

TARAS SHEVCHENKO NATIONAL UNIVERSITY OF KYIV

Institute of Geology
Department: Geology of mineral deposits

Hrinchenko O.V.

THEORY OF ORE FORMATION

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Рецензенти:

Дубина О.В., Доктор наук, доцент; Київський національний університет імені Тараса Шевченка

Бондаренко С.М., Кандидат геологічних наук, старший науковий співробітник; Інститут геохімії, мінералогії та рудоутворення, НАН України.

Грінченко О.В.

ТЕОРІЯ РУДОУТВОРЕННЯ

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Розглядаються поняття про рудогенез та особливості утворення головних типів родовищ корисних копалин. Наведені данні про сучасні класифікації родовищ корисних копалин з описом головних критеріїв розподілу родовищ на класи – структурний контроль, морфологія рудних покладів, співвідношення з вмисними породами, типи мінералізації, генетичні чинники та особливості прояву рудоформувальних процесів.

В розділах навчального посібника охарактеризовані головні геологічні процеси, що спричиняють утворення родовищ корисних копалин магматогенного, гідротермального (постмагматичного) та осадового генезису. Надаються відомості про головні фактори магматогенного (кристалізаційна диференціація, ліквіація, фільтр-пресинг), гідротермального (джерела водних флюїдів, розчинення та перенос рудних компонентів у водних флюїдах, рудовідкладання), приповерхневого (залишкова концентрація, приповерхневе/вторинне збагачення) та осадового (кластогенна, хемогенна та біогенна седиментація) рудогенезу.

Надається класифікація родовищ корисних копалин з визначенням та коротким описом головних їх типів. Коротко охарактеризовані економічні аспекти корисних копалин та закономірності поширення їх у просторі та часі.

Для студентів які навчаються на другому і третьому рівнях вищої освіти за програмами спеціальностей Науки про Землю, а також фахівців і викладачів.

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Автор:

Грінченко О.В., кандидат геолого-мінералогічних наук, доцент кафедри геології родовищ корисних копалин

TABLE OF CONTENTS

Introduction	5
Part 1. Formation and interpretation of mineral deposits	
1.1 Mineral deposit classification	
(1) Relation to host rocks	7
(2) Geographic localization.....	8
(3) Occurrence depth.....	9
(4) Structural control.....	9
(5) Mineralization style	10
(6) Morphology	11
(7) Genetic features and ore-forming processes.....	12
1.2. Nature of minerals	
(1) Classification of ore minerals.....	14
(2) Mineral grain size.....	16
1.3. Mineral economics	
(1) Ore-grade and tonnage.....	17
(2) Mineral resources and ore reserves.....	18
1.4. Distribution of mineral deposits	
Mineral deposits and plate tectonics	22
Part 2. Magmatic ore formation	
2.1. Magma types and metallogeny.....	24
2.2. Magmatic ore-forming processes	
(1) Fractional crystallization.....	29
(2) Liquid immiscibility.....	31
(3) Filter pressing.....	32
2.3 Magmatic type deposits	
(1) Chromite deposits.....	33
(2) Nickel (copper) sulfide deposits	35
(3) Platinum Group Element (PGE) deposits	37
(4) Diamond deposits.....	38
(5) Carbonatite associated deposits.....	40
(6) Pegmatite deposits	41
Part 3. Hydrothermal ore formation	
3.1 Hydrothermal ore-forming processes	
(1) Water properties	45
(2) Factors essential of hydrothermal ore formation.....	46
3.2 Hydrothermal type deposits	
(A) Metasomatic-hydrothermal:	
(1) Greisen and albitite deposits	51
(2) Skarn deposits.....	53
(B) Magmatic-hydrothermal:	
(3) Porphyry deposits.....	55
(4) Volcanogenic Massive Sulfide (VMS) deposits	57
(5) Iron Oxide Copper Gold (IOCG) deposits.....	59

(C) Sedimentary-hydrothermal:	
(6) Sedimentary Exhalative (SEDEX) deposits.....	60
(7) Mississippi Valley Type (MVT) deposits	62
(8) Stratiform Sediment-hosted Copper (SSC) deposits.....	63

Part 4. Surficial and sedimentary ore formation

4.1 Surficial and sedimentary ore-forming processes	
(A) Weathering:	
(1) Residual concentration	66
(2) Supergene enrichment	68
(B) Sedimentation:	
(3) Clastic sedimentation.....	69
(4) Chemical precipitation	70
(C) Fossil fuel formation.....	70
4.2 Surficial type deposits	
(1) Bauxites.....	72
(2) Ni laterites.....	73
(3) Supergene copper deposits.....	74
4.3 Sedimentary type deposits	
(4) Placer deposits	75
(5) Ironstones and Banded Iron Formations.....	76
(6) Manganese deposits	79
(7) Phosphorites.....	81
(8) Evaporites and Li-brines	82
4.4 Fossil fuels	
(1) Oil and gas.....	84
(2) Peat and coal	89

References and recommended literature	92
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Introduction

Mineral deposits are economic concentrations of useful elements in the Earth's crust, from which they can be extracted at a profit. For this reason, the existence of a concentrating geological process is crucial.

There are four basic geological requirements for any ore deposit to be formed:

- 1) possible source for useful ore components;
- 2) transportation of these components to the site of ore deposit formation
- 3) deposition (accumulation) of these components in the ore body as ore minerals;
- 4) geological setting that allows to preserve ore deposit in the geologic time.

One of the most typical characteristics of mineral deposit is the association of specific ore types with certain assemblages of crustal host-rock. In general, this association represents the geological environment and processes that result in formation of mineralization.

The main aim of ore geologists is to know the nature of these ore-forming processes and to understand how these processes work within certain geological environment. This knowledge has been commonly and successfully utilized for searching new deposits.

The particular elemental composition of a mineral deposit results from a complicated interaction of favorable combinations of source, transport, and depositional variables. Thus, the type, character, and abundance of an ore deposit reflect the environment in which it was formed. It preserves evidence for the evolution of ore-forming processes and tectonic setting as well as the characteristics of the atmosphere and hydrosphere.

In order to describe and define any mineral deposits ore geologists commonly use basic terminology which is not used in other Earth's Science disciplines.

A term *mineral deposit* is used to define a several ore bodies that includes useful elements (or minerals) which average abundance is enough to have potential economic importance.

An *orebody* refers to a specific volume of material in a mineral deposit that can be mined and marketed at a reasonable profit under the prevailing conditions of commodity prices, costs, and technology.

Such terms as metallogenic maps, metallogenic provinces, and metallogenic epochs are usually used in the branch of metallogeny. *Metallogeny* is the study of the genesis of mineral deposits, with emphasis on their relationships in space and time to geological features of the Earth's crust. A *metallogenic province* may be defined as a mineralized area or region containing mineral deposits of a specific type or a group of deposits

that possess features (e.g., morphology, style of mineralization, or composition) suggesting a genetic relationship; a *metallogenic epoch* is a geological time interval of formation of one or more kinds of mineral deposits. The size of a metallogenic province can be of regional scale (e.g. Ukrainian Shield), and a metallogenic epoch can be as broad as whole geologic period (e.g. Archean period of gold greenstone mineralization).

To describe spatial and temporal relations between ores and host rocks such terms as *syngenetic* and *epigenetic* are used in genetic descriptions of mineral deposits. Syngenetic indicates that ore minerals have formed at the same time as their host rock and it is commonly used for sedimentary rocks. By contrast, epigenetic means that the ore minerals have emplaced in pre-existing host rocks (e.g., veins).

Other used terms are *hypogene* and *supergene*. The former refers to ores formed by ascending solutions, whereas the latter deals with ore formation by descending solutions, classically meteoric waters interacting with rocks during surficial weathering.

Many terms are used in relation to the shape of a mineral deposit since it is very variable, from concordant tabular and stratiform to discordant veins and breccia bodies.

Mineral deposits can be named according to different criteria. Sometimes the name of a place, region, or city is used (e.g., Alpine type, Sudbury type, Cyprus type, Mississippi Valley type). Other times the deposits are known using their acronyms (e.g., BIF means banded iron formation ores, MVT means Mississippi Valley-type lead-zinc ores, or SEDEX means sedimentary exhalative ore). In addition, the deposits may be called according to the rock type, like pegmatitic (large crystals), porphyry copper (disseminated stockwork linked to plutonic intrusives), and skarn (calc-silicate rock). Finally, deposits can be known by their shape, being the most representative example a type of uranium deposits, namely, roll-front uranium deposit.

To describe all the variety of mineral deposits different type classifications are widely used in common geological practice.

Part 1. Formation and interpretation of mineral deposits

1.1. Mineral deposit classification

There are two main classifications of mineral deposits that are widely used in the world. The first one, industrial classification is based on commodities produced as a result of mining activity with subsequent treatment of mineral raw material, whereas the other one, geological classification is made according to the ore-forming processes and ore genesis. A combination of both classifications makes it possible to describe in detail the overall characteristics of mineral deposits.

According to *industrial classification*, all mineral deposits can be grouped into three broad categories:

- (a) metallic (ore) minerals – deposits of iron, manganese, chromium, copper, lead, zinc, gold, etc.
- (b) nonmetallic (industrial) minerals – deposits of bentonites, clay, mica, fluorite, asbestos, molding sands, etc.
- (c) combustible (power) minerals – oil and gas fields, shale-oil, tight gas, tar sands, etc.

At the same time, some geologists think that industrial classification based on the commodity is geologically useless. For example, uranium deposits can occur in sandstone and in granites, but their formation processes are radically different.

The *geological classification* of mineral deposit can be based on single or multiple criteria. Among them are:

- 1) relation to host rocks
- 2) geographic localization
- 3) occurrence depth
- 4) structural control
- 5) mineralization style
- 6) morphology
- 7) genetic features and ore-forming processes.

It is unlikely for two mineral deposits to be exactly identical, but in a broad sense it will fall into one or another group or class.

(1) Relation to host rocks

Crustal rocks that can host ore deposits are commonly classified in terms of a threefold subdivision – igneous, sedimentary and metamorphic. This classification reflects the global processes active in the Earth's crust. At the same time, ores can be treated as «metallic-rich rocks» and easily attributed to igneous or sedimentary origin. Such a classification of ores also reflects the genetic process involved in their formation, since igneous and

sedimentary deposits are commonly syngenetic and formed at the same time as the host rock.

Although many ores are metamorphosed it is evident that metamorphism does not itself represent a fundamental process ore deposits are created. Hydrothermalism, however, is a viable analogue in ore-forming processes for metamorphism and also involves modification of either igneous or sedimentary rocks.

A very simple classification of ores might be made on the basis of igneous, sedimentary and hydrothermal categories. At the same time, igneous processes become magmatic-hydrothermal as intrusions cool and crystallize and sediments undergo diagenesis and metamorphism as they are progressively buried. Ore-forming processes can, therefore, span more than one of the three categories, and there is considerable overlap between igneous and hydrothermal and between sedimentary and hydrothermal. Figure 1 shows the three major categories of ore types – Igneous (Part 1), Hydrothermal (Part 2), and Sedimentary/surficial (Part 3).

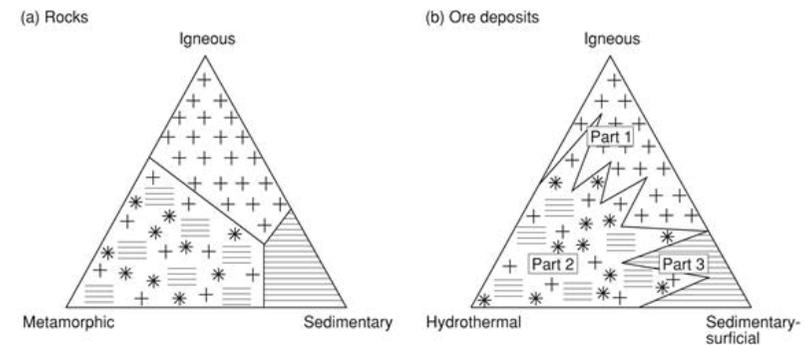


Figure 1. Classification of (a) crustal host rocks and (b) ore deposit types (after Robb, 2005).

(2) Geographic localization

Mineral deposits can be broadly described based on geographic location and dimension. There are some mineralized area that can be distinguished based on area size and regional scale.

Province or metallogenic province is a large specific area having essentially notable concentrations of certain characteristic metals or several metal assemblages or a distinctive style of mineralization to be delineated and developed as economic deposits. The metallogenic province can be formed on various processes such as plate tectonic activity, subduction, igneous intrusives, metal-rich hydrothermal solution, and expulsion of pore water enriched in metals from a sedimentary basin.

Region is similar to a province but is relatively smaller in size and controlled by stratigraphy and/or structure for the occurrence of specific mineral(s) at commercial quantity.

District is comprised of one geographical area known for the occurrence of a particular mineral.

Belt is a narrow linear stretch of land having series of deposits of associated minerals.

Deposit is a single or a group of mineral occurrences of sufficient size and grade separated by a natural barren parting.

(3) Occurrence depth

Mineral deposits can be classified based on their occurrence depth (distance from the Earth's surface).

Some mineral deposits are *exposed to the surface* and are easy to mine. There are ample possibilities of finding new «surficial» deposits but the best prospecting effort is look for fresh rock exposure.

Deposits can be covered by altered oxidized capping or exist at *shallow depth* or under thick overburden of bed rock. Geochemical prospecting and ground geophysical survey will be useful to discover deposits at shallow depths.

Because near-surface deposits are mostly discovered *deep-seated hidden deposits* is the future aim of mineral exploration. The key exploration procedures suitable for the discovery of these deposits require clear understanding of regional geologic structure, applications of high penetrative methods, and interpretation by simulation tools to identify, describe, and delineate. Exploration for such deposits is expensive and associated with considerable economic risk.

(4) Structural control

Structure and tectonics play a significant role in the passage of hydrothermal flow of mineralized fluids, accumulation and concentration at favorable locations. The features related to mineralization control are deformation, joints, fractures, folds, faults and breccia.

Most of the residual and placer deposits might be related to *undeformed* type. Many deposits show varied degrees of deformation. *Joints and fractures* caused by regional stress break in the rocks along which little or no movement has occurred. Mineralization often concentrates along these regular and irregular fracture planes.

Semiplastic deformation creates folding of strata (*fold*). The fold closure, limb zone, and axial planes are suitable for mineral localization. These mineral deposits are often folded during or after ore formation.

The joints and fractures along which noticeable movements have occurred are called *faults*. Deposits can be faulted with displacement from millimeters to kilometers. Fault zones are favorable for localization of mineralized solution as well as its movement and metal concentration.

Shear is the result of rock deformation generating particular textures like foliation, deformation, and microfolding. A *shear zone* is a wide region of distributed shearing in crushed rock mass with widths varying between a few centimeters and several kilometers. The interconnected openings of the shear zone serve as channelways for mineral-bearing solutions and subsequent formation of deposits.

Breccia is commonly used for clastic sedimentary rocks composed of large sharp-angled fragments embedded in a fine-grained matrix of smaller particles or mineral cement. The breccia generated by folding, faulting, magmatic intrusions, and similar forces is called tectonic breccia. Breccia and conglomerate are similar rocks but with a difference in the shape of larger particles due to the transportation mechanism. Igneous, flow, or pyroclastic breccias are rocks composed of angular fragments of preexisting igneous rocks of pyroclastic debris ejected by volcanic blast or pyroclastic flow.

(5) Mineralization style

The style of mineralization refers to the pattern of distribution of ore minerals in a host rock, and it varies from being very subtle (even invisible to the naked eye as in some precious metal deposits) to quite pronounced (as in the case of massive sulfide deposits).

The mineralization style is the expression of mineral formation as a natural process of different types – disseminated, massive, vein-type, stock work, and many more.

Disseminated types of mineralization are formed by crystallization of deep-seated magma. The early formed in situ metallic and nonmetallic minerals can be sparsely disseminated or scattered as fine grains throughout the host rock. As a result, ore minerals dispersed through the whole volume of host rock

Massive deposits include mineralization comprising more than 50% of the host rock. Massive deposits with more than 60% sulfides (volcanogenic massive sulfide) are formed due to accumulations on or near the sea floor in association with volcanic activity or hydrothermal emanations along with sedimentary deposition.

Mineralization in *veins* is commonly discordant to the host rock layering. Veins and lodes are tabular deposits usually formed by deposition of ore and gangue minerals in open spaces within fault, shear, and fracture

zones. Veins often have great lateral and/or depth extents but are usually of narrow width. Veins frequently pinch and swell in all directions.

Stock work types of ore deposits are characterized by a large mass of rock impregnated with a dense interlacing network of variously oriented irregular ore-bearing veins and veinlets. The stock works are formed by a group of hydrothermal systems of metal-bearing fluids from hot mineralized solutions circulating through the fissured rocks. The veins and veinlets commonly contain ore minerals. Stock work mineralization may occur as a separate body or in association with other styles.

(6) Morphology

The shapes of mineral deposits are also highly variable ranging from concordant tabular and stratiform to discordant veins and breccia bodies.

Stratiform deposits contain mineralization confined to a specific bed and, thus, broadly conformable to the layering of host rock.

Hydrothermal and volcanogenic mineralization can resemble stratification of sedimentary formation. The stratification is formed by upward-moving metal-bearing hydrothermal solution through a porous aquifer. Ore minerals are deposited in the overlying pile of sedimentary strata of shale and dolomite. These deposits may contain a significant amount of organic matter and fine pyrite.

Ore minerals in *stratabound* deposits are exclusively confined within a particular stratigraphic interval. Stratabound deposits include various orientations of mineralization representing layers, veinlets, and disseminated and alteration zones, strictly contained within the stratigraphic unit. These mineralized structures may or may not be conformable with bedding of host rocks.

Layered and bedded types of deposits are formed generally by deposition and consolidation of sediments that may be metamorphosed. The type of ore deposit will depend on the composition of the transported sediments. Layered features of mineralization can be also developed during fractional crystallization and segregation of mafic and ultramafic magma in a huge magma chamber over a prolonged time. The early crystallization, settling, and consolidation of heavy metal-rich layers is followed by late crystallization and solidification of residual magma. The process repeats with addition of fresh magmatic cycles.

Porphyry is a diversity of igneous rock consisting of large-grained crystals such as quartz and feldspar scattered in a fine-grained groundmass. The groundmass is composed of indistinguishable crystals (aphanites as in basalt) or easily distinguishable crystals (phanerites as in granite). Porphyry refers to the texture of the igneous rocks, and used as suffix after granite-,

rhyolite-, and basalt-porphyry. The porphyry deposits are formed by differentiation and cooling of a column of rising magma. The different stages of cooling create porphyritic textures in intrusive as well as in subvolcanic rocks. The process leads to a separation of dissolved metals into distinct zones responsible for forming rich deposits in the intrusive rocks.

Tabular is an ore zone that is extensive in two dimensions, but has a restricted development in its third dimension. The magmatic segregation deposits are formed by fracture filling within the host rock, and are generally irregular, roughly spherical, and more often *tabular* or *lenticular* in shape. The width/thickness ranges between a few centimeters and a few meters. The length may exceed 1 km.

Pipe-like deposits are relatively small in the horizontal dimension and extensively large in the vertical direction. Pipes may be formed by infillings of mineralized breccias in volcanic pipes. Another common type of volcanic pipe is a deep narrow cone of solidified intrusive magma represented by kimberlite or lamproite.

(7) Genetic features and ore-forming processes

The genetic classification of ore deposits is the most commonly used since it can incorporate all the above mentioned criteria (relation to host rocks, geographic localization, occurrence depth, etc.) which other classifications might be based on. These classifications make it possible to create predictive geological models that can be used to search for geological environments in which appropriate ore-forming processes have possibly operated.

A simplified genetic classification encompassing all ore deposit types is shown in Figure 2. This scheme highlights the broad categories of ore-forming processes and the later overprints that may affect the deposits. Deposits can also be broadly subdivided into syngenetic (formed with the enclosing rocks) and epigenetic (introduced into pre-existing rocks). Deposit form and geometry can vary greatly but, in many cases, these features also reflect the nature of the ore-forming process. Thus, hydrothermal deposits show forms related to the geometry of the fluid channelways (e.g., veins or stockworks along fractures). Syngenetic deposits are commonly stratabound (i.e., confined to a particular stratigraphic layer or unit) or stratiform (i.e., confined to the stratigraphy and internally stratified or layered).

Many geologists believe that linking of deposit types directly to ore-forming processes and genesis is the preferred way to classify. Because it provides better criteria for understanding the deposits with respect to

associated features such as its association with igneous rock suites, alteration patterns, etc. This will also lead to creation of more efficient exploration models for their discovery and evaluation.

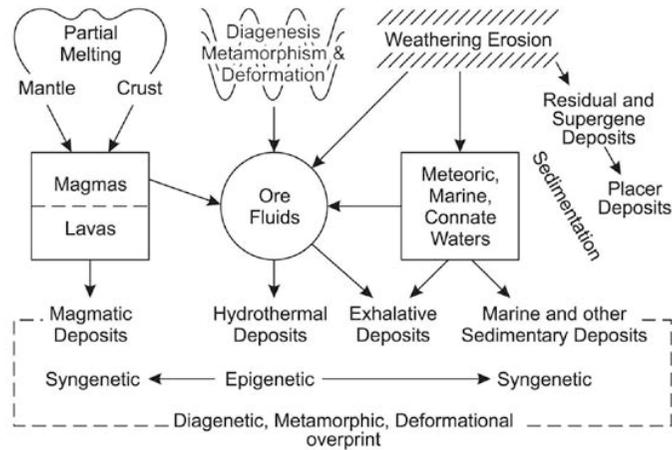


Figure 2. Genetic classification of ore deposits (after Arndt, 2012).

1.2. Nature of minerals

(1) Classification of ore minerals

There are about 4000 known minerals that have been identified and classified. Only a very small proportion of these make up the bulk of the Earth's crust, as the common rock forming minerals. Likewise, a relatively small number of minerals make up most of the economically viable ore deposits.

Each deposit comprises useful part represented by orebodies (ore minerals) and waste part represented by host rocks (or gangue). Ore deposit can also include some accessory minerals that are described as ore minerals (e.g., pyrite, arsenopyrite, magnetite), although they constitute part of the gangue.

All known ore minerals can be subdivided in terms of chemical classes based essentially on the anionic part of the mineral formula. They can be classified into six classes – namely (1) native elements, (2) halides, (3) sulfide and sulfo-salts, (4) oxides and hydroxides, (5) oxy-salts (such as carbonates, phosphates, tungstates, sulfates), and (6) silicates.

(1) Native elements

Both metals and non-metals exist in nature in the native form, where essentially only one element exists in the structure. Copper, silver, gold, and platinum are all characterized by cubic close packing of atoms, have high densities, and are malleable and soft. The carbon atoms in diamond are linked in tetrahedral groups forming well cleaved, very hard, translucent crystals. Sulfur occurs as rings of eight atoms and forms bipyramids or is amorphous.

(2) Halides

The halide mineral group comprises compounds made up by ionic bonding. Minerals such as halite NaCl and sylvite KCl are cubic, have simple chemical formulae, and are highly soluble in water. Halides sometimes form as ore minerals, such as chlorargyrite AgCl and atacamite $Cu_2Cl(OH)_3$.

(3) Sulfides and sulfo-salts

This is a large and complex group of minerals in which bonding is both ionic and covalent in character. The sulfide group has the general formula $A_M X_p$, where X, the larger atom, is typically S but can be As, Sb, Te, Bi, or Se, and A is one or more metals. The sulfo-salts, which are much rarer than sulfides, have the general formula $A_M B_N X_p$, where A is commonly Ag, Cu, or Pb, B is commonly As, Sb, or Bi, and X is S. The sulfide and sulfo-salt

minerals are generally opaque, heavy and have a metallic to sub-metallic lustre.

This group includes such sulfides as chalcocite Cu_2S , bornite Cu_5FeS_4 , galena PbS , sphalerite ZnS , chalcopyrite CuFeS_2 , pyrrhotite Fe_{1-x}S , pentlandite $(\text{Fe},\text{Ni})_9\text{S}_8$ and others. Tetrahedrite $(\text{Cu},\text{Ag})_{12}\text{Sb}_4\text{S}_{13}$, tennantite $(\text{Cu},\text{Ag})_{12}\text{As}_4\text{S}_{13}$, and enargite Cu_3AsS_4 are known as sulfosalts.

(4) Oxides and hydroxides

This group of minerals is variable in its properties, but is characterized by one or more metal in combination with oxygen or a hydroxyl group. The oxides and hydroxides typically show ionic bonding. The oxide minerals can be hard, dense, and refractory in nature (magnetite Fe_3O_4 , cassiterite SnO_2) but can also be softer and less dense, forming as products of hydrothermal alteration and weathering (hematite Fe_2O_3 , anatase TiO_2 , pyrolucite MnO_2). Hydroxides, such as goethite $\text{FeO}(\text{OH})$ and gibbsite $\text{Al}(\text{OH})_3$, are typically the products of extreme weathering and alteration.

(5) Oxy-salts

The carbonate group minerals form when anionic carbonate groups (CO_3^{2-}) are linked by intermediate cations such as Ca, Mg, and Fe. Hydroxyl bearing and hydrated carbonates can also form, usually as a result of weathering and alteration. The other oxy-salts, such as the tungstates, sulfates, phosphates, and vanadates, are analogous to the carbonates, but are built around an anionic group of the form XO_4^{n-} .

This group includes such type of minerals as carbonates (calcite CaCO_3 , dolomite $\text{CaMg}(\text{CO}_3)_2$, etc.), tungstates (scheelite CaWO_4 , wolframite $(\text{Fe},\text{Mn})\text{WO}_4$), sulfates (baryte BaSO_4 , anhydrite CaSO_4), phosphates (xenotime YPO_4 , monazite $(\text{Ce},\text{La},\text{Th})\text{PO}_4$), vanadates (carnotite $\text{K}_2(\text{UO}_2)(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$).

(6) Silicates

Silicate minerals that can be subdivided into several mineral series based on the structure and coordination of the tetrahedral SiO_4^{4-} anionic group – tekto (framework), neso (ortho), cyclo (ring), soro (di), phyllo (sheet) and ino (chain) silicates.

Silicate minerals are generally hard, refractory and translucent. Most of them cannot be regarded as ore minerals in that they do not represent the minable part of an ore body, and only some of the silicates are associated with mineral occurrences as gangue or alteration products. Some silicate minerals, such as zircon $\text{Zr}(\text{SiO}_4)$ and spodumene $\text{LiAlSi}_2\text{O}_6$, are ore minerals and represent important sources of metals such as zirconium and lithium, respectively. Others, such as kaolinite $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$, are mined for their intrinsic properties (e.g. as a clay for the ceramics industry).

(2) Mineral grain size

Grain size of rock-forming and ore-forming mineral varies widely between very fine and very coarse. The different minerals are of different grain sizes and even the same mineral may show large variations in grain size influenced by the process of formation and postmineralization – postdepositional structure, remobilization, and metamorphic grade. Grain sizes are broadly grouped into three categories.

Fine grained minerals are defined as less than 0.1 mm in diameter. *Medium grained* minerals are minerals which grain size varies between 0.1 and 2 mm. These minerals are easily identified based on their distinguishable physical properties. *Coarse grained* minerals have the size that is more than 2 mm in diameter. Much larger and very large size minerals are unique to identify.

1.3. Mineral economics

(1) Ore-grade and tonnage

Ore is any naturally occurring material that comprises orebody, from which a mineral or aggregate of value can be extracted at a profit under the prevailing conditions of market prices, production costs, and up-to-date technologies of mining and mineral processing. Many mineral deposits are non-economic (not mined) because they fail to pass the test of profitability at current market conditions. In every day practice, the general term ore deposit is used a broader sense to include both economic and non-economic mineral deposits. For ore deposit to be economic it must contain high-enough concentration of the valuable substance, and more than a given tonnage of this substance.

Detailed exploration of any deposit is aimed at collection of geological- and- economic data and determination of cut-off grade, which is used for calculation of *reserves (tonnage)* and *average grade* of any orebody on the basis of geologic certainty and economic feasibility.

Grade (or tenor) is the average concentration of a valuable substance in a mineral deposit. *Cut-off grade* is the minimum concentration of a valuable substance that is treated as lower economic limit at current market conditions.

Figure 3 shows how an increase in ore price results in a decrease of cut-off grade which, in turn, increases the volume of ore that can be mined at profit.

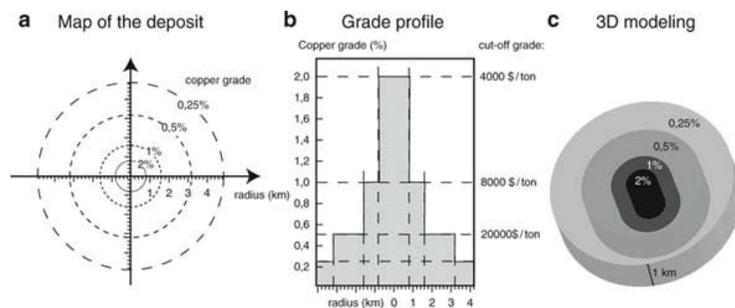


Figure 3. Ore deposit and variations in ore grade (after Arndt, 2012).

Deposits can be classified on the basis of concentration of mineral or metal grade. *High-grade* deposits are economically the most encouraging type for the mineral industry. *Medium-grade* deposits are also equally important as sources of metal. *Low-grade* deposits are exploited on account of available existing infrastructure. These deposits are workable with high mechanization for huge production and improved process recovery.

(2) Mineral resources and ore reserves

Depending on the degree of geologic certainty that is estimated from drilling results and results of different exploration methods ore reserves can be subdivided into *measured*, *indicated* and *inferred*. Subeconomic materials of any mineral deposit, that may be profitably mined in the future, constitute *potential resources*. On the basis of economic feasibility mineral resources can be subdivided into *paramarginal* and *submarginal* (Fig. 4).

Measured (proved) ore reserves are estimated based on samples from outcrops, trenches, development levels and diamond drilling. The drilling interval would be 200 or even 400 m for simple sedimentary bedded deposits (coal seam, iron ore) with expected continuity along strike, other than structural dislocation. The sample interval would be at 50 by 50 m for base metal deposits. The deposit is either exposed by trenches or trial pit for open-pit mines and by development of one or two levels for underground drilling. Further stope delineation drilling and sampling will continue to upgrade the category to developed reserves. The confidence of estimate is ~80%.

Indicated (probable) ore reserves are estimate essentially based on wide-spaced sampling, surface and underground drilling at 100-400 m interval depending on the complexity of the mineralization. The opening of the deposits by trial pit or underground levels is not mandatory to arrive at this category. The confidence of estimate is ~70%.

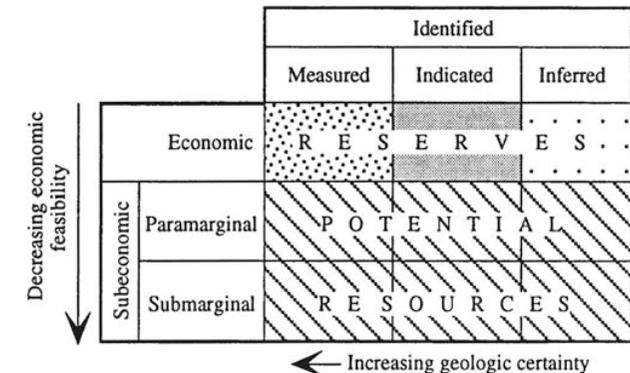


Figure 4. Classification of mineral resources and ore reserves (after Misra, 2000).

Inferred (possible) reserves/resources are based on few scattered sample information in the strike and dip extension of the mineral deposit. There would be sufficient evidences of mineralized environment within broad

geological framework having confidence of about 50%. The possible resource will act as sustainable replacement of mined out ore.

The resource classification scheme gives emphasis to identified sub-economic resources for future target. It also initiated the concept of probability of existence of undiscovered resources simply on hypothetical and speculative ground.

Paramarginal are sub-economic resources that exist at the margin of economic-uneconomic commercial border and can be exploited at marginal profit only with application of innovative mining and metallurgical techniques. The other type of paramarginal resources is treated as unviable because of current safety, legal or political circumstances. **Submarginal** are sub-economic resources that would be mined at much higher price of commodity (ore or mineral) or in case of cost reduction in technologies of mining and metallurgical recovery.

Mineral resources and ore reserves are the results of estimation of deposit tonnage and ore grade. However, this estimation is mostly based on certain interpretations and assumptions of ore body (deposit) continuity, shape, and grade. As a results, they are always approximate (not certain) until the deposit is worked out by mining.

The mineral resource and ore reserves classification system and reporting code have evolved over the years by different countries exclusively based on geological confidence, convenience to use, and investment need in the mineral sector. There are several mineral resource and ore reserves classification systems and reporting codes used in the world:

- 1) UNFC = United Nations Framework Classification scheme;
- 2) USGS/USBM = US Geological Survey / US Bureau of Mines classification scheme, (USA);
- 3) JORC code = Joint Ore Reserve Committee Code, (Australia);
- 4) CIMC = Canadian Institute of Mining classification, (Canada);
- 5) SAMREC = South African Code for the Reporting of Mineral Resources and Mineral Reserves, (South Africa);
- 6) Reporting Code, (United Kingdom);
- 7) Classification of Mineral Reserves and Resources of the State Subsoil Fund, (Ukraine).

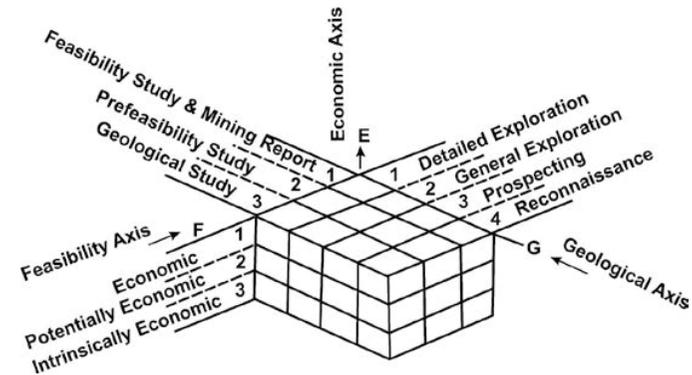


Figure 5. United Nations Framework Classification (UNFC) scheme

Among all the classification schemes the UNFC scheme is currently treated as the most internationally understandable and it is accepted in many countries. This scheme gives emphasis to three criteria of equal importance – exploration, investment, and profitability of mineral deposits. These criteria include (1) stage of geological exploration and assessment, (2) stage of feasibility appraisal, and (3) degree of economic viability. In common practice, this scheme might be shown graphically as multiple cubes with geological (G), feasibility (F), and economic (E) axes (Fig. 5).

Table 1. Codification codes of United Nations Framework Classification (UNFC).

Economic axis	Feasibility axis	Geological axis	Code
Economic	Feasibility Study and Mining Report	Detailed Exploration	111
Economic	Pre-feasibility Study	Detailed Exploration	121
Economic	Pre-feasibility Study	General Exploration	122
Potentially Economic	Feasibility Study and Mining Report	Detailed Exploration	211
Potentially Economic	Pre-feasibility Study	Detailed Exploration	221
Potentially Economic	Pre-feasibility Study	General Exploration	222
Intrinsically Economic	Geological Study	Detailed Exploration	331
Intrinsically Economic	Geological Study	General Exploration	332
Intrinsically Economic	Geological Study	Prospecting	333
Intrinsically Economic	Geological Study	Reconnaissance	334

A National Code is a standard whose utilization is obligatory in the certain country. Each codified class (Table 1) displays a specific set of assessment stages with associated economic viability. Most of the national codes are derived from the JORC Code (Australia, since it was established earlier and has been relatively reliable. There are many national codes, but only some of them are accepted worldwide.

Table 2 shows subdivision of Mineral Reserves and Resources and Class Codes utilized in Ukraine. The Code applies to the reporting of all mineralized material to be potentially economic in the future. This includes mineralized fill, remnants, pillars, low-grade mineralization, stockpiles, and dumps and tailings where there are reasonable prospects for economic extraction.

Table 2. Codification system of Ukraine (after Rudko, 2013)

Commercial value	Degree of technical and economic investigation	Degree of geological exploration	Class code
1. Balance reserves	EGE-1	Explored (proved) reserves	111
	EGE-2	Explored (proved) reserves	121
	EGE-2	Prospected (probable) reserves	122
2. Conditionally balance and off-balance reserves	EGE-1	Explored (proved) reserves	211
	EGE-2	Explored (proved) reserves	221
	EGE-2	Prospected (probable) reserves	222
3. Commercial value undetermined	EGE-3	Prospected (probable) reserves	332
	EGE-3	Prospective resources	333
	EGE-3	Prognostic resources	334

Note: EGE = economic-geological evaluation

1.4. Distribution of mineral deposits

Mineral deposits have formed throughout the Earth's geologic history and in a wide range of geologic environments. The space-time distribution of mineral deposits, however, is not uniform. Certain types of mineral deposits tend to be concentrated in specific parts of the Earth's crust, often in clusters or arranged in linear belts, and/or particularly well represented within restricted intervals of geologic time.

A first-order control on the localization of mineral deposits is tectonic setting that, in turn, controls other factors favorable for the formation of mineral deposits. These factors include, for example, the form and composition of the associated igneous bodies, the formation of sedimentary basins and the characteristics of sediments that fill the basins, the development of faults and shear zones that provide conduits for mineralizing fluids or places for ore localization. As a result, many geologists have made an attempt to relate the distribution of mineral deposits to plate tectonics.

Mineral deposits and plate tectonics

Plate tectonics is a theory showing that the lithosphere is divided into a finite number of plates that migrate across the surface of the Earth. Classification of mineral deposits based on plate tectonics is intensively used because plate tectonics can determine the origin and distribution of many ore deposits, particularly when discussing their broad-scale distribution.

Most mineral deposits can usually be assigned to defined tectonic settings. Tectonic setting controls factors favorable for the formation of mineral deposits such as the form and composition of igneous bodies, the formation of sedimentary basins and the characteristics of sediments that infill the basins, and the development of faults and shear zones that provide conduits for mineralizing fluids or places for ore location. Tectonics not only controls the architecture of a mineral basin but also facilitates the interaction between ore-bearing fluid and rocks.

Some scientists define all the list of the tectonic settings including as ocean ridges, settings related to mantle plumes, continental rifts, cratons and passive margins, arc systems and orogens. Others considered tectonic settings in terms of convergent and divergent plate environments (Fig. 6).

The study of relationships between mineral deposits and plate tectonics has been particularly successful for many kinds of deposits (e.g., porphyry copper deposits, volcanic-hosted massive sulfide deposits, and much more). But some plate tectonic settings, especially during the Precambrian, are still highly controversial.

Before plate tectonics geosynclines and the geotectonic cycle were very popular in the geologic community. They provided framework to metallogenic provinces and metallogenic epochs that assisted mineral discovery especially in the former Soviet Union.

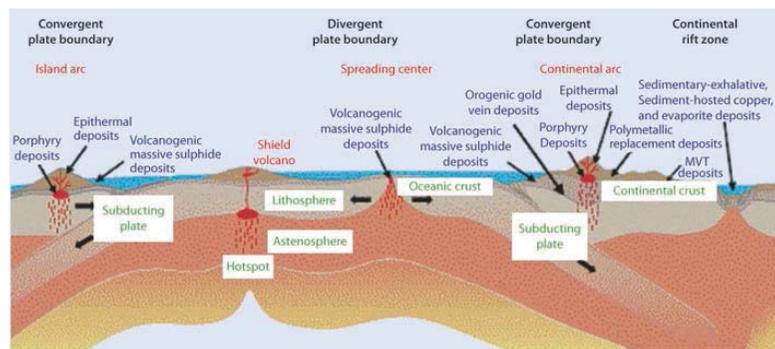


Figure 6. Distribution of mineral deposits in relation to plate boundaries (after Pirajno, 2009).

Although the concept of geosynclines has been out of date for several decades now, it left behind some terminological heritage that is still locally used in an official way because of tradition. The two geosynclinal megadomains: eugeocline (volcanic sedimentary oceanic and convergent margin assemblage) and miogeocline (stable continental margin sedimentary successions) are still in use as convenience terms to rapidly identify contrasting megadomains in composite orogens (e.g. North American Cordillera).

Questions for self-testing:

1. Analyze the criteria used for classifications of different type mineral deposits.
2. Describe key features of classifications based on such criteria as ore-body relation to host rocks and geographic localization of mineral deposit.
3. Describe key features of classifications based on such criteria as ore-body occurrence depth and structural control.
4. Describe key features of classifications based on such criteria as mineralization style and ore-body morphology.
5. Analyse classifications based on genetic features and ore-forming processes that result in formation of mineral deposit.
6. Characterise the nature of ore and gangue minerals.
7. Classify ore minerals by their subdivision into six classes.
8. Describe possible relation between ore mineral grain-size and ore-grade.
9. Which mineral resource and ore reserve classifications commonly used.
10. Describe the main plate tectonic settings and associated patterns of ore deposit distribution.

Part 2. Magmatic ore formation

Igneous rocks contain a large number of different ore deposit types. At the same time, different igneous rocks host ore deposits with different metal associations. Chalcophile and siderophile elements (Ni, Co, Pt, Pd, and Au) are more likely to be associated with mafic rock types, whereas lithophile elements (Li, Sn, Zr, U, and W) are typically found in association with felsic or alkaline rock types. This fact should be somehow related to the environments in which magmas are generated or, in general, to the tectonic settings of their formation.

2.1. Magma types and metallogeny

Magmas can be treated as essentially silicate melts with variable amounts of ore metals and other elements, water, and relatively minor amounts of volatile constituents (e.g., CO₂, H₂S, SO₂, HCl, HF, H₂). Almost infinite range of magma compositions (from ultramafic to highly alkaline) can be subdivided into four groups or magma types – basalt, andesite, felsic, and alkaline magmas.

Basalt magma

Basalts are generated in almost every tectonic environment, but the majority of basaltic magma is formed in the mid-ocean ridges and hot-spot (mantle plumes) within oceanic crust. In addition, basalts are formed together with a variety of more felsic magmas, along island arcs, active continental margins, as well as in intra- and intercontinental rifts.

Basalts are supposed to be formed by partial melting of mantle material. Laboratory experiments have shown that such mantle rocks as lherzolite (peridotite which contains olivine, ortho pyroxene, and garnet or spinel) can produce basaltic liquids on melting within mid-ocean ridges. At the same time alpine-type peridotite (peridotite which contains olivine and orthopyroxene) is too refractory to produce basaltic melt. These rocks are treated to be residues left behind after extraction of basaltic magma from the mantle. Komatiites, which are ultramafic basalt magmas (MgO > 18%) mainly restricted to Archean are generally believed to represent high degrees of partial melting of mantle during the high heat-flow conditions, at tectonic settings of greenstone belts being predominant in Archean (prior to 2500 Ma).

Ore deposits associated with mafic igneous rocks commonly comprise mainly siderophile and chalcophile metal assemblage (Ni, Co, Cr, V, Cu, Pt, and Au). This fact might be explained by primary enrichment of the source materials from which the basaltic magmas are formed. In addition,

high abundances in siderophiles can also reflect the chemical affinity between these ore and rock-forming elements (Mg and Fe) that mostly comprise minerals of solidified basaltic magma (olivine and pyroxenes).

As possible good example of such an affinity might be the substitution of Ni^{2+} for Mg^{2+} in olivine. Figure 7 shows good correlation between Ni and MgO contents in basaltic magmas. The high initial Ni content of ultramafic basalts and komatiites suggest possible formation of magmatic nickel deposits of economic importance. This fact is proved by common presence of world class nickel deposits hosted in the Archean komatiites – e.g. Kambalda deposit in Australia and elsewhere in the world.

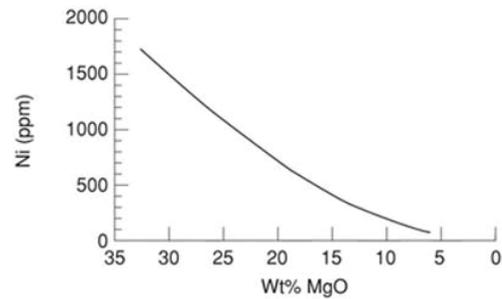


Figure 7. The relationship between Ni and MgO contents of basalts (after Robb, 2005)

Andesite magma

Andesites are rocks that crystallize from magmas of composition that is intermediate between basalts and felsic magmas. As to tectonic settings of their formation, andesites commonly occur along island arcs or active continental margins, within the subduction zone of oceanic crust.

The petrogenesis of andesites is still under debates. Geological evidences support that andesites can be formed in two ways. It can represent a primary magma produced by direct melting of hydrated basalts of subduction oceanic crust. Alternatively, andesitic magma can be produced as an evolved melt through fractional crystallization (differentiation) of originally mafic magma, or by mafic melt contamination with felsic (crustal) material (Gill, 2010).

Irrespective of the debates, andesites do not show any primary association with metals or ore deposits, and are characterized by intermediate position between basalts and felsic magmas. It looks like that most ore deposits show the tendency to be associated with the end member of magma composition range. There are no any class deposits in the world that show close/direct association with andesite type magma. Most deposits associated with andesite are formed during late «post-magmatic» stages,

while intensive andesite alteration at circulation of ore-bearing hydrothermal fluids (porphyry- and epithermal-type deposits).

Felsic magma

Felsic magmas can be formed in various geological environments ranging from oceanic (as evolved products of deeply differentiated mafic magmas). But most felsic magmas are derived from the partial melting of crustal material as products of orogenic (Himalayan-type continent collision) and anorogenic (intracontinental crustal thinning) magmatism.

Ore deposits associated with felsic igneous rocks commonly comprise concentrations of certain lithophile elements (Li, Be, F, Sn, W, U, and Th). The relative enrichment of lithophile elements in felsic magmas is partially related to their geochemically incompatible nature. An incompatible element is one whose high ionic charge (HFSE, high field strength elements) and large ionic radius (LILE, Large Ion Lithophile Elements) make it difficult to substitute for any major elements in rock-forming minerals. Incompatible elements are characterized by tendency to be excluded from crystalline rock-forming mineral and concentrated into evolved residual melts, such as felsic magmas (Fig. 8).

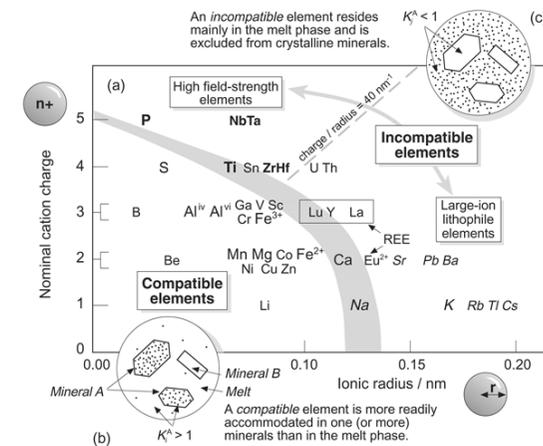


Figure 8. Diagram showing distribution of compatible («mineral loving») and incompatible («melt loving») elements. (after Gill, 2010)

There are also some evidences that origin and composition of the felsic magma can also control ore mineral assemblages of the associated deposit. Granitic magma can inherit metallogenic «endowment» of the rocks from which it was produced. According to classification scheme of granitic rocks proposed early, granitic magma can be derived from melting of a sedimentary protolith (S-type granites) or igneous protolith (I-type granite).

This scheme also has metallogenic significance. Porphyry-type Cu-Mo mineralization (with Pb-Zn-Au-Ag) is typically associated with I-type granites, whereas Sn-W mineralization (with high U and Th) is more commonly hosted by S-type granites.

Alkaline magma

Most magma compositions of the Earth's crust can be represented by the continuous basalt-andesite-felsic range. Alkali rocks that are formed from alkaline magma constitute no more than 1% of all igneous rocks exposed on the Earth's surface. These are the rocks formed from magmas depleted in SiO₂ but so highly enriched in the alkali elements (Na and K) that they can precipitate «unusual» sodium- and potassium-bearing minerals (feldspathoids, aegirine and sodic amphiboles).

At the same time, alkaline magmas may be of high economic importance because they commonly contain high concentrations of a wide range of ore metals – Cu, Fe, P, Zr, Nb, REE, F, U, and Th (Fig. 9). In addition, kimberlitic and lamproitic magma types that are rich in potassium represent the main economic source of diamonds.

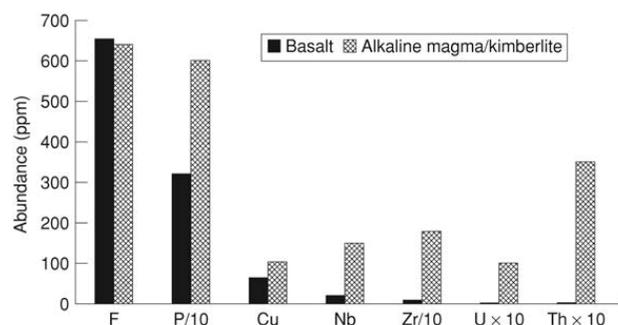


Figure 9. Metal abundances in alkaline magma/kimberlite relative to basalt. (after Robb, 2005)

The most common alkaline mafic magma is nephelinite, which crystallizes to give a range of rock types (the ijolite suite) comprising rather unusual minerals, such as feldspathoid, calcic-pyroxene, and carbonate assemblages.

Nephelinite lavas are found as formed in oceanic (Hawaiian islands) and continental settings (East African rift). Old alkaline igneous complexes are rare. Among the best preserved is the Phalabora complex (deposit) of South Africa that is dated at 2050 Ma and mined mostly for copper and phosphate as well as for some other rare elements.

Nephelinite and rarely occurring carbonatite (rich in CaCO₃) melts are treated as magmas derived by small-degree of partial melting of ultramafic rocks (mostly garnet peridotites) at high pressure of the Earth's upper mantle. The origin of kimberlitic magmas is similar to that of the alkaline magmas. They are supposed to be formed at high pressure partial melting of garnet peridotite source that includes additional phlogopite or K-amphibole (richterite), as well as carbonates.

2.2. Magmatic ore-forming processes

Magmatic deposits may form as a result of (a) solid phases crystallizing as a differentiate as the magma cools, (b) minerals crystallizing from the enriched residual fluids formed as magma cools and crystallizes, (c) the formation of a sulfide melt that developed by immiscibility from a coexisting silicate melt, or (d) where a magma transports xenolithic or xenocrystic phases that it has picked up on its passage through the Earth's crust.

Among ore-forming processes that are considered to be particularly important for the formation of magmatic deposits are:

- (1) Fractional crystallization
- (2) Liquid immiscibility
- (3) Fitter pressing

(1) Fractional crystallization

The formation of magmatic deposits with massive style mineralization requires that ore minerals can be concentrated by some mechanism in a part of the magma chamber. The lack of efficient segregation from the silicate minerals result in formation of relatively low-grade, disseminated mineralization.

Once minerals are removed from the magma by settling of crystals (cumulates) at the bottom of magma chamber there is no chemical reactions (equilibration) between the solid minerals and liquid melt. The crystallization of mafic magma might be also treated as a process of chemical fractionation, since minerals of one composition are physically separated from the compositionally different magma from which they form. This process is known as *fractional crystallization* and schematically shown on Figure 10.

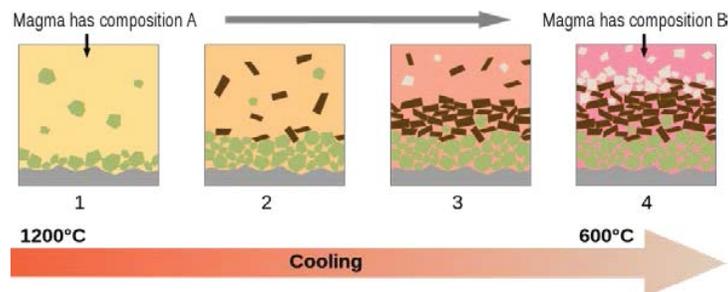


Figure 10. Fractional crystallization sequence with cumulate mineral formation.

Layered mafic intrusions

A possible mechanism of crystal-liquid separation in a magma undergoing crystallization is gravitative settling (or floating) of crystals as a result of their density differences relative to the liquid.

Gravitationally induced settling of minerals in mafic intrusions would seem to be the most logical way of explaining the well layered mafic intrusions so commonly observed in these bodies. The subhorizontal layers that form in mafic intrusions arise from the initial accumulation of early formed minerals (such as olivine and orthopyroxene), followed, in a stratigraphic sense, by accumulations of later formed minerals such as the pyroxenes and plagioclase. Minor oxide minerals such as chromite and magnetite are also observed to accumulate among the major silicate mineral phases.

The viscosity of mafic magma is relatively low, as illustrated by the eruption of basaltic magmas flows. The densities of mafic minerals are typically greater than 3 g/cm^3 , whereas mafic magma has a density of around 2.6 g/cm^3 . The low viscosity of mafic magma and the high densities of minerals crystallizing from it imply that minerals such as olivine and the pyroxenes will typically sink in a magma chamber. By contrast, less dense minerals, such as the feldspathoids, might float in an alkaline magma as they have densities less than 2.5 g/cm^3 . Plagioclase would float in a basaltic magma at pressures greater than about 5 kbar, but would sink in the same magma emplaced at high crustal levels.

Felsic intrusions commonly do not exhibit the well-defined sub-horizontal layering that typifies large mafic intrusions. This is largely due to the fact that felsic magmas are much more viscous than mafic ones. In addition, the density contrasts that exist in crystallizing mafic magma chambers are not as marked as they are with respect to quartz and feldspars forming in felsic chambers.

At the same time, most felsic plutons record a concentric zonation, with the outer zones preserving more mafic compositions (i.e. diorite, tonalite, granodiorite) and rock types becoming progressively more felsic toward the center. Since many granite plutons intrude at shallow crustal levels and most of their heat is, therefore, lost to the sidewalls, this type of zonation is attributed to crystallization that started from the sides and roof of the magma chamber and progressed inwards. Although crystals are not being removed from the magma by the settling process applicable in mafic intrusions, they are effectively isolated from the residual melt by the crystallization front which advances in towards the center of the chamber. This process, referred to as *sidewall boundary layer differentiation*, can also, therefore, be regarded as a form of crystal fractionation (Robb, 2005).

(2) Liquid immiscibility

Liquid immiscibility is the process of separation of a cooling magma into two liquid phases of different composition. The two liquid fractions may be mineralogically similar (silicate-silicate immiscibility) or be very different (silicate-oxide, silicate-carbonate or silicate-sulfide immiscibility). There are three possible modes of liquid immiscibility that can be observed under geological conditions:

(a) separation of Fe-rich tholeiitic magmas into two liquids, one felsic and the other mafic (rich in Fe);

(b) splitting of CO₂-rich alkali magmas into one melt rich in carbon dioxide (carbonatite magmas) and the other rich in alkalis and silica (nephelinites);

(c) segregation of sulfide melts from silicate mafic or ultramafic magmas.

Segregation of sulfide melts from silicate ones (*silicate-sulfide immiscibility*) is widely accepted idea about basic and ultrabasic magma crystallization. There are many large ore deposits associated with the development of an immiscible sulfide fraction in mafic and ultramafic magmas.

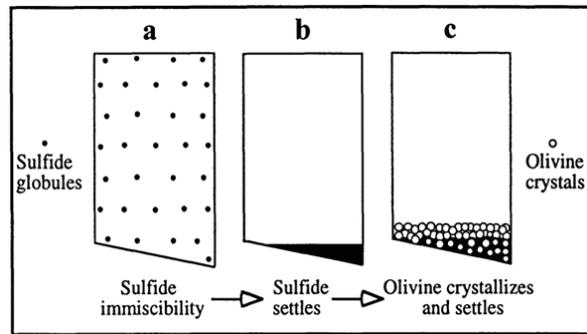


Figure 11. Segregation of sulfide melt from cooling silicate magma (after Misra, 2000).

a) Formation of sulfide globules due to sulfur saturation in the magma; b) Sulfide settlings with formation of sulfide layer; c) Crystallization and settling of silicates (olivine, etc.)

Sulfur as sulfide is dissolved in mafic magmas by displacing oxygen bonded to ferrous iron. Sulfide solubility is, therefore, a function of FeO activity in the magma, but is also controlled by oxygen fugacity (fO_2), decreasing as fO_2 increases. Sulfide solubility, or the amount of sulfide dissolved in the magma at saturation, will vary as magma progressively crystallizes and, at any point when saturation is reached, small immiscible globules of sulfide melt will form. Since the sulfide globules have a high density, they might also accumulate as a separate sulfide layer at the lower

part of the magma chamber (Fig. 11). The immiscible sulfide melt that segregated from basaltic magma subsequently solidified to form such ore mineral as pyrrhotite, chalcopyrite, and magnetite.

Among various factors that can promote sulfide immiscibility in a mafic or ultramafic magma are: (a) cooling of the magma, which not only decreases its sulfur solubility, but also causes crystallization of silicate minerals, thereby increasing the sulfur concentration in the residual magma; (b) silica enrichment of the magma by reaction with felsic country rocks; (c) mixing of a more fractionated magma with a less fractionated magma, both of which were nearly saturated with sulfur; and (d) assimilation of sulfur from country rocks; (f) distinct difference in densities of sulfide and silicate melts.

(3) Filter pressing

The separation of crystal phases from residual melt during the solidification of magma is generally attributed to gravitational segregation where crystals of either higher or lower density than the magma settle or float to form horizontally layered cumulate rocks. Another mechanism by which crystal melt segregation can occur is the process known as *filter pressing*. The residual magma within a network of accumulating crystals in a partially solidified chamber can be pressed out into regions of lower pressure such as overlying non-crystalline magma or fractures in the country rock.

A mafic magma and low oxygen fugacity (fO_2) that is not enough for early crystallization of Fe-Ti oxide minerals would produce enrichment of iron and titanium in the residual magma. This heavier liquid, then, may drain downward, collect below as a segregation resting on a solid floor of early formed sunken crystals, and crystallize into a layer with significant concentration of Fe-Ti oxide minerals. In some situations, the residual magma may be squeezed out by filter pressing and form magmatic injection deposits. The Fe-Ti oxide deposits associated with anorthosites and anorthositic gabbros are believed to have formed by gravitative accumulation and injection of residual magmas that are filter pressed into adjacent fractures created during hydrofracturing.

2.3. Magmatic type deposits

A magmatic ore deposit is formed by an accumulation of ore minerals. Some of them are extremely rare and almost never encountered in nature (e.g., alloys of the platinum group metals). However, other minerals such as magnetite are commonly found. The type of ore mineralization in magmatic deposits is directly linked to the composition of the host rock. For example, deposits of nickel, chromium, and platinum group elements (PGE) are related to mafic-ultramafic hosts. Deposits associated with ultramafic and mafic rocks span most of the history of the Earth, being well represented in all continents.

Classification of magmatic type deposits can be made according to the host rock association. Six types of magmatic ore deposits can be defined: (1) chromite, (2) nickel (copper) sulfide, (3) platinum group element (PGE), (4) diamond, (5) carbonatite and (6) pegmatite deposits.

(1) Chromite deposits

Chromite deposits constitute the only primary source of chromium metal, with chromite $(\text{Mg,Fe}^{2+})(\text{Cr}^{3+},\text{Al,Fe}^{3+})_2\text{O}_4$ being the only ore mineral of chromium known in nature.

Chromite deposits that are associated with ultramafic-mafic igneous rocks commonly classified according to their forms and textures as: (a) *stratiform* deposits; and (b) *podiform* deposits. The stratiform deposits occur as conformable layers of great lateral extent in Precambrian layered intrusions emplaced within stably continental crust. The podiform deposits typically occur as irregular (lenticular), concordant to discordant chromite-rich bodies in tectonically-emplaced alpine-type peridotite complexes (ophiolites) that formed in oceanic settings.

Most of the world's chromium resources are located in stratiform chromite deposits such as the Bushveld Complex (South Africa) and the Great Dyke (Zimbabwe). Important podiform chromite deposits are located in Kazakhstan, Turkey and the Philippines. The major stratiform chromite deposits also contain important contents of platinum and PGE.

Stratiform chromite deposits are hosted by layered intrusions of large, sill-like ultramafic-mafic complexes. These intrusions are ultrabasic and basic in composition and owe their layering to differentiation by fractional crystallization. The layers are composed of a framework of cumulus crystals which nucleate and settle down in the magma chamber) with the interstices filled by postcumulus crystals. In general, layered intrusions consist of two zones: a lower ultramafic zone of olivine \pm clinopyroxene

cumulates; and an upper mafic zone of plagioclase \pm olivine \pm pyroxene cumulates.

Ore bodies of chromite deposits are typically represented by thin but laterally continuous and conformable layers of chromitite (massive chromite containing 50% to more than 95% of cumulus chromite). Massive chromitite layers (more than 90% of chromite) or seams of disseminated chromite (more than 60% of chromite) are commonly found as confined to the lower ultramafic zone of the layered intrusions. Intrusions are formed by emplacement in stable cratonic settings or during rift-related events throughout the Archean or early Proterozoic time. The intrusions extend from 2 to 180 km in diameter and can reach thicknesses of as much as 15 km.

The thickness of chromitite layers ranges from less than 2 cm to more than 1 m, but the lateral extent may be traced or correlated over distances measured in kilometers or even tens of kilometers. Individual chromitite layers have been traced for almost 20 km in the Stillwater Complex, for more than 30 km in the Bushveld Complex, and for at least 185 km in the Great Dyke (Fig. 12).



Figure 12. Chromitite layers in the Bushveld Complex (after Arndt, 2012).

Podiform chromite deposits are mostly associated with alpine-type ultramafic-mafic complexes. Compared with layered complexes, alpine-type complexes are relatively small in size, are highly serpentinized, occur in orogenic belts, often show evidence of tectonic emplacement, and overwhelmingly are Phanerozoic in age. Alpine-type complexes may be subdivided into two classes: (a) ophiolites; and (b) mantle diapirs.

Ophiolites are believed to have been generated initially at spreading centers of mid-oceanic ridges and subsequently obducted onto continental margins during plate convergence. Mantle diapirs occur as small bodies of ultramafic (peridotitic) composition and represent diapiric emplacement of

mantle material in a solid state. Chromite concentrations in these bodies are limited to a few small pods and lenses of little economic potential.

Chromite that occurs in podiform deposits has a geotectonic environment distinctly different from the model in stratiform chromite deposits. In podiform deposits, chromite shows different textures such as massive aggregates and banded, nodular, net, or graded layers, which indicate relict cumulate features. Nodular texture is probably the most important feature to distinguish podiform chromite deposits from stratiform deposits.

(2) Nickel (copper) sulfide deposits

Nickel is one of the metals which is depleted in the crust but enriched in the mantle. Thus, ultramafic and mafic rocks formed from mantle-derived magmas tend to have relatively high nickel contents. The nickel in these rocks resides in olivines and pyroxenes, substituting for Mg^{2+} and Fe^{2+} , and may amount to as high as 0.3% in some dunites and peridotites. Mineable orebodies of nickel commonly contain in excess of 1% Ni.

Nickel (copper) deposits are referred as magmatic sulfide-rich Ni-Cu \pm PGE deposits related to mafic and/or ultramafic dyke-sill complexes. The name of the deposits emphasizes the relation of these Ni-Cu sulfide-rich deposits to mafic and ultramafic rocks and to mostly small- to medium-sized dykes and sills, as opposed to the generally much larger layered mafic-ultramafic intrusive complexes that typically host sulfide-poor PGE-enriched deposits such as Stillwater Complex in USA.

All the deposits can be classified into two principal types based on the petrology of the host rocks:

- (a) peridotite-dunite type (komatiitic association)
- (b) gabbroic type (tholeiitic association).

Deposits included in the peridotite-dunite class are hosted by komatiite associations of Precambrian greenstone belts of Archean age. The gabbroid type deposits occur in differentiated mafic-ultramafic intrusive complexes of predominant gabbroic composition, ranging in age from Precambrian to Phanerozoic.

Sulfide deposits containing nickel and copper with or without (\pm) platinum-group elements (PGE) account for approximately 60% of the world's nickel production and they form where mantle-derived, sulfur-undersaturated tholeiitic basalt magma becomes sulfide-saturated. Sulfur saturation results in formation of an immiscible sulfide liquid, which tends to segregate in the lower parts of dike- or sill-like intrusions (Fig. 13).

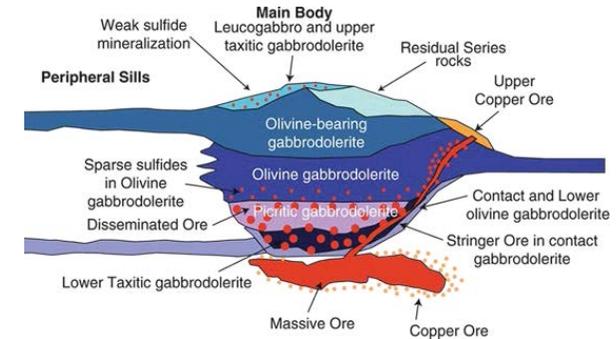


Figure 13. Cross section through ore-bearing sill with massive ore (after Arndt, 2012).

The ore minerals of nickel, copper, and the PGE are all chalcophile and show a tendency to partition into the sulfide. Nickel is lithophile as well as chalcophile, and in normal ultramafic rocks, it is distributed between olivine and sulfide. Copper is moderately chalcophile, but the PGE are enormously chalcophile. This means that any droplet of sulfide will extract most of the copper and nickel and effectively all of the PGE from the surrounding silicate liquid. In this sense, if the sulfide droplets can then be concentrated effectively, for instance, by gravitational processes, then an ore deposit is formed.

Deposits of magmatic Ni-Cu sulfides occur with mafic and/or ultramafic bodies emplaced in diverse geological settings. They generally are found in penetrating faults, which permit the efficient transport of magma undersaturated in sulfur from the mantle to relatively shallow crustal depths. Sulfur-bearing crustal rocks (black shales, evaporites, or paragneisses) are supposed to be a potential source of sulfur in many to many deposits.

The major Ni-Cu sulfides mineralogy typically consists of an intergrowth of pyrrhotite, pentlandite, and chalcopyrite. In most cases, the ores are zoned, with copper-rich zones relatively enriched in gold, palladium, and platinum. Those zones, as footwall dykes and veins, either overlie or are separated from Cu-poor zones relatively enriched in osmium, iridium, ruthenium, and rhodium.

Cobalt, PGE, and gold are extracted from most magmatic Ni-Cu ores as by-products. The sulfide-rich Ni-Cu \pm PGE deposits contain ore grades of between 0.5% and 3% of nickel and between 0.2% and 2% of copper. Tonnages of individual deposits range from a few tens of thousands to tens of millions of tons bulk ore.

Two giant Ni-Cu districts, with more than 10 Mt nickel, dominate world nickel sulfide resources and production. These are the Sudbury district in

Ontario (Canada) where sulfide ore deposits are at the lower margins of a meteorite impact-generated igneous complex and contain 19.8 Mt of nickel and the Noril'sk-Talnakh district in Siberia (Russia) where the ore deposits are in subvolcanic mafic intrusions and contain 23.1 Mt of nickel.

(3) Platinum Group Element (PGE) deposits

The platinum group elements (PGE) comprise a geochemically coherent group of siderophile to chalcophile metals that includes osmium (Os), iridium (Ir), ruthenium (Ru), rhodium (Rh), platinum (Pt), and palladium (Pd). Based on association, the PGE may be divided into two subgroups: the Ir-subgroup consisting of Os, Ir, and Ru and the Pd-subgroup consisting of Rh, Pt, and Pd (Fig. 14).

The concentration of PGE in the Earth's crust ranges from sub-ppb (part per billion) level in rocks of felsic and intermediate composition to generally 1-100 ppb in mafic and ultramafic rocks. Economic deposits typically contain 5-10 ppm (part per million) of PGE. and involve concentration factors in the order of 1000, similar to those for gold deposits.

Platinum-Group Elements (PGE)				
	44 Ru hcp mp 2607 K	45 Rh fcc mp 2237 K	46 Pd fcc mp 1828 K	
75 Re hcp mp 3469 K	76 Os hcp mp 3306 K	77 Ir fcc mp 2739 K	78 Pt fcc mp 2041 K	79 Au fcc mp 1337 K

Figure 14. Platinum group elements (PGE); position in the periodic table.

High concentrations of PGE are known from high-temperature magmatic to low-temperature hydrothermal and sedimentary environments, but significant amounts of PGE are restricted to ultramafic rocks.

Two types of deposits, both associated with Ni-Cu sulfides, account for about 98% of the PGE resources in the world:

- stratiform (or strata-bound) deposits occurring in large, layered complexes (Bushveld, Stillwater, and Great Dyke), mined mostly for PGE;
- Ni-Cu sulfide deposits mined mostly for Ni-Cu sulfides, but containing recoverable amounts of PGE as byproducts (Sudbury, Noril'sk-Talnakh, and Kambalda deposits).

Most stratiform deposits of PGE occur as dissemination of sulfide minerals in silicate rocks at specific horizons («reefs» or mineralized rock layers) within large layered intrusions. In the Bushveld Complex, platinum group elements are predominantly confined to two specific horizons. The upper one is the Merensky Reef, a thin (1-10 m) layer of pegmatoid

pyroxenite. The second principal mineralized layer (UG2), is a group of thick chromite reefs that, in addition to high PGE concentration, are also mined for their chromium contents.

The large layered intrusions contain about 90% of the world's PGE resources, with the Bushveld Complex accounting for about 80%. About two-thirds of total world production of PGE comes from the Bushveld Complex. Among other important producers of PGE in the world are Noril'sk-Talnakh deposits (Siberian Platform), the Great Dyke (Zimbabwe), and Stillwater Complex (USA). The rest of the world, including the Sudbury Complex (Canada), provides less than 5% of the world's PGE production.

There is no consensus regarding the origin of these types of PGE deposits: one line of thinking argues that these deposits formed through magmatic processes, whereas the opposing view ascribes an important role to the migration of volatile-rich fluids. In the first case, a plume of primitive magmatic liquid was injected into the base of the Earth's crust and then mixed with evolved liquid to produce a hybrid magma that became saturated in sulfide. The other view propose that volatile-rich fluids migrated up through the cumulus pile, leaching out the PGE from the cumulus minerals then redepositing them at favorable horizons.

(4) Diamond deposits

Diamonds are formed mainly in the Earth's lithosphere where pressure conditions are appropriate for carbon to crystallize as diamond, and they are brought to the surface, mostly through the eruption of fluid-enriched magmas.

A variety of mantle-derived igneous rocks comprise the primary sources of diamond, with the principal hosts being kimberlite and lamproite. Kimberlite is a special type of ultramafic magma and derived from the Earth's mantle at more than 140 km depth.

Kimberlites are volatile-rich (dominantly CO₂), potassic (up to about 5% K₂O), ultramafic (< 35% SiO₂) rocks with a distinctive inequigranular texture resulting from the presence of relatively large (0.5-10 mm), rounded to anhedral crystals set in a fine-grained matrix. The larger crystals include olivine (the dominant phase), phlogopite, magnesian ilmenite, Ti-poor chrome spinel, pyrope-rich garnet, Cr-poor clinopyroxene, and enstatite. The matrix assemblage consists of second-generation euhedral olivine, phlogopite, serpentine, pyroxene (Al- and Ti-poor), perovskite, Ti-Mg-Al chrome spinel, Fe-Ti spinel, monticellite, carbonate (usually calcite), and apatite. Lamproite, a rock type similar to kimberlite, can also contain commercial diamond deposits.

All kimberlite-hosted diamond mines which exist in the world, like in south-central and Southern Africa, western Africa, Canada, China, Russia, and the USA, are located in Archean continental blocks. They are virtually restricted to ancient (>2.4 Ga) cratons and the younger (>1.0 Ga) accreted belts of cratonized regions that are underlain by cratons. The Cretaceous was a major period of kimberlite magmatism, particularly in Africa, but the ages of kimberlites range from Proterozoic to Tertiary. It is important to note that some southern African kimberlites dated at about 90 Ma contain diamonds older than 2.0 Ga.

The typical diamond deposit is pipe-shaped with a circular surface diameter of 50-500 m and a depth extent of several hundred to one thousand meters or more (Fig. 15). Diamonds in kimberlites are not truly magmatic because kimberlite magma only transports the diamonds rapidly to the surface under conditions that prevent them from reverting to graphite. Kimberlites or lamproites originate either within or below the mantle source region and intrude fast enough for the diamonds to survive transport to the surface or near-surface emplacement site. Probably, kimberlites move to the surface through the mantle at velocities of 10-30 km/h by crack propagation processes.

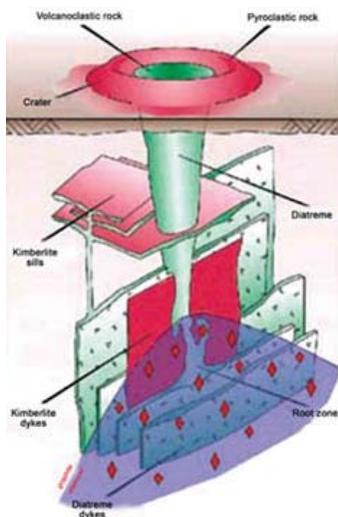


Figure 15. Schematic illustration of diamond-bearing kimberlite pipe (after Arndt, 2012).

The origin of diamonds in kimberlites is controversial, but there is wide agreement that kimberlites have formed under upper mantle conditions. At the same time there are two models as to the diamond origin:

a) *phenocrystal model* treat the diamonds as genetically related to the early crystallization products of kimberlite magmas within the upper mantle.

b) *xenocrystal model* – that the diamonds are xenocrysts, which were picked up from fragmented diamond-bearing eclogite and peridotite in the upper mantle and transported by the kimberlite magma.

Two other problems of diamond genesis that still remain unresolved are the mechanism of diamond growth and the source of carbon in the mantle. Some geological evidences favor the formation of diamonds either directly from an igneous melt or from some type of fluid (with dissolved CO₂ or CH₄) which metasomatise upper mantle rocks – the process known as «*mantle metasomatism*».

Although diamond deposits are often very low grade, the value of the individual diamonds makes the overall deposit highly valuable. Grade values in diamond deposits commonly range from 0.25 to 1.5 carats/t. The value of the diamonds can be very variable depending on its size, shape, color, and quality. Large, equidimensional, colorless, and clear diamonds without defects are most highly valued. Therefore, the common measure used to assess the economic potential of a deposit is a combination of the grade of the deposit (carats per ton) and the dollar value per carat of the diamonds in the deposit.

It is important to remember that most kimberlites and lamproites contain no diamonds. Of the approximately 1000 individual kimberlite intrusions known in South Africa, only about 50 carry significant quantities of diamonds. Of these, many are considered subeconomic either because the quantity or quality of the diamonds or the quantity of ore is insufficient.

(5) *Carbonatite associated deposits*

Carbonatites are carbonate-rich rocks of apparent magmatic origin. They occur as both intrusive (dikes, sills, sheets, pipes, and stocks) and extrusive (flows and pyroclastics) bodies. They are typically associated with nephelinitic and phonolitic magmatism, although the carbonatite itself forms a very small component of the associated alkali igneous complex.

Carbonatites are located predominantly in tectonically stable continental, cratonic, or peripheral-cratonic areas, with close relationships to zones of major faulting. They range in age from Proterozoic to Recent, with an apparent trend of increasing carbonatite production with time and a maximum peak starting at 200 Ma.

Carbonates are the most diagnostic minerals of carbonatites, which may be further subdivided into calcite-carbonatite (sovite, alvikite), dolomite-carbonatite (beforsite), ferrocarbonatite (ankerite), and natrocarbonatite

(Na-K-Ca carbonates). Sovite is the most common variety of carbonatite. The accessory minerals include apatite, pyroxene, olivine, K-feldspar, albite, phlogopite, wollastonite, riebeckite, pyrochlore, barite, fluorite, strontianite, sulfides, and Fe-Ti oxides. Alkali metasomatism (finitization) of wallrocks is a characteristic feature of carbonatites.

Carbonatites are commonly enriched in a characteristic set of minor elements: Nb, REE (especially LREE), P, F, Th, Ti, Ba, Sr, and Zr. The most important products of industrial minerals are calcite for cement and apatite for phosphatic fertilizer. As to the ore minerals carbonatites are considered a major resource of niobium and REE; some carbonatites also contain significant concentrations of Fe (magnetite, hematite), Ti (rutile, brookite, ilmenite, perovskite), Cu-sulfides, barite, fluorite, and strontianite, which may be extracted as by-products.

Most carbonatites contain minor amounts of disseminated sulfides, predominantly as pyrite and pyrrhotite, but much below ore-grade concentration. A notable exception is the carbonatite of the Palabora ultramafic-alkaline igneous complex located in South Africa. The complex intrudes Archean gneisses and is believed to be older than 2060 Ma. It is estimated to contain about 700 million tons of copper ore averaging 0.68% Cu. The principal copper sulfides are chalcopyrite and bornite. Ti-bearing magnetite (0.6-2.8% TiO₂) is a major constituent of the ore and is recovered as a by-product.

(6) Pegmatite deposits

Pegmatites represent another type of magmatic ore deposit that are formed from deeply evolved phases of felsic melts. Pegmatites are formed by the crystallization of melts expelled from granitic magmas. Pegmatites are very coarse-grained rocks abundant in quartz, feldspar, and mica that can include megacrystals of rock-forming or rare-element minerals. Most pegmatites show a paragenesis of orthoclase, microcline, albite, mica, quartz, and common minor minerals including topaz, tourmaline, cassiterite, beryl, and lithium.

Granite pegmatites commonly occur as dikes, oval and lenticular bodies, being homogeneous (without a change of mineralogy or texture) and inhomogeneous (zoned or complex pegmatites). Most pegmatites are relatively small in size which thickness rarely surpass tens of meters and length of a few hundred meters. But at the same time, pegmatites may host many useful materials such as ores of Be, Li, Rb, Cs, Ta-Nb, U, Th, REE, Mo, Bi, Sn, and W; industrial minerals (muscovite, feldspar, kaolin, quartz, spodumene, fluorite), and gemstones (Fig. 16);



Figure 16. Gemstones from granitic pegmatites (after Laznicka, 2010).

Left to right: *spodumene* (kunzite, California, USA, 284 g), *spodumene* (triphane, Afghanistan, 196 g), *beryl* (Heliodor, Ukraine, 303 g, 14 cm tall), *tourmaline* (Brazil, 25 g), *beryl* (aquamarine, Vietnam, 37 g), *topaz* (China, 375 g), and *quartz* (smoky quartz, Namibia, 219 g).

Rare-element complex-type pegmatites are commonly classified into two families:

- LCT family is represented by pegmatites enriched in lithium, cesium and tantalum, being an important source of rare elements.
- NYF pegmatites are of different family and enriched in niobium, yttrium, and fluoride.

Pegmatites of the LCT family were emplaced in orogenic settings by intruding metasedimentary rocks, typically at low-pressure (amphibolite to upper greenschist) metamorphic facies. All the largest deposits of LCT family pegmatites are Archean in age. Among them are such pegmatite deposits as Tanco in Canada (2.1 Mt at 0.215% Ta₂O₅), Greenbushes in Australia (70.4 Mt at 2.6% Li₂O), and Bikita in Zimbabwe (12 Mt at 1.4% Li₂O). Current economic importance of NYF pegmatites is much less than that of the LCT family, but these pegmatites could be a source in the future for rare earth elements and other strategic metals.

Questions for self-testing:

- Characterize magma types and their associated metallogeny.
- Describe the main magmatic ore-forming processes with detailed explanation of fractional crystallization.
- Describe the main magmatic ore-forming processes with detailed explanation of liquid immiscibility.
- Give classification of the magmatic type deposits.
- Characterize the main features of chromite deposits.
- Analyze the main ore-forming features favorable for formation of nickel (copper) sulfide deposits.

7. Characterize the main types and distribution patterns of platinum group element deposits
8. Describe the main theories applicable for explanation of diamond deposits formation.
9. Carbonatites and their mineralization; age distribution of carbonatites.
10. Rare-metal and gemstone mineralization of pegmatite deposits.

Part 2. Hydrothermal ore formation

Hydrothermal ore formation can develop in almost all geological environments of the Earth's crust. Although there are several natural processes that can concentrate elements and form mineral deposits, the most important is the hydrothermal process. Igneous processes become magmatic hydrothermal as the intrusion cools and crystallizes. At the same time, hydrothermal fluids can be formed from metamorphic dehydration reactions, from the expulsion of pore fluids during compaction of sediment, and from meteoric waters. Sea water can be also considered as a hydrothermal fluid that takes active part in formation of base metal deposits on the ocean floor.

Hydrothermal fluids form as a result of magma cooling and crystallization. The magmatic system can be a source of heat that drives the circulation of fluids through adjacent fractured Earth's crust (host rocks). As the magma cools and crystallizes, it becomes more concentrated and eventually forms an immiscible fluid phase which can collect ore components. These metal-rich fluids can migrate away from the magma and interact with minerals of outside (host) rocks. These minerals become altered by chemical reaction and new mineral phases (including the ore minerals) can be precipitated.

Surface or seafloor hydrothermal fluids are generated as deeply penetrating *meteoric or seawater* heated in the Earth's crust. In the case of seafloor, this phenomenon is common where a new ocean is formed by the seafloor spreading through the formation of seafloor *hydrothermal vents*. On land, such hydrothermal fluids can be generated in zones of crustal attenuation with formation of *hot springs*.

Diagenesis results in the transformation from uncompact particles of sediment into lithified sedimentary rock and can produce aqueous solutions. *Diagenetic fluids* are commonly involved in the formation of ore deposits. This process may develop on a large scale in a sedimentary basin undergoing burial and lithification and is a related process to hydrocarbon generation. The released water can pick up dissolved salts to form *brines* which have an ability to transport and precipitate different elements to form an ore deposit. In sedimentary basins, evaporite beds may be a specific source of salts that can be dissolved by the basinal water. Basins undergoing diagenesis become heated, and thus the basinal brine may be a highly effective solvent for dissolving large quantities of metals. These basinal brines can then migrate via crustal faults and permeable horizons to depositional environments.

Diagenetic process evolves to metamorphism as rocks are gradually buried and temperatures rise. *Hydrothermal fluids* are formed as a result of

metamorphic mineral-chemical alterations that may release volatiles dominated by water and carbon dioxide (CO₂). Metamorphism might be caused by external heat or pressure. Heat may be provided by the deep burial of a rock mass or by the intrusion of a magma body. Pressure to cause metamorphism may be provided during deep burial or by tectonic dislocations.

3.1. Hydrothermal ore-forming processes

(1) Water properties

Water (H₂O) occurs as liquid at room or standard temperature and pressure (STP). In nature water exists as three different phases, solid (ice), vapor (steam), and liquid. H₂O-ice typically exists below about 0°C and forms when water molecules are arranged in a hexagonal crystalline structure similar to many rock forming silicate minerals. When H₂O-ice melts only a small proportion of the hydrogen bonds are broken and H₂O-liquid retains a large measure of tetrahedral coordination. At temperatures close to the freezing point, this structure is more tightly knit than ice, which explains why the liquid water phase of is more dense than solid, and ice floats.

The density of H₂O-liquid varies mainly as a function of temperature, but also pressure. Density defines the difference between the liquid phase and coexisting vapor. Lines of equal density in P-T space are referred to as isochores. The phase boundary along which liquid and vapor are in equilibrium (i.e. between the triple point and the critical point) defines the saturation vapor pressure, also known simply as the boiling point curve. On the Earth's surface, water effectively can boil when vapor pressure exceeds the atmospheric pressure and vapor can bubble off from the liquid.

As temperature rises the density of H₂O-liquid decreases. The boiling point temperature of pure water increases progressively with pressure until a maximum limit is reached, called the critical point, at 374°C and 221 bar. The critical point is where it is no longer possible to increase the boiling point by increase of pressure and is effectively defined as the stage where there is no longer a physical distinction (density contrast) between liquid and vapor. Since the terms «liquid» and «vapor» no longer have any meaning at the critical point, the term «supercritical fluid» is used to describe the homogeneous single phase that exists at pressures and temperatures above the critical point (Fig. 17).

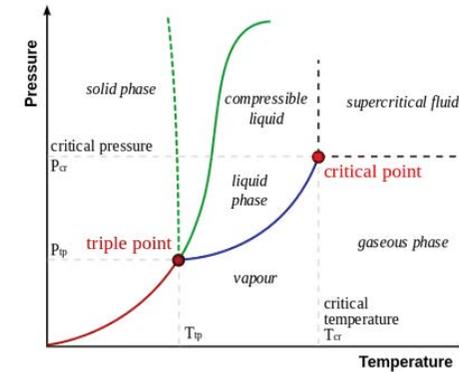


Figure 17. Pressure-temperature phase diagram of water.

The physical properties of water that make it so important for natural as well as geological processes include: (1) high heat capacity, which means that it can conduct heat more readily than other liquids; (2) high surface tension implying that it can easily «wet» mineral surfaces; (3) density maximum at temperatures just above the freezing point, which means that solid-H₂O (ice) will float on liquid-H₂O; (4) high dielectric constant and, hence, an ability to dissolve more ionic substances, and in greater quantities, than any other natural liquid.

The last property is particularly important to the hydrothermal ore-forming processes, since water is largely responsible for the dissolution, transport, and, concentration of a wide range of elements and compounds, including metals.

(2) Factors essential of hydrothermal ore formation

Possible formation of a hydrothermal type deposit requires combination of favorable ore-forming factors that include:

- A) Water sources
- B) Sources of ore constituents
- C) Dissolution and transportation to deposition sites
- D) Ore precipitation

A) Water sources

The most useful data in deducing the possible source of water are obtained from: (a) fluid inclusion studies of ore and gangue minerals for information about the temperature and chemical composition of the fluids; (b) analysis of stable isotope ratios (D/H, ¹⁸/¹⁶O) of fluid inclusions in

minerals (Fig. 18), and (c) studies of natural waters and active geothermal systems.

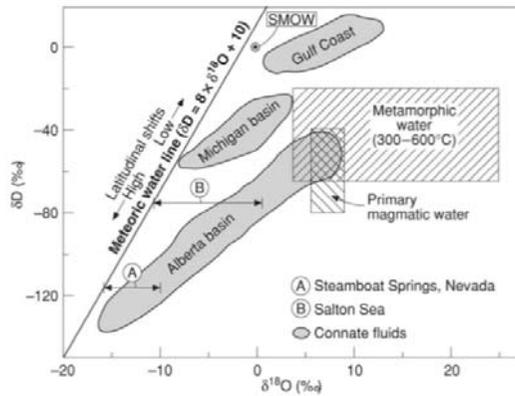


Figure 18. Hydrogen (δD ‰) and oxygen ($\delta^{18}O$ ‰) isotopic ratios for various types of water; SMOW = Standard Mean Ocean Water (after Robb, 2005).

The waters of hydrothermal fluids may be classified into four following types: (1) *meteoric water* that is involved in atmospheric circulation; (2) *connate or formational water* trapped in the pores of sediments deposited in sedimentary basins; (3) *metamorphic water* produced by metamorphic dehydration reactions; and (4) *magmatic water* that is derived from crystallizing magma.

Any types of water can evolve into a potential ore-forming fluid. But at the same time, many deposits are formed from waters of at least two or more sources of water. So, source of water cannot be treated as the key controlling factor in the formation of hydrothermal mineral deposits.

B) Sources of ore constituents

Among possible sources of ore constituents for hydrothermal fluids might be: (a) magmas, which can concentrate constituents in the fluids and separate them as a result of magmatic crystallization (magmatic hydrothermal fluids); (b) crustal rocks with which hydrothermal fluids interact during their migration.

The potential of crustal rocks as sources of ore constituents depends on many variables. These include: (a) primary concentrations of ore-forming elements in the host rock, (b) volume of rock affected by hydrothermal circulation, and (c) the extent of chemical interaction between host rock and hydrothermal fluids.

With a few exceptions (Fe, Al), crustal rocks commonly contain ore metals only at trace levels, predominantly as components of silicate minerals (bound in the crystal structure of minerals) – for example, Pb in potassium feldspars, Cu and Zn in micas, Cr and Ni in olivines and pyroxenes, Ti in amphiboles, etc.

Extraction of metals can take place only during destruction of the host minerals by dissolution or during conversion of the host mineral into alteration assemblage. Circumstances favorable to both types of reactions are hydrothermal alteration and metamorphism.

C) Dissolution and transportation to deposition sites

The solubility of metals in pure water is very low even at moderate to high temperature. Most of the common ore metals – such as lead, zinc, copper, silver, molybdenum, mercury – occur chiefly as sulfide and sulfosalt minerals, and they are precipitated from aqueous solutions at moderate temperatures. This raises a serious problem about hydrothermal ore deposits, because sulfide and sulfosalt minerals are extremely insoluble in aqueous solutions at such temperatures.

For the fluid to be capable of transporting and re-depositing ore minerals it must contain salt and other anions in solution. Recent experimental works has shown that the solubility of ore metals is greatly increased in saline solutions by the formation of metal complexes. In chemistry, a coordination complex consists of a central atom or ion, which is usually metallic and is called the coordination center, and a surrounding array of bound molecules or ions, that are in turn known as ligands or complexing agents. A coordination complex whose center is a metal atom is called a metal complex (Fig. 19).

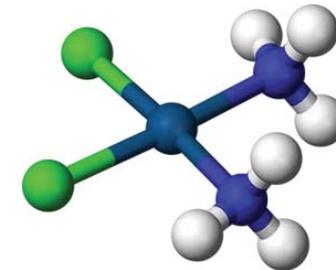


Figure 19. Coordination complex of platinum ($PtCl_2(NH_3)_2$) with two chloride and two ammonia ligands.

Three kinds of coordination complexes have been considered as likely candidates for many ore metals: (a) chloride complexes; (b) sulfide complexes; and (c) organometallic complexes. But above the limit of 300°C, organic complexes are commonly dissociated and are unlikely to be important for high-temperature ore formation. A ligand that promotes formation of coordination complexes typically increases the solubility of metals in aqueous ore-bearing solutions.

In natural (geologic) conditions, the major complexing agents (ligands) are represented by hydroxide (OH), Cl, S and in some cases by HCO₃/CO₃ and F. The nature of metal complexes depends on the metal-ligand chemical affinities: so-called «hard metals» like Al, REE, Zr, U, preferentially form complexes with ligands like OH, F, and CO₃, whereas «soft metals» like Au, Pt strongly prefer to form metal complexes with HS or H₂S. Most base metals (Ni, Pb, Zn, Cu, etc.) are complexed largely with Cl ligands.

D) Ore precipitation

The key factor of the ore-forming process is the precipitation of the ore metals or minerals at sites of deposition. There are two main types of deposition site – open fractures and replacement zones. Many hydrothermal deposits form at shallow levels in the crust where fractures remain open and ore deposition takes place by open space filling. Ore bodies formed this way consist of a multitude of veins and patches of ore minerals dispersed through the host rock.

At deep levels of Earth's crust where porosity is restricted, replacement of existing minerals tends to occur. Hot hydrothermal fluids are chemically aggressive and capable of reacting with a wide range of rock types. Alteration zones surround most hydrothermal systems and ore minerals occur in many of these zones. In some cases the minerals are disseminated or restricted to veins; in other cases wholesale replacement of the original rock is evident.

What is required are mechanisms that can cause the metals to precipitate out of aqueous solution. Among them are (a) temperature change; (b) boiling (separation of water/vapour phases); (c) fluid interaction with wallrocks; and (d) fluid mixing.

The most common cause of precipitation is cooling of the solution (temperature change), which decreases the solubility of the metals. Cooling takes place when hot magmatic fluids enter cool wall rocks, when fluids emerging from a seafloor spring mix with cold seawater or when warm basin fluids mix with cooler near-surface waters.

Fluid circulation through open space (fractures) can be accompanied by pressure decrease that lead to boiling – separation of vapor phase from liquid solution. Separation of water phases results in destruction of metal-ligand complexes that can cause the metal precipitation.

Another process is reaction with wall rocks, which changes the fluid composition. Particularly important are redox reactions, which happen when oxidized basin waters come into contact with reduced materials such as hydrocarbons or organic-rich shales. This type of interaction is crucial in the formation of most uranium deposits and many of the base-metal deposits in sedimentary basins.

Mixing of fluids of different temperature and composition is considered to be an effective precipitation mechanism of ore constituents. For example, dilution of the hydrothermal brines decreases the concentration of the complex-forming anions and consequently decreases the solubility of the metals leading to their precipitation.

3.2. Hydrothermal type deposits

Hydrothermal type deposits represent an essential group of ore minerals because they are the source for most of the metal production of the world. Hydrothermal deposits provide almost 100% of lead, zinc, molybdenum, and silver and 60-90% of copper, gold, and uranium as well as gemstones and industrial materials such as clay minerals and quartz. Hydrothermal deposits are diverse, being present in a wide range of geological settings and tectonic environments. Some deposits are closely associated with granitic intrusions, others form on the ocean floor and still others are in sedimentary basins. All the deposits have common origin via the precipitation of metals or ore minerals from hot aqueous fluids.

All known hydrothermal type ore deposits can be subdivided into three groups: (A) **Metasomatic-hydrothermal**: 1) Greisen and albitite, (2) Skarn; (B) **Magmatic-hydrothermal**: (3) Porphyry, (4) Volcanogenic Massive Sulfide (VMS), (5) Iron Oxide Copper Gold (IOCG) deposits; and (C) **Sedimentary-hydrothermal**: (6) Sedimentary Exhalative (SEDEX), (7) Mississippi Valley Type (MVT), (8) Stratiform Sediment-hosted Copper (SSC) deposits.

(A) Metasomatic-hydrothermal:

(1) Greisen deposits

The term greisen (after german «Tin stone») is used to refer quartz+muscovite assemblage accompanied by varying amounts of other distinctive minerals such as fluorite, topaz and tourmaline. Greisens are formed as a result of complex late- to post-magmatic metasomatic processes that take place within a nearly consolidated granitic intrusion and the adjacent country rocks.

Greisenisation is typically linked with highly fractionated felsic magmas that have intruded into crustal depths ranging from 3 to 5 km, with greisenising fluids emanating from deep-seated granite batholiths. The highly evolved granitic melts that promote the development of greisenisation and associated mineralization (Sn, W, U, Mo, Be, Bi, Li and F) are strongly enriched in volatile components (Cl, B, F, OH⁻).

Greisens are formed in the apical portions (cupolas) of granites and commonly associated with vein systems. There are two types of greisens: one in which the greisenising fluids are contained within the granitic cupola (closed system, or *endogreisen*), and one in which the fluids are channelled along fractures and faults, from within the parent cupola into the country rocks (open system or *exogreisen*).

Different types of exogreisens can be distinguished depending on the lithology of country rocks. Greisenisation of host sedimentary sequence containing pelitic and psammatic rocks (alumino-silicates) is characterised by the formation of muscovite, albite and locally tourmaline. Quartz-sericite, albite and adularia, all of which may occur along fractures, may be associated with quartz vein material containing sulphides and oxides (pyrite, chalcopyrite, cassiterite, wolframite, scheelite, arsenopyrite, molybdenite). In mafic rocks greisenisation is characterised by the presence of chlorite-talc, phlogopite-actinolite, quartz-plagioclase and quartz-muscovite assemblages. Greisen alteration of carbonate rocks result in neutralization of greisen solution, as the anionic species (e.g. F⁻, OH⁻) become fixed by Ca and Al to form fluorite and topaz (Fig. 20).

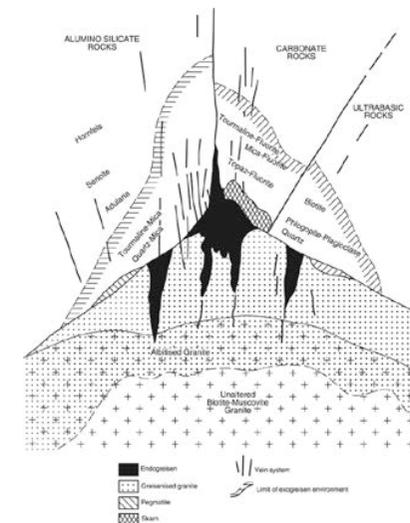


Figure 20. The endo- and exogreisens that occur in alumino-silicate, carbonate and ultramafic rocks (after Pirajno, 2009).

Greisenisation can follow the early stage of Na-metasomatism manifested by direct replacement of K-feldspar with newly formed albites (granite albitisation). At the same time second phases of sodic metasomatism may occur following the phase of greisen alteration, as indicated by the replacement of greisen minerals (topaz and muscovite) by albite. The development of albite-rich rocks is usually associated with formation of rare element mineralisation (Nb, Ta, Sn, W, Li, Be).

Greisens are typically associated with Sn and W mineralisation, usually accompanied by numerous other ore elements such as Cu, Zn, Bi, Mo, U, F. Common ore minerals are cassiterite, stannite, wolframite, scheelite,

arsenopyrite, pyrite, chalcopyrite, molybdenite, sphalerite, bismuth and bismuthinite. Other important minerals are topaz, fluorite and apatite. Most greisen type Sn and W deposits are spatially and genetically related to S-type granitic rocks forming dome-like (cupolas) intrusions.

Greisen-related Sn mineralisation occurs as lenses, generally subparallel to the arcuate contacts of the granitic intrusion with the enclosing country rocks. In open system (exogreisen), fracture-controlled, sheeted veins, and stockworks emanate from the greisenised granite into the country rocks. Greisen mineral systems may have distinct metal zonations. These are usually manifested by a lower zone of Sn+Mo, extending upward and sometimes laterally through W+Bi to Cu, Zn, and Pb. In some cases Au may also be present (Timbarra greisen).

Classical examples of greisen type deposits include: Sn and W deposits of Cornwall (England), Sn greisen of Erzgebirge (Czech Republic), Sn-W-Mo greisen of Sisson Brook (Canada), Au-Mo greisens of Timbarra (Australia) and others.

(2) Skarn deposits

Skarn deposits occurred in contact aureoles around igneous intrusions are essentially formed from metasomatic fluids derived from the magma, and, in such a way, can be also regarded as metasomatic-hydrothermal. At the same time, some geologists relate them to metamorphic type due to the contact metamorphism occurred at the contact area between igneous intrusion and host rocks.

The term *skarn* (old Swedish mining term) was originally used to describe a type of calc-silicate gangue (garnet + pyroxene + epidote), or waste rock, associated with iron-ore (magnetite) and sulfide (chalcopyrite) deposits. In modern usage, the term encompasses a wide variety of generally coarse-grained calc-silicate rocks that are rich in calcium, iron, magnesium, aluminum, and manganese and are formed by replacement of originally carbonate-rich rocks by metasomatic processes.

Hornfels is a term commonly used for the fine-grained calc-silicate rocks that result from isochemical (H₂O and CO₂) metamorphic recrystallization of «impure» carbonate host rocks, (silty limestone or calcareous shale). *Skarnoid* is a descriptive term for fine-grained, iron-poor, calc-silicate rocks of uncertain origin. It takes intermediate position between metamorphic (isochemical) hornfels and metasomatic (allochemical) skarn.

Carbonate rocks (limestones and dolostones) represent the most common host rocks, although occurrences of skarns in shales, quartzites, and igneous rocks are also known. Skarn deposits can occur in a wide range

of geologic setting and vary in age from Precambrian to late Tertiary. Most economic deposits are relatively young in age and closely related to metasomatic-hydrothermal activity associated with dioritic to granitic intrusions formed in orogenic belts (Fig. 21).

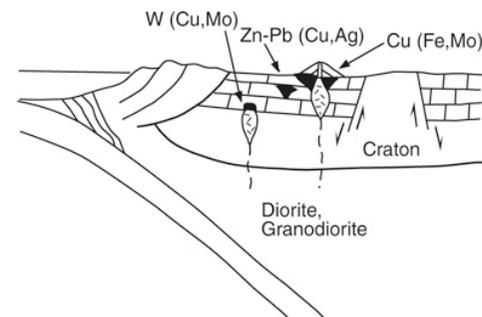


Figure 21. Skarn deposits with associated mineralization, occurred in orogenic setting of active continental margin (after Pirajno, 2009).

A diagnostic feature of typical skarns is their mineral assemblages. The «primary» assemblage is characterized by presence of anhydrous Ca-Fe-Mg silicates. Among them are include pyroxenes (including pyroxenoids) and garnets (wollastonite; salite of diopside-hedenbergite series), and grandite (grossularite-andradite series with varying amounts of spessartine and almandine). Hydrous minerals such as tremolite, talc, epidote, and serpentine are also found in skarns.

Skarns commonly show zonal structure manifested by a sequence of monomineralic or bimineralic layers relative to sedimentary or igneous contacts. The generalized zoning pattern is marked by an increase in the pyroxene/garnet ratio away from the igneous contact and the occurrence of idiochase (or pyroxenoid such as wollastonite, bustamite, or rhodonite) at the contact between skarn and marble.

As to their origin, skarns can be subdivided into two general types: (a) *reaction skarns* involving bimetasomatic diffusion of components; and (b) *infiltration skarns* formed by reaction with the infiltrating metasomatic-hydrothermal fluids. It is only the infiltration type skarns that commonly treated as ore skarns characterized by presence of associated mineralization of economic importance. A commonly used classification scheme is based on the position of the skarn relative to contact zone between intrusive and host rocks, with skarns being subdivided into endo- (intrusive replacement) exo- (host rock replacement) skarns.

At the same time, skarn deposits are best classified on the basis of the dominant economic metal (s): iron, copper, molybdenum, gold, tungsten,

tin, and zinc-lead skarns. The main ore minerals of these skarn types are, respectively, magnetite, chalcopyrite ± bornite, molybdenite, electrum, scheelite, cassiterite, and sphalerite-galena.

Skarns constitute the world's premier source of tungsten (more than 70% of world's production) and serve as important sources of copper, iron, molybdenum, and zinc. They are also mined for many industrial minerals, including wollastonite, graphite, asbestos, magnesite, talc, boron, and fluorite. From an economic point of view, seven major skarn types are distinguished: iron (calcic), iron (magnesian), copper (calcic), molybdenum (calcic), tungsten (calcic), tin (calcic), and zinc-lead (calcic).

(B) Magmatic-hydrothermal:

(3) Porphyry deposits

Porphyry-type deposits refer to disseminated and stockwork mineralization spatially associated with and genetically related to felsic intrusions. The most important porphyry-type deposits are of copper, molybdenum, and tin, but similar low-grade deposits of other metals, such as uranium and gold, related to granitic intrusions may also be included in this group.

Porphyry copper deposits are large, low- to medium-grade, $\text{Cu} \pm \text{Au} \pm \text{Mo}$ hydrothermal deposits. Despite relatively low grades (0.3-2.0% copper), these deposits have significant economic importance due to their large size (hundreds of millions to billions of metric tons), high tonnage (greater than 100 million tons), long mine lives, and high production rates (billions of kilograms of copper per year). With rising molybdenum/copper ratio, these deposits are treated to be low fluorine (quartz-monzonite type) porphyry molybdenum deposits; with rising gold/copper ratio, they are considered to be porphyry gold deposits. Most porphyry-type deposits can be classified into several subtypes according to the dominant mineralization present: porphyry Cu, porphyry Cu-Au, and porphyry Cu-Mo.

Porphyry deposits derive their name from the phenocryst-bearing felsic to intermediate shallow-level intrusions with which they are associated. Mineralization is thought to derive from hydrothermal fluids generated near the top of a cooling magma body at depths between 1 and 5 km. The close spatial and temporal association between the ore bodies and granitic intrusions is clearly indicative that magmas are directly linked to the ore-forming process.

Ore bodies commonly occur as superimposed on the upper parts of relatively small granitic plutons which represent offshoots from larger batholiths occurring at greater depths. Porphyry copper systems are mainly

formed by magmatic fluids that were released during shallow emplacement of porphyritic granitoid stocks. The fluids create a fracture network in the rocks as they travel, thereby producing *stockwork* texture that is typical of this type of deposits. The ores are not only confined to the plutons but extend outwards into the surrounding rocks.



Figure 22. Large open pit of Chuquicamata deposit in Chile (11 billion tons of 0.56% Cu and 0.06% Mo); mined since 1915 year.

The ore minerals crystallize out of the hydrothermal fluids as a result of cooling of the fluid as it moves away from the magma body. The mineralization consists of small concentrations of sulfide minerals, disseminated or dispersed in small veins and replacement patches in the highly altered upper portions of the intrusion and in surrounding rocks.

Original sulfide minerals are represented by pyrite, chalcopyrite, bornite, and molybdenite. Gold is often in native form and is found as tiny blobs along borders of sulfide crystals, or it occurs in sulfosalts like tetrahedrite. Most of the sulfides occur in veins or fractures and form intergrowths with quartz or sericite.

The composition of the intrusion exerts a fundamental control on the metal content of the deposit. Low-silica and relatively mafic plutons, ranging in composition from calc-alkaline diorite and granodiorite to alkalic monzonite, are associated with porphyry Cu-Au deposits; intermediate to felsic, calc-alkaline granodiorites and granites are associated with Cu-Mo deposits; and felsic, high silica, strongly differentiated granites are associated with Mo, W, and Sn deposits.

Porphyry type deposits have formed throughout most of Earth's history, but more than 90% of known deposits are Cenozoic or Mesozoic in age. This is interpreted to be a result of their occurrence in the upper crust level and possible destruction by erosion.

Porphyry deposits are the world's most important source of Cu and Mo. They account for about 50-60% of world Cu production and more than 95% of world Mo production. Among the best-known deposits are those occurred in the cordilleras of North and South America, the Bingham mine in the USA (2.7 billion tons of 0.7% Cu and 0.05% Mo), and the Chuquicamata mine in Chile (11 billion tons of 0.56% Cu and 0.06% Mo) (Fig. 22).

(4) *Volcanogenic Massive Sulfide (VMS) deposits*

VMS deposits are among the best understood of all ore deposits. There are various reasons for this: the ore bodies are relatively simple, both in their structure and their composition and mineralogy, and they have also been studied intensively over the last decades. These deposits were among the first ever to be mined because this mineralization was mined in Cyprus and in Spain more than 2000 years ago, providing much of the copper utilized in the weapons of the ancient Roman Empire. In modern times, VMS deposits have become a major focus of scientific studies since the discovery of active high-temperature (more than 300°C) hydrothermal vents («black smokers») in the ocean-floor ridge-rift systems of Pacific ocean.

The distinctive feature of a VMS deposit is its association with volcanic rocks. Depending on the particularly setting, these can be mafic (basaltic) or felsic. Invariably they were deposited under water, either in a mid-ocean ridge setting or more commonly in island arcs or during arc-continent collision. Sedimentary rocks form an important part of the host sequence in certain classes of VMS deposits. The term volcanogenic implies a genetic link between mineralization and volcanic activity, but siliciclastic rocks can dominate the stratigraphic assemblage in some settings.

Volcanogenic massive sulfide deposits are stratabound concentrations of sulfide minerals precipitated from hydrothermal fluids in extensional seafloor environments. Among the main tectonic settings of their possible formation are mid-oceanic ridges, volcanic arcs (intraoceanic and continental margin), back-arc basins, rifted continental margins, and pull-apart basins.

The deposits are formed by two parts: a concordant massive sulfide lens (>60% sulfide minerals) and discordant vein-type sulfide mineralization, commonly called the stringer or stockwork zone. Individual lenses are 2-20 m thick and extend for tens to hundreds of meters laterally. Large lenses can reach more than 100 m thick and extent for more than 1000 m laterally.

They show different mineralization textures such as breccias, layering, and laminations.

The mineralogy of the most deposits is relatively simple. As with almost all sulfide deposits, with the exception of those in purely sedimentary settings, iron sulfides predominate. In VMS deposits, abundant Fe sulfides (pyrite or pyrrhotite) make up about 90% of the sulfide assemblage, which may also include chalcopyrite, sphalerite and galena, and in some cases and in minor amounts, bornite, arsenopyrite, magnetite, and tetrahedrite.

Depending on the dominant metal, host-rock lithology and tectonic setting of their formation VMS deposits are classified into two groups: (a) Cu-Zn; and (b) Zn-Pb-Cu deposits. The first Cu-Zn group deposits occur in two principal geologic settings: (a) Archean and Proterozoic greenstone belts dominated by mafic volcanites; and (b) Phanerozoic back-arc setting characterized by equal amounts of mafic volcanic and sedimentary rocks. Deposits of the second Zn-Pb-Cu group are mostly Phanerozoic in age, occur in arc-related setting and characterized by bimodal (mafic-felsic) volcanism where felsic volcanic rocks, with or without associated sedimentary strata, are dominant.

Deposits of first Cu-Zn group are further can be subdivided into four types: *Noranda and Mattabi* hosted by mafic-felsic volcanites; *Cyprus* hosted by ophiolites; and *Besshi* type deposit, hosted by sediments in volcanic terranes. The second Zn-Pb-Cu group includes only one type – *Kuroko* deposit (Fig. 23).

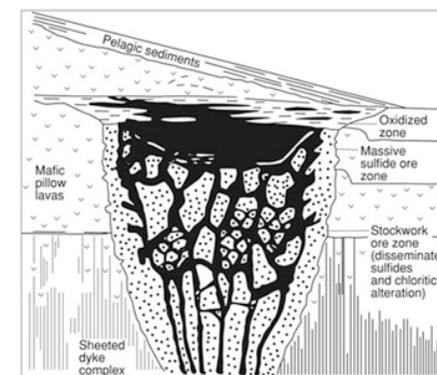


Figure 23. Ophiolite-hosted Cyprus type VMS deposit (after Misra, 2000)

VMS deposits occur in volcanic belts of submarine origin, emplaced in a wide spectrum of tectonic settings and ranging in age from Early Archean (3.55 Ga) to Tertiary. Of particular importance are the Archean and early

Proterozoic greenstone belts of the Canadian Shield, the Lower Paleozoic volcanic belts of the Caledonides in Scandinavia and the northern Appalachians of Newfoundland (Canada), the Upper Paleozoic Iberian pyrite belt extending from southern Portugal to southern Spain, and the Miocene Green Tuff belt of Japan (Kuroko-type).

Volcanogenic massive sulfide deposits are normally small (1-5 Mt) but of high-grade (3-10% ore metals) $\text{Cu} \pm \text{Zn} \pm \text{Pb} \pm \text{Au} \pm \text{Ag}$ hydrothermal deposits hosted in volcanic and/or sedimentary rocks. They are significant sources of copper and zinc and, to a lesser extent, lead, silver, gold, cadmium, selenium, tin, bismuth, and minor amount of other metals. The polymetallic and high-grade ores make these deposits a preferential target for exploration and mining.

(5) Iron-Oxide Copper Gold (IOCG) deposits

An Iron-Oxide Copper Gold (IOCG) deposit is defined as a polymetallic, breccia-hosted hydrothermal type deposit in which ore is spatially and temporally associated with granite and with iron oxide alteration. The Olympic Dam deposit in Australia is the best example of IOCG-type deposit known in the world. Other typical example is represented by Kiruna deposit in Sweden.

The Olympic Dam deposit is located within a funnel-shaped, hematite-rich hydrothermal breccia that formed close to the surface at the upper (brecciated) part of granitic intrusion. The ore minerals are diverse and complicated, comprising some 30 varieties of Cu, U, Au, Ag, Ni, Co sulfides, sulfosalts, oxides, carbonates, and native metals. They occur as veins, disseminations, irregular patches and breccia fillings that occur together with zones of intense (calcic-sodic, iron and potassic) alteration.

Due to the very recent discovery of Olympic Dam in 1975, theories of ore formation for IOCG-type deposits are subject to continual revision. According to the most widely accepted theory large-scale magmatic events (granite intrusion) drive large-scale flow of oxidized probably magmatic hydrothermal fluids into mid to upper crustal levels along fault zones. Mixing of these fluids with near surface meteoritic water or brines has caused the formation of rich-ores zones in brecciated granite and host rocks.

The Olympic Dam deposit is treated as the most reach (supergiant) deposits of the world. It contains almost eight billion tons of copper-uranium-gold ore. It is the world's biggest uranium resource, the fifth largest gold deposit, and one of the biggest copper deposits. Proved ore reserves of the deposit are estimated to be greater than 600 Mt with ore-grades averaging 1.8% Cu, 500 g/t U_3O_8 , 0.5 g/t Au, and 3.6 g/t Ag) and

mineral resources reach 31810 Mt averaging 1% Cu, 0.5 g/t Au and 400 g/t U_3O_8 .

(C) Sedimentary-hydrothermal:

(6) Sedimentary Exhalative (SEDEX) deposits

The term SEDEX, derived from «sedimentary exhalative», is based on the interpretation that the finely laminated or bedded sulfide ores represent chemical sediments precipitated from hydrothermal fluids exhaled onto the seafloor. SEDEX deposits are medium to large sizes, moderate to high grade, $\text{Zn} \pm \text{Pb} \pm \text{Ag}$ hydrothermal deposits hosted in sequences of marine basin sedimentary rocks.

SEDEX ore deposits are formed by fluids rich in metals (Cu, Pb, Zn, Ag and Ba) that ascend along basin graben-bounding faults to exhale at higher levels. The composition of the fluids depends on the nature of the basin lithologies (volcanic-dominated, sedimentary-dominated, presence of evaporites).

Ores typically occur as tabular bodies composed predominantly of Zn and Pb sulfides (sphalerite and galena) and they usually contain economically important amounts of Ag. The Zn and Pb sulfides are interbedded with iron sulfides (pyrite and pyrrhotite) and with generally fine-grained detrital or chemical sediments. Chert, quartz, barite, fluoroapatite and various carbonates are common gangue minerals. Carbonates commonly include calcite, siderite, ankerite, dolomite and Ba-carbonates. A characteristic feature of the deposits is the fine grain-size of the original ore minerals. Another striking feature of a SEDEX deposit is the banding displayed in many ores – stratiform and stratabound ore bodies.

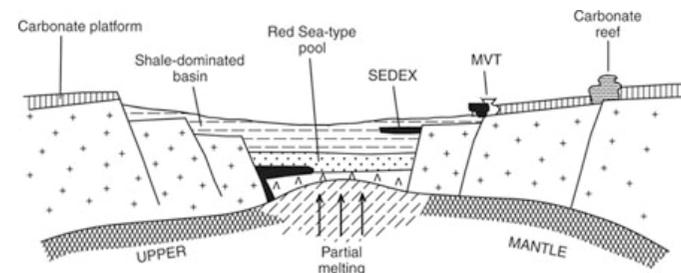


Figure 24. SEDEX and MVT ore deposits formed in the rift setting. (after Pirajno, 2009)

Deposits are believed to have formed from hydrothermal fluids that were expelled from mostly reduced sedimentary basins in continental rifts. The evolution of continental rifts, from incipient graben structures to

protooceanic and oceanic sea-floor spreading, is commonly accompanied by the development of sedimentary basins. Rift-related sedimentary basins are host to a variety of hydrothermal mineral systems, including disseminated and massive sulphide ores.

The key factor that is widely considered to be responsible for the origin of sedimentary-exhalative deposits is the deep circulation of hot (up to 350 °C) fluids within sedimentary sequence in the ocean basin. Saline (dense Na-Ca-K-Cl brine) fluids become enriched in Fe, Zn, Pb and Cu that are leached from coatings of detrital sedimentary minerals. The metals are transported in the hydrothermal fluids as chloride (Cl) and sulfate (SO₄) complexes. When the fluids are discharged along faults to the sea basin floor, metal sulphides can precipitate by mixing with much cooler oceanic water or by reaction with hydrogen sulfide (H₂S). The most likely S source is biogenic H₂S that is typically enriched in the reduced anoxic layer at the base of the sea water column.

Based on the lithology of rocks that host sedimentary exhalative deposits they can be subdivided into two types – the first «Broken Hill type», which is associated with bimodal volcanic rocks and Fe- or Mn-rich sediments, and the second «Irish-type» deposits which are hosted predominantly by carbonate rocks.

SEDEX deposits are mainly formed during two main age intervals: in Early to Middle Proterozoic (1700-1400 Ma) and Lower to Middle Paleozoic (500-320 Ma). Most of the giant deposits are hosted by Early to Middle Proterozoic rocks and are related to the first type (Broken Hill and McArthur River in Australia, Sullivan in Canada, etc.). Important examples of Paleozoic deposits are mostly of the second type (Navan in Ireland, Rammelsberg in Germany, etc.). The known younger deposits are small and very few in numbers. They are mostly restricted to the Jurassic strata of Pakistan, Cuba, and Azerbaijan.

Sediment-hosted exhalative, stratiform, massive sulphide deposits, are a major source of base metals. They comprise 50% of the world's zinc and lead reserves, and 25% of world zinc and lead production. The dominant economic minerals are sphalerite and galena, and in some deposits chalcopyrite, with silver primarily contained with galena. The deposits are characterized by moderate to high grades of zinc and lead, and copper as an important by-product in some deposits.

(7) Mississippi Valley Type (MVT) deposits

Mississippi Valley-type (MVT) deposits form wide group of deposits that contains a substantial amount of the reserves of zinc and lead in the world. The name «MVT» comes from the valley of the Mississippi River in

central USA where these deposits were first recognized. These are low-temperature (50 to 200 °C) epigenetic and stratabound Zn-Pb ± fluorite ± barite deposits that occur mostly in dolostones, less commonly in limestone or sandstone. Among the most favorable settings of their formation are shallow depths (carbonate reef facies) at the flanks of sedimentary basins (Fig. 24).

All the deposits are mineralogically simple. Among dominant minerals present are sphalerite, galena, pyrite, marcasite, dolomite, calcite, and quartz. Textures of sulfide mineral are extremely varied, ranging from coarse and crystalline to fine-grained, from massive to disseminated.

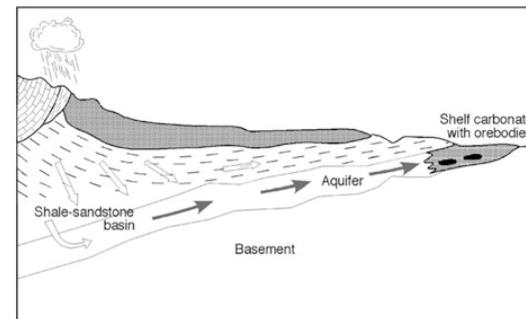


Figure 25. Formation of MVT deposits at shallow (shelf area) depth (after Arndt, 2012).

According to the widely accepted genetic model of ore formation both the metals and the sulfides that comprise ore bodies of MVT deposits are derived from the detrital sedimentary rocks of the sedimentary basin. Ore-bearing hydrothermal fluid was connate water; i.e. the fluid, initially seawater, that filled the pore-space between the detrital grains of the poorly consolidated sedimentary rocks. Basinal fluids are relatively oxidized and they most probably transported the metals as chloride or sulfate complexes. The geochemical environment of the carbonates that now host the ores was very different – it was reduced and contained abundant reductants in the form of hydrocarbons (oil or gas) and other organic material. The redox reaction destabilized and reduced the chloride or sulfate complexes, causing the precipitation of Pb and Zn sulfides with formation of ore bodies within carbonate sequences (Fig. 25). Platform carbonates are often highly porous, due to the presence of the breccias and cavities and the ores were precipitated in these cavities or in zones of reaction between the fluid and the carbonate rocks.

Most MVT deposits constitute parts of ore «districts» that contain numerous small to large deposits. These ore districts (clusters) may extend

over hundreds of square kilometers and contain up to 500 million tons of ore. These ore districts are the main source of base metals in the USA and contribute significantly to the production of lead and zinc in Canada and Europe.

Within each ore district, deposits display remarkably similar features, including mineral assemblages, isotopic compositions, and textures. This fact is interpreted to be the result of formation of the most MVT ore districts through hydrological processes manifested at regional or subcontinental scale.

(8) Stratiform Sediment-hosted Copper (SSC) deposits

Stratiform sediment-hosted copper deposits are hosted in black, gray, green, or white (reduced) sedimentary strata within or above a thick section of red-beds (oxidized). Mineralization consists of fine-grained copper and copper-iron-sulfide minerals that occur as stratabound to stratiform disseminations in siliciclastic or dolomitic sedimentary rocks.

Sedimentary rocks that host ore mineralization range in age from Early Proterozoic to Cenozoic, but most deposits belong to two geologic age intervals – Proterozoic and Paleozoic (Permo-Carboniferous). So far, no any typical SSC deposit has been discovered in the Archean rocks.

Regarding their tectonic setting of these deposits formation, they are found in intracontinental rift-related sedimentary sequences and vary considerably in size, grade, and metal association. Ore bodies can be commonly found at junction between aeolian (oxidised) sandstones and more reduced shales, carbonates and evaporates. Thus, ore formation occurred at the redox interface between oxidised and reduced sedimentary rocks.

Ore constituents are dissolved and transported in basin-derived sedimentary-hydrothermal fluids. The metals are leached from detrital minerals of sedimentary basin represented by such minerals as magnetite and biotite and are transported as chloride complexes. SSC deposits are characterized by distinct zoning of ore minerals expanded laterally along and across bedding of sediment strata, from pyrite and chalcopyrite to bornite and chalcocite.

Genetic models of SSC deposit formation fall into two main groups: syngenetic (syngenetic) and diagenetic (syndiagenetic). According to the first syngenetic model, ore sulfides are precipitated in an anoxic water column containing H₂S resulted from bacterial sulfate reduction (similar to that of present Black Sea environment). The second diagenetic model treats the ore-formation processes as those occurred during diagenesis of the host sedimentary strata. Some geologic evidences indicate that copper

mineralization might be derived from sedimentary hydrothermal fluids generated during diagenesis and lithification in sedimentary basins.

As to economic importance, stratiform sediment-hosted copper (SSC) deposits occupies minor place (after porphyry-copper type) as a source of copper and they represent the most important source of Co. Some deposits are rich in Pb, Zn, Ag, U, and Au. Among the most famous deposits of this type are Kupferschiefer deposit in Central Europe, Copperbelt in Central Africa, and Dzhezkazgan deposit in Kazakhstan.

Questions for self-testing:

1. *Analyze the nature of hydrothermal ore-forming processes.*
2. *In which way metasomatic-hydrothermal and magmatic-hydrothermal type deposits can be classified.*
3. *Describe typical features of greisen and albitite deposits.*
4. *Characterise typical features of the main skarn deposits.*
5. *Describe the main features of porphyry-type deposits.*
6. *Characterise the main features of Volcanogenic Massive Sulfide (VMS) deposits.*
7. *Describe typical features of Iron Oxide Copper Gold (IOCG) deposits.*
8. *Which way sedimentary-hydrothermal type deposits can be classified in.*
9. *Analyse existing models of Sedimentary Exhalative (SEDEX) deposit formation.*
10. *Characterise typical features of Iron Oxide Copper Gold (IOCG) deposits.*
11. *Describe features of Mississippi Valley Type (MVT) deposits.*
12. *Analyse existing genetic models of Stratiform Sediment-hosted Copper (SSC) deposits.*

Part 4. Surficial and sedimentary ore formation

Low-temperature surface processes can be responsible for the formation of economic ore deposits at or near the Earth's surface. Under favorable conditions, sediments and sedimentary rocks become selectively enriched in some elements of potential economic value. Two main processes which may produce such enrichment are:

- (A) Weathering
- (B) Sedimentation

Weathering may lead to *residual concentration* of weathering-resistant minerals of the parent rock or of relatively insoluble elements reconstituted into stable minerals. It is an important ore-forming process resulting in chemical change and redistribution of components in surface rocks by migrating solutions. Under these conditions, ore formation is driven by the circulation of largely meteorically derived water at the Earth's surface, although similar analogous processes can take place on the seafloor. These subsurface waters can dissolve and reprecipitate components at favorable mineral sites or surface interfaces.

Supergene processes usually originate different types of raw materials such as iron, manganese, or aluminum ores. A special case of weathering would be the so-called supergene enrichment process, which involves the leaching of ore-forming elements (e.g., copper) from surficial parts of a low-grade sulfide deposit and reprecipitation below the water table. The process involves the release of ore metals from unstable sulfide minerals to downward percolating meteoric water and precipitation of more stable secondary oxide and sulfide mineral assemblages in the subsurface environment.

Sedimentation may also lead to the formation of mineral deposits through either *clastic accumulation* (placer deposits) or *chemical/biochemical precipitation* of economically important constituents.

In clastic accumulation, physical processes such as physical erosion, transportation, and deposition lead directly to the redistribution and accumulation of specific minerals. Thus, these deposits are formed as a result of the differing physical and chemical behavior of minerals that form the original rock, either hydraulic (water) or aeolian (wind) being the physical processes. Typical of these deposits are diamond placer deposits in river sediments and deposits of heavy minerals in beach sands.

Chemical precipitation can occur in lake water or seawater to comprise chemical sedimentary rocks. Some metals or minerals are soluble in surface waters but can precipitate when their concentrations reach saturation levels with formation of a sedimentary type deposit. These are salt deposits that result

from the evaporation of waters in lakes or shallow seas, and Fe- or Mn-rich sediments that can be formed as a result of different composition water mixing or changes of redox states.

Sedimentation processes commonly occur at the surface of the Earth, which is also the realm of life. Thus, sedimentary ore formation will almost always show biogenic components that are very obvious in phosphate deposits made of bones and coprolites. Living bacteria can enhance dissolution of rocks and minerals containing metals, aid in metal transport, affect porosity and permeability of rocks, and cause the precipitation of biogenic sulfur, sulfides, and carbonates. In particular, iron-reducing bacteria and sulfate-reducing bacteria may play important roles in low-temperature ore genesis.

Organic compounds produced by bacterial degradation of a more complex organic matter could enhance metal transport by formation of metal-organic complexes. Similarly, biogenic H₂S could form stable aqueous metal-sulfide complexes leading to transport of certain metals such as Ag at low temperature.

4.1 Surficial and sedimentary ore-forming processes

Sediments and sedimentary rocks can be selectively enriched in certain elements of potential economic value. There are two main processes which may produce such enrichment are: (a) weathering processes; and (b) sedimentation. Fossil fuels represent a special case «organic» sedimentation when remains of organic matter became trapped and altered in sedimentary rock

(A) Weathering:

(1) Residual concentration

Weathering includes processes by which rocks that occur at or near the Earth's surface tend to achieve equilibrium with the surface environment. Water is the most important agent of chemical weathering. Among other substances, which may take active part in weathering reactions are free oxygen, inorganic and organic acids. The simplest of the weathering reactions is the dissolution of soluble minerals either by ionization (e.g., dissolution of NaCl) or by formation of acids (e.g., H₄SiO₄ by dissolution of quartz). More complex reactions include hydration, hydrolysis, carbonation, oxidation, and sulfidation. The most important weathering reactions involve hydrolysis of rock-forming silicates. The parameters commonly used to evaluate the stability of minerals under weathering conditions are Eh and

pH; other parameters, which can be used in appropriate cases, are the partial pressures of oxygen, sulfur, and CO₂.

Weathering provides mechanisms for leaching of more mobile constituents from the parent rock, thus resulting in residual concentration of the less mobile ones in the soil profile. The most important controls of soil profiles formation (*pedogenesis*) are climate and drainage which, in turn, control the release of elements by the breakdown of primary minerals and their entrapment in secondary minerals depending on Eh-pH conditions.

Arid regions produce neutral to alkaline soils, which selectively concentrate alkaline and alkaline-earth elements. Humid climates give rise to acidic soils where the alkaline and alkaline-earth elements, and to a lesser extent silica, are leached out and relatively immobile elements (e.g., iron, aluminum, and manganese) are concentrated mostly as hydroxides. In well-drained locations under the hot and humid conditions of tropical climate, the leaching of silica becomes very efficient, and the resulting soil with very high residual concentrations of iron and/or aluminum is commonly called *laterite*. Laterites are generally well layered, due to alternating downward percolation of rainwater and upward movement of moisture in the regolith during seasonal dry spells.

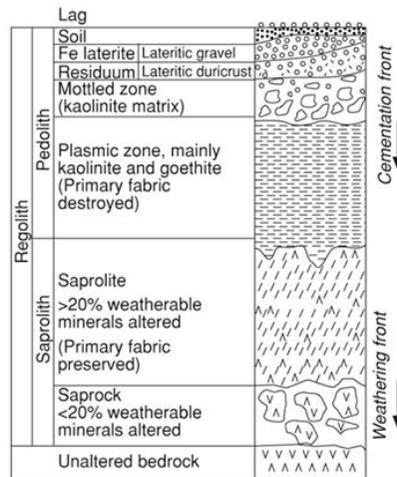


Figure 26. A generalized lateritic profile (after Robb, 2005).

Figure 26 shows a generalized lateritic regolith profile. The base of a lateritic regolith profile is characterized by the *saprolith zone*, which is highly weathered rock where the primary texture and fabric is still preserved. The lowermost *saprock zone* is characterized by the destabilization of sulfides and carbonates and the associated leaching of

most chalcophile metals and alkaline/alkaline earth elements. The lower *saprolite zone* is characterized by the destruction of feldspars and ferromagnesian minerals, with Si and Al retained in clay minerals (kaolinite and halloysite). The upper part of the regolith profile, the *pedolith zone*, is characterized by complete destruction of rock fabric and leaching of all but the most stable elements. This zone is dominated compositionally by Si, Al, and ferric Fe occurring mainly in kaolinite, quartz, and hematite/goethite.

(2) Supergene enrichment

The process which causes metal enrichment during weathering of hypogene sulfide body is called *supergene enrichment*. It involves the release of ore metals from unstable sulfide minerals to downward percolating meteoric water and precipitation of more stable secondary oxide and sulfide minerals in the subsurface environment.

The processes involved in the formation of supergene mineralization are similar to those that results in concentration of useful element in lateritic weathering zones. The end-product varies depending on the factors that govern chemical weathering and on the physical and chemical nature of the sulfide assemblages and host rocks.

Figure 27 shows the typical profile of the supergene enrichment zone that can be formed above original copper sulfide ore body. The uppermost layer, of hydrated iron oxides, is called a *gossan*. These layers are void of ore metals but they have distinctive textures that signal the presence of buried sulfides and they are commonly used in mineral exploration.

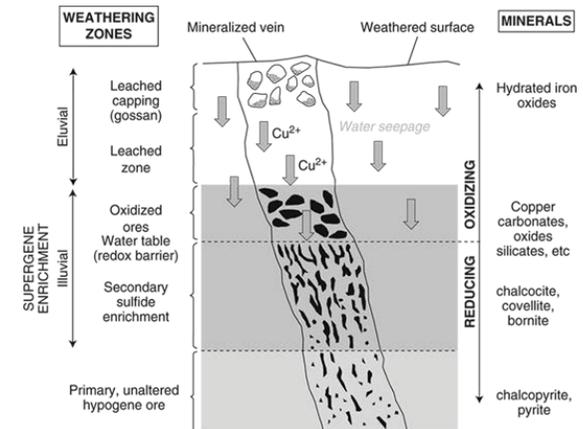


Figure 27. Typical profile of supergene enrichment zone (after Arndt, 2012).

Two enriched layers underlie the leached zone. The upper zone of «oxidized» ores contains a wide variety of secondary minerals – carbonates,

silicates, sulfates, phosphates – that are commonly well crystallized, brightly coloured, and highly prized by mineral collectors. It is underlain by a «*reducing*» zone of sulfide enrichment where the original iron-bearing sulfides, such as chalcopyrite (CuFeS₂) are replaced by secondary sulfides that are iron-free or iron poor and have high Cu contents. Examples include chalcocite (Cu₂S), covellite (CuS) and bornite (Cu₅FeS₄).

(B) Sedimentation:

(3) Clastic sedimentation

The term placer was used by the early Spanish miners in North and South America for gold deposits found in the sands and gravels of streams. The term has since been used in a more general way to describe deposits formed by mechanical accumulation of economically important detrital (*clastic*), resistant minerals – minerals that are stable in the weathering environment. Resistant minerals that are relatively inert and heavy can be released by weathering from source rocks and concentrated in modern placer and paleoplacer deposits. The formation of placer deposits is essentially a process of sorting light from heavy minerals during transportation and sedimentation.

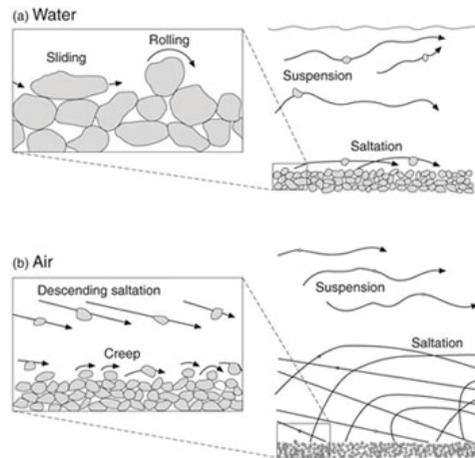


Figure 28. Sediment transportation in water (a) and air (b) environments (after Robb, 2005).

The transportation and deposition of sediment in fluvial and related systems are complex in nature. The types of fluid flow in water (or air) define the character and efficiency of mass (sediment) transport. A particle

or grain will move through a fluid as a function of its size, shape, and density, as well as the velocity and viscosity of the fluid itself.

In water, sediment particle will move in one of three ways: the heaviest particles (boulders, gravel) roll or slide along the channel floor to form the bedload; intermediate sized particles (sand) effectively bounce along with the current (a process known as *saltation*); while the finest or lightest material (silt and clay) will be carried in *suspension* by the current. In air the types of movement are similar, but the lower density and viscosity of air relative to water dictate that moving particles are smaller, but their motion is more vigorous. Deposition can occur either as flow velocity decreases or grain size increases (or both), and these parameters are very relevant to the formation of placer deposits (Fig. 28).

Based on the geologic environment of accumulation, placer deposits may be classified into: eluvial (sometimes referred to as residual), colluvial, fluvial (or alluvial), eolian, lacustrine, beach, and marine.

(4) Chemical precipitation

In contrast to the clastic sedimentation, where detrital sediment is sorted and deposited by water and wind, chemical sedimentation refers to the precipitation of dissolved components from solution, essentially out of sea water or brine. A wide variety of rocks are formed by the compaction and lithification of chemical precipitates and these include carbonate sediments (limestone and dolomite), siliceous sediments (chert) and iron-rich sediments (ironstones and banded ironformations), as well as less voluminous accumulations of manganese oxides, phosphates, and barite.

Most chemical sediments form in marine or marginal marine environments. The continental shelves, together with intratidal and lagoonal settings, represent the geological settings where chemical sediments and associated deposits are generally located. The chemical processes by which ore concentrations form are complex and controlled by parameters such as oxidation-reduction and pH, as well as climate, paleolatitude, and biological-atmospheric evolution.

(C) Fossil fuel formation:

«Organic» sedimentation is a process of fossil fuels formation through trapping and subsequent alteration of organic remains (plants and animals) in sedimentary rock. Typical hydrocarbon deposits (fossil fuels) are formed during the burial and degradation of organic matter that store a significant proportion of energy imparted into living organisms by the sun. Among the the most typical fossil fuels are coal and petroleum (crude oil and natural gas).

The global carbon cycle involves both gaseous carbon (CO₂ and CH₄) circulation and solid carbon (reduced carbon or carbonate minerals) storage in different reservoirs – deep ocean and sedimentary rocks. Organic photosynthesis ensure carbon trapping as combined with hydrogen and oxygen to form the organic molecular of various biota that inhabit the Earth's surface.

When organisms die they can be decomposed by bacterial decay (or oxidation) into relatively simple molecules such as CO₂ and CH₄. Such a process that can occur at or near the Earth's surface would not result in the formation of fossil fuels, which requires preservation of much complex organic molecules in reducing environment.

The widely accepted theory for formation of fossil fuel (coal and petroleum and) is based on the idea that organisms are buried during the sedimentary process accompanied by consequently series of alteration stages at condition of pressure and temperature increase. Progressive burial of phytoplankton results in the early liberation of CO₂ and H₂O and formation of kerogen (sedimentary organic matter with polymer like structure). As the kerogen «matures» the long-chain covalent bonds of organic molecules are progressively broken to form lower molecular weight compounds. At around 100-120°C and burial depths of 3-4 km, a liquid hydrocarbon fraction (oil) develops and can migrate from the source rock. This interval is known as the «oil window».

With further burial and cracking of molecular bonds, significant volumes of gas (mainly methane, CH₄) develop, which are also amenable to migration. The solid residue remaining in the sediment is referred to as kerogen, but with progressive burial it devolatilizes further and has a composition approaching pure carbon (graphite). By contrast, when humic, land-derived vegetation is buried, little liquid oil is formed, although significant volumes of gas can be generated. In this case, more voluminous and compact solid residue remains to form coal seams. The nature of the solid coal residue changes with depth ranging from peat and lignite formed at shallow burial depths (less than 500 m) to bituminous and anthracitic coals (at depths of 5000 m). The calorific value of the coal (amount of energy produced on coal combustion) increases with maturity or burial depth.

4.2. Surficial type deposits

(1) Bauxites

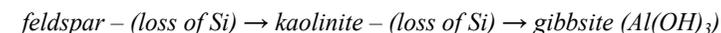
Bauxites represent the most important source of aluminum metal in the world. Just as for iron, the reserves of bauxite are enormous and reach about 25 billion tons. It will be enough for more than 300 years even at increased industrial consumption of this metal.

Bauxite deposits vary in age from Late Proterozoic to Cambrian but the most intense period of bauxite formation was from Cretaceous to Recent. The large lateritic bauxite deposits were formed during this time interval on stable continental platforms. The most important deposits of this type occur in Guinea, Brazil, Australia, India, Guyana, and West Africa.

These deposits, referred to as «high-level» laterites because of their occurrence at high elevations of the Earth's surface, are considered by most workers as ancient peneplains. Geographically, all the Cenozoic deposits are restricted to latitudes from 30°N to 30°S, indicating a strong climatic control on bauxite formation. Bauxites are composed dominantly of three modifications of Al-hydroxide minerals: gibbsite [γ -Al(OH)₃], boehmite [γ -AlOOH], and diaspore [α -AlOOH].

The accumulation of an alumina-rich residuum, as opposed to one enriched in iron, in the upper zone of a lateritic profile is a function of higher rainfall, lower average temperatures (around 22 °C) and higher humidity. Actual alumina enrichment in the upper parts of laterite profiles is due to relatively high Si mobility compared to Al, and reflects near neutral pH conditions (between 4.5 and 9).

This results in dissolution of minerals such as feldspar and kaolinite, where Si is leached in preference to Al, yielding a gibbsite-like residue. This process might be described schematically as:



Seasonal climatic variations are also important to the formation of bauxitic ores as the alternation of wet and dry spells promotes fluctuations in groundwater levels and, hence, dissolution and mass transfer.

Variations in bauxitic profiles, as well as transformation from hydrated gibbsite to the relatively dehydrated version, boehmite, or to diaspore (AlO(OH)), result from such fluctuations. The mineralogical profiles of bauxite mineralization may be quite variable. In humid, equatorial laterite zones, hydrated minerals such as gibbsite and goethite predominate, whereas in seasonally contrasted climates the ores are relatively dehydrated and boehmite-hematite assemