topogenous rheotrophic mires. The classification of the two hydrological categories of mire lists a number of widely used terms. Moore (1987) has defined a number of these:

- *Mire* is now accepted as a general term for peat-forming ecosystems of all types.
- *Bog* is generally confined to ombrotrophic peat-forming ecosystems.
- *Bog forest* consists of ombrotrophic forested vegetation, usually an upper storey of coniferous trees and a ground layer of *sphagnum moss.*
- *Marsh* is an imprecise term used to denote wetlands characterized by loating vegetation of different kinds including reeds and sedges, but controlled by rheotrophic hydrology.
- *Fen* is a rheotrophic ecosystem in which the dry season water table may be below the surface of the peat.

- *Swamps* are a rheotrophic ecosystem in which the dry season water table is almost always above the surface of the sediment. It is an aquatic ecosystem dominated by emergent vegetation.
- *Floating swamps* develop around the fringes of lakes and estuaries and extend out over open water. These platforms can be thick and extensive particularly in tropical areas.
- *Swamp forest* is a specific type of swamp in which trees are an important constituent, e.g. mangrove swamps.

The resultant characteristics of coals are primarily influenced by the following factors during peat formation:

- type of deposition,
- the peat-forming plant communities,
- the nutrient supply,
- acidity,
- bacterial activity,
- temperature and
- redox potential.

In order for a mire to build up and for peat to accumulate, the following equation must balance.

$$\textit{Inflow} + \textit{Precipitation} = \textit{Outflow} + \textit{Evapotranspiration} + \textit{Retention}$$

The conditions necessary for peat accumulation are therefore a balance between plant production and organic decay. Both area function of climate, plant production and organic decay; such decay of plant material within the peat profile is known as humification. The upper part of the peat profile is subject to fluctuations in the water table and is where humification is most active. The preservation of organic matter requires rapid burial or anoxic conditions (McCabe and Parrish 1992), the latter being present in the waterlogged section of the peat profile. In addition, an organic-rich system will become anoxic faster than an organic-poor one as the decay process consumes oxygen. This process is influenced by higher temperatures, decay rates being fastest in hot climates. Rates of humification are also affected by the acidity of the groundwater, as high acidity suppresses microbial activity in the peat.

Peat formation can be initiated by:

- terrestrialisation, which is the replacement, due to the setting up of a body of water (pond, lake, lagoon, interdistributary bay) by a mire;
- paludification, which is the replacement of dry land by a mire, e.g. due to a rising groundwater table.

As peat is relatively impermeable, its growth may progressively impede drainage over wide areas, so that low-lying mires may become very extensive. In those areas where annual precipitation exceeds evaporation, and where there are no long dry periods, a raised mire may develop. Such mires are able to build upwards because they maintain their own water table. The progression of a peat-forming environment from the infilling of a watercourse or lake, to a low-lying mire and finally to a raised mire should produce zonation in the peat accumulated.

## *V.4. Coal Petrography*

Coal petrology (or coal petrography) is the study of the organic and inorganic constituents of coal and their transformation via metamorphism. Coal petrology is applied to the studies of the depositional environments of coals, correlation of coals for geological studies, and the investigation of coals for their industrial utilization. Traditionally, the latter has been dominated by the use of coal petrology in the optimization of coal blends for the production of metallurgical coke, but can also include the use of petrology in evaluating coals for beneficiation (coal preparation for downstream utilization) and combustion. Recently, significance of coal petrology has been demonstrated in coalbed methane exploration and in potential $CO_2$ sequestration into the coal seams. Techniques developed in the study of coal are also used in the investigation of organic-rich rocks to evaluate source rocks in petroleum and natural gas exploration.

Coal is the product of the deposition of the peat, its degradation (for example, by insects or micro-organisms), selective preservation of the surface litter; the growth of roots though the peat; the subsurface action of aerobic and anaerobic micro-organisms; and the metamorphic changes of this organic mass through time. The organic constituents in coal and non-coal organic-rich rocks are termed macerals (in the broader sense, and particularly for dispersed organic material, the term kerogen is also used). By convention, maceral names always have an “*-inite*” suffix.

*Macerals are the (optical) microscopically identifiable constituents in coal, somewhat analogous to minerals in an inorganic rock.*

Macerals are generally divided into:

- the vitrinite group, or huminite in lower rank coals;
- the inertinite group, and;
- the liptinite or exinite group.

### V.4.1. The huminite/vitrinite group

Huminite/vitrinite macerals are derived from humic substances, the alteration products of lignin and cellulose. Huminite refers to macerals in lignite and subbituminous rank coals and vitrinite to maceral of bituminous and anthracitic ranks. The distinction of huminite with vitrinite is based on the textural and physical changes associated with gelification. *Huminite* is divided into three subgroups based on the texture/morphology of the maceral:

- Telohuminite, with constituent macerals textinite and ulminite, the recognizably textured huminite macerals;

- detrohuminite, with macerals attrinite and densinite, the detrital huminite macerals; and
- gelohuminite, with macerals corpohuminite and gelinite,

Huminite macerals showing some degree of gelification.

*Vitrinite* follows a comparable division:

- the telovitrinite subgroup, with constituent macerals telinite and collotelinite;
- the detrovitrinite subgroup, with macerals vitrodetrinite and collodetrinite; and
- the gelovitrinite subgroup, with macerals corpogelinite and gelinite.

Inertinite macerals are, to a normally derived from the same starting materials as the huminite/vitrinite macerals.

## V.4.2. The inertinite group

In contradiction of vitrinite/huminite group, the inertinites have been oxidized at high temperatures and/or by fire. This is assumed to be the most important cause of their formation. The following macerals present:

- *The macerals fusinite and semifusinite*: They are the products of such oxidation and, in most coals, are the most abundant inertinite macerals.
- *Secretinite:* It is a product of the oxidation of plant secretions.
- *Macrinite*: It is complex, since it is partly confused with now understand as to be secretinite. Many proposals are under discussion for a macrinite division sensu stricto.
- *Funginite*: It has a fungus type origin and it is grouped with inertinites derived from plant cells. Fungi, however include two distinct eukaryote kingdoms, Fungi and Protoctista-kingdom slime molds.
- *Micrinite*: It is a secondary maceral derived from the decomposition of hydrogen-rich liptinites.

## V.4.3. The liptinite or exinite group

The liptinite or exinite maceral group stem from hydrogen-rich plant parts, i.e.:

- From sporopollenin, cutin, suberin, resin, wax, etc.;
- from the bacterial degradation products of carbohydrates, cellulose, and proteins; and
- from algae.

The maceral names of certain liptinite group macerals follow the *origin of the maceral*:

- sporinite,
- cutinite,

- suberinite,
- resinite,
- alginite.

*Secondary macerals* can develop from the liptinite, for example:

- the fracture-filling exsudatinite, basically a variety of resinite, and;
- fluorinite, a derivative of elemental oils.

### V.4.4. Coal petrographical nomenclature

The nomenclature follows the scale of the observation:

- macerals: components of the microscopic level of the texture as discussed previously.
- microlithotypes: microscopic assemblages defined as smaller than 50 μm.
    - The microlithotypes, all with the suffix "-ite," are the monomaceral assemblages (vitrite, inertite, and liptite);
    - the bimaceral assemblages (clarite [vitrinite + liptinite], durite [inertinite + liptinite], and vitrinertite [vitrinite + inertinite];
    - the trimaceral assemblages (duroclarite [vitrinite dominant], clarodurite [inertinite dominant], and vitrinertoliptite [liptinite dominant]); and the mineral-richcarbominerites.
- megascopic scale assemblages of microlithotypes: these lithotypes all have an "-ain" suffix (e.g., vitrain, clarain, durain, fusain) and they are the assemblages of microlithotypes.
- Inorganic elements can be included in coal in minerals or as elements incorporated in the organic structure of macerals. For example; the incorporation of sulfur into macerals as "organic sulfur." Minerals can be added into the peat during sedimentation, but also during epigenetic or metamorphic processes. Other commoninorganic minerals are clay minerals, quartz, calcite, siderite, and pyrite/marcasite.

## *V.5. Coalification*

Coal metamorphism is the effect of burial (predominantly due to the dewatering from peat to lignite to subbituminous) and increase in temperatures (burial at different geothermal gradients, thermal water/brine influx and occasionally contact metamorphism near igneous intrusions). Chemical parameters are used to delineate coal rank:

- At lower ranks, the equilibrium moisture is used as a measure of coalification.
- In bituminous coals, heating value, carbon, and volatile matter, both as defined by standards are applied.
- At higher ranks, the measurement of hydrogen content.

The coal rank series, from the minimum to the maximum degree of metamorphism, is:

- peat,
- lignite,
- subbituminous,
- high volatile bituminous,
- medium volatile bituminous,
- low volatile bituminous,
- semi-anthracite,
- anthracite, and, meta-anthracite.

The degree of change undergone by a coal as it matures from peat to anthracite (known as coalification) has an important bearing on its physical and chemical properties. Low rank coals, such as lignite and sub-bituminous coals are typically softer, friable materials with a dull, earthy appearance. They are characterized by high moisture levels and low carbon content, and therefore a low energy content. Higher rank coals are generally harder and stronger and often have a black vitreous luster. They contain more carbon, have lower moisture content, and produce more energy. Anthracite is at the top of the rank scale and has a correspondingly higher carbon and energy content and a lower level of moisture.

### V.5.1.Coal microscopy

The intensity of the luster is caused by the presence of vitrinite. Petrographers use the vitrinite reflectance method by using a reflected-light microscope, oil-immersion optics, and a 546-nm band pass filter, as a broad standard. Vitrinite reflectance is also used in the evaluation of organic-rich petroleum source rocks. Coal petrography techniques are the basic tool in determining the maceral- and microlithotypes.

## *V.6. Coal characterization for utilization*

Coal can be classified according to many criteria depending on the background of its use. For example; In relation to the exploitation of coal, an international classification of coal makes the difference between hard coal and brown coal:

- Hard coal has a caloric value (combustion energy) of 23,8 MJ/kg or higher;
- Brown coal or lignite has a maximum caloric value of less than 23,8 MJ/kg.

Another often used classification is the difference between:

- steam coal, which is suitable under steam boilers, and;
- cokes coal, a solid carbonaceous material derived from destructive distillation of low ash and low sulfur bituminous coal. This coal type is used in metallurgical processes.

## *V.7. Coal quality*

Other, more mineralogical and petrographical qualities of coal characterize the quality of coal for various purposes, such as:

- Application: Is the coal good enough to be used as steam coal, or;
- Is the “dirty component” not to high, i.e. environmental effects (SOx, NOx, etc.);
- Is the carbon component sufficient for the production of coke coal;
- What is the ash content (non-caloric part of the coal).

### V.7.1. How to analyze coal properties

First of all coal analyses can be presented in the form of “proximate” and “ultimate” analyses, whose analytical conditions are prescribed by organizations such as the ASTM.

- The parameters of proximate analysis are moisture, volatile matter, ash, and fixed carbon. (Fixed carbon is the material, other than ash, that does not vaporize when heated in the absence of air.)
- Ultimate analysis covers the quantitative determination of carbon, hydrogen, nitrogen, sulfur and oxygen within the coal.

One also has to know what type of coal has been analyzed. The following definitions are used at the basis of an analysis:

- As Received (ar): includes Total Moisture (TM)
- Air Dried (ad): includes Inherent Moisture (IM) only
- Dry Basis (db): excludes all Moisture
- Dry Ash Free (daf): excludes all Moisture & Ash

The Proximate Analysis of coal ( thus, the (%) content of Moisture, Ash (A), Volatile Matter (VM), Fixed Carbon (FC), Sulfur (S) and Calorific Value (CV) can be expressed on any of the above bases.

So criteria for the choice of coal quality for a specific purpose or installation are standardized in procedures. Distinguished in coal are:

- Caloric value
- Humidity
- Volatile matter
- Sulfur content
- Ash content
- Baking properties: Volatile constituents of coal (water, coal-gas and coal-tar) are removed in airless ovens at temperatures as high as 2000°C.
- Hardness

### V.7.2. Caloric value

The amount of created energy per mass-unit of coal. This varies from about 14 to 38 MJ/kg.

### V.7.3. Humidity or moisture

Coal contains inherent fluids in the micro-pores, mostly consisting of water, varying from a few wt.% in anthracite up to more than 50 wt.% in lignites. Also free water is present in the cleat system. This water can be fresh but also may contain high concentrations of salts and other components. The composition primarily depends on the environment of deposition and burial history. Further ground water flow (i.e. climate conditions) and human intervention (i.e mining/exploration) exert influence on the composition. Groundwater and other extraneous moisture are known as *adventitious moisture* and are readily evaporated. Moisture held within the coal itself is known as *inherent moisture* and is analyzed. Moisture may occur in four possible forms within coal:

- *Surface moisture*: water held on the surface of coal particles or macerals
- *Hydroscopic moisture*: water held by capillary action within the micro fractures of the coal
- *Decomposition moisture*: water held within the coal's decomposed organic compounds
- *Mineral moisture*: water which comprises part of the crystal structure of hydrous silicates such as clays

Total moisture is analyzed by loss of mass between an untreated sample and the sample once analyzed. This is achieved by any of the following methods;

- Heating the coal with toluene
- Drying in a minimum free-space oven at 150 °C within a nitrogen atmosphere
- Drying in air at 100 to 105 °C and relative loss of mass determined

The first two methods are suitable with low-rank coals but the last one is only suitable for high-rank coals as free air drying low-rank coals may promote oxidation. Inherent moisture is analyzed similarly, though it may be done in a vacuum.

### V.7.4. Volatile matter.

The volatile components consist of light hydro-carbons is usually a mixture of short and long chain hydrocarbons, aromatic hydrocarbons and some sulfur, i.e.; methane and ethane, hydrogen, carbon monoxide, carbon dioxide and minor amounts of sulfur oxide. A part of these components is inflammable. The amount of volatile matter varies with depth and maceral composition. In coalbed methane exploration, up to 30 $m^3$ methane per ton of coal is not uncommon. However, gases may also migrate during the burial history and create gasfields such as the Groningen gasfield. The gas content has also to be considered in the development of a boiler or furnace. For these purposes coals are also divided in Germany in Gaskohle and Flammkohle.

The volatile matter of coal is determined under rigidly controlled standards. In Australian and British laboratories this involves heating the coal sample to 900 ± 5 °C for 7 minutes in a cylindrical silica crucible in a muffle furnace. American Standard procedures involve heating to 950 ± 25 °C in a vertical platinum crucible. These two methods give different results and thus the method used must be stated. Coal is also assayed for oxygen content, hydrogen content and sulfur.

### V.7.5. Sulfur content

Sulfur is mainly associated to pyrite ($FeS_2$), gypsum ($CaSO_4.n(H_2O)$ or biochemically associated with organic compounds. The sulfur content is usually in between 0.2 to 10 wt.%, with less than 1 wt.% named “low sulfur” and more than 2.5 wt.% as “high sulfur” coal. Sulfur is analysed on whether it is a sulfide mineral or a sulfate. This is done by dissolution of the sulfates in hydrochloric acid and precipitation as barium sulfate. Sulfide content is measured with the iron content, here thus as the amount of iron in pyrite.

### *V.7.6. Ash content*

Ash is the remnant of coal after combustion, or the non-combustible residue. It represents the bulk mineral matter after carbon, oxygen, sulfur and water (including from clays) has been driven off during combustion. In commercial coal it varies from 3 to 20 wt.%. Analysis is quite straightforward, with the coal thoroughly burnt and the ash material expressed as a percentage of the original weight. Carbonate minerals are analysed by measuring the amount of carbon dioxide emitted when the coal is treated with hydrochloric acid. The carbonate content is necessary to determine the combustible part and incombustible part (carbonate carbon) of the carbon content. Chlorine, phosphorus and iron are also determined to characterize the coal's suitability for steel manufacture. An analysis of coal ash may also be carried out to determine not only the composition of coal ash, but also to determine the levels at which trace elements occur in ash. These data are useful for environmental impact modeling, and may be obtained by spectroscopic methods such as ICP-OES or AAS

In general the caloric value is of importance and increase of ash content increases the costs for transport, storage and processing (grinding, etc.). Pre-processing and removal of ash from coal often occurs during the washing procedures at the mine site. However, in some heating processes, as in fluidized bed combustion, the ash component is an advantage since it helps to increase the heat capacity of the heating medium. In other cases the ash may cause sintering and clogging in the furnace. All coal fired installations are developed and constructed according with in mind the use of specific coal types! After combustion fly ash has to be removed from the flue gas with special filtering techniques. Sintered rock, or slag, remains as a viscous or solid substance, which has to be removed from the bottom of the furnace (examples: iron/steel/steamproduction).

## V.7.7. Fixed carbon content

The fixed carbon content of the coal is the carbon found in the material which is left after volatile materials are driven off. This differs from the ultimate carbon content of the coal because some carbon is lost in hydrocarbons with the volatiles. Fixed carbon is used as an estimate of the amount of coke that will be yielded from a sample of coal. Fixed carbon is determined by removing the mass of volatiles determined by the volatility test, above, from the original mass of the coal sample.

*Summary of coal composition*

| Coal rank | Humidity [%] | C-content [%] | Volatile matter [%] | Caloric upper value [MJ/kg] | Caloric upper value [Btu/lb] 1) |
|---|---|---|---|---|---|
| Lignite | 30–50 | < 40 | - | 14–19 | 7000 |
| Subbituminous | 20–30 | 40–60 | - | 19–24 | 9000 |
| Bituminous | 2–15 | 50–86 | 14–50 | 24–32 | 12000 |
| Anthracite | < 2 | 86–98 | 2–14 | 32–38 | >12000 |

1) British thermal unit per pound; 1 Btu/lb is ca. 2.32 kJ/kg.

## V.7.8 .Calorific value Q

The calorific value Q of coal is the heat liberated by its complete combustion with oxygen. *Q* is a complex function of the elemental composition of the coal. *Q* can be determined experimentally using calorimeters. *Q* is given in kilojoules per kilogram.

## V.7.9. Baking properties

During heating of coal, its texture and structure changes. Depending on the texture and chemical composition coal may start to swell, particles start to be viscous and start to stick together (baking). In some coal conversion techniques baking coals cannot be used as a heating source. In general, the swelling and baking behavior increases with carbon content.

## V.7.10. Hardness

Preparation of coal for transport or for commercial operations is common. Crushing to fine powder (pulverizing) is essential for feeding into a boiler. Easiness of pulverization depends on the coal strength, which is measured by the Hardgrove grindability index (HGI, *Hardgrove* °H ). Harness increases with decrease in °H-value. Most coals have values in between 45°H and 70°H. Hardness is also associated to physical and mechanical properties of coal, as explained in the subsequent section.

## *V.8I. Physical and mechanical properties of coal*

### V.8.1.Relative density

Relative density or specific gravity of the coal depends on the rank of the coal and degree of mineral impurity. Knowledge of the density of each coal ply is necessary to determine the properties of composites and blends. The density of the coal seam is necessary for conversion of resources into reserves. It is determined by the loss of a sample's weight in water. This is best achieved using finely ground coal, since bulk samples are porous.

### V.8.2.Particle size distribution

The particle size distribution of milled coal depends partly on the coal rank of the coal. It gives an picture of its brittleness, and on the handling, crushing and milling it has undergone. Coal for furnaces and coking ovens need to have specified sizes. Therefore the crushability must be established and its behavior quantified. Before mining these data must be known so that crushing machinery can be prepared for the required particle size for transport and use.

### V.8.3. Float-sink test

Coal blocks and particles have different densities due to variation in vitrinite- and mineral content, rank and porosity. Coal is washed by passing it over a bath of liquid of known density, which removes high-ash content particles and increases the salability of the coal as well as its energy content per unit volume. Therefore, coals are subjected to a float-sink test in the laboratory. Here the optimum particle size for washing and the best density of the wash liquid are determined to remove maximum ash with a minimum of work.

### V.8.4. Abrasion testing

It is already mentioned in relation to *Hardness*. Abrasion is the property of the coal which describes its propensity and ability to wear away machinery and undergo autonomous grinding. While carbonaceous matter in coal is relatively soft, quartz and other mineral constituents in coal are quite abrasive. This is tested in a calibrated mill, containing four blades of known mass. The coal is agitated in the mill for 12,000 revolutions at a rate of 1,500 revolutions per minute. The abrasion index is determined by measuring the loss of mass of the four metal blades.

## *V.9. Special combustion tests*

In relation to the previously mentioned *Calorific value Q* and *Baking Properties* of coal, a series of combustion tests have been developed.

### V.9.1. Specific energy

Aside from physical or chemical analyses to determine the handling and pollutant profile of a coal, the energy output of a coal is determined using a bomb calorimeter which measures the specific energy output of a coal during complete combustion. This is required particularly for coals used in steam-raising.

### V.9.2. Ash fusion tests

The behavior of a coal's ash residue at high temperature is a critical factor in selecting coals for steam power generation. Most furnaces are designed to remove ash as a powdery residue. Coal which has ash that fuses into a hard glassy slag known as clinker is usually unsatisfactory in furnaces as it requires cleaning. However, furnaces can be designed to handle the clinker, generally by removing it as a molten liquid. Ash fusion temperatures are determined by viewing a moulded specimen of the coal ash through an observation window in a high-temperature furnace. The ash, in the form of a cone, pyramid or cube, is heated steadily past 1000 °C to as high a temperature as possible, preferably 1600 °C. The following temperatures are recorded:

- Deformation temperature: This is reached when the corners of the mould first become rounded
- Softening (sphere) temperature: This is reached when the top of the mould takes on a spherical shape.
- Hemisphere temperature: This is reached when the entire mould takes on a hemisphere shape
- Flow (fluid) temperature: This is reached when the molten ash collapses to a flattened button on the furnace floor.

### V.9.3. Crucible swelling index (free swelling index)

The simplest test to evaluate whether a coal is suitable for production of coke is the free swelling index test. This involves heating a small sample of coal in a standardized crucible to around 800 degrees Celsius (1500 °F). After heating for a specified time, or until all volatiles are driven off, a small coke button remains in the crucible. The cross sectional profile of this coke button compared to a set of standardized profiles determines the Free Swelling Index.

## *V.10. The production of coke.*

Volatile constituents of the coal, including water, coal-gas, and coal-tar, are removed by baking in an airless oven at temperatures as high as 2,000 degrees Celsius. This fuses together the fixed carbon and residual ash. Most coke in modern facilities is produced in "by-product" coke ovens and the resultant coke is used as the main fuel in iron-making blast furnaces. Today, the hydrocarbons are considered to be by-products of modern coke-making facilities (though they are usually captured and used to produce valuable products). Non by-product coke ovens burn the hydrocarbon off gasses produced by the coke making process to drive the carbonization process.

## *V.11. Distribution and transport of coal*

After winning, the coal is transported from the mine by bulk transporters, such as a ship, train or by slurry pipe line. After transshipment on a central point, it is blended and distributed. Costs for coal can roughly be divided in:
35-45% for mining, 15-30% free on board (fob) delivery, 20-30% for costs for insurance of the fright (cif), 2% for ex-ship and 3% for transhipment to the customer.

The variety in within the cost structure depends on:

- Way of mining (open pit, sub-surface)
- Transport option from the exporting region (Rail, river, harbour capacity for ship size, etc.);
- Distances for transport;
- Market price.

Coal transport for the Northwest Europe is mostly carried out with ships with a tonnage of about 50000 to 250000 tons. After transhipment coal can be transported in various ways however, river transport is the cheapest for distances over more than 40 km. The United States, the former Soviet Union, China and India have the largest reserves of coal, but large deposits also exist in South Africa, Australia Germany and Eastern Europe. Canada has about 0.6% of worldwide coal reserves and these are concentrated in western Canada.

From an environmental point of view, river transport is preferred. One push tug with four barges transports in 1.5 hours as much as a 2000-tons train per 20 minutes or two 25-tons lorries per minute.

## *V.12 References*

Diessel, C.F.K. (1992) Coal Bearing Depositional Systems. Springer Verlag, Berlin, 721 pp.

McCabe, P.J. and Parrish, J.T. (1992) Tectonic and climatic controls on the distribution and quality of Cretaceous coals, in McCabe, P.J., and Parrish, J.T., eds., Controls on the Distribution and Quality of Cretaceous Coals: Geological Society of America Special Paper 267, p. 1-15.

Thomas, L. (2005) Coal Geology, John Wiley and Sons, Ltd. 384 pp.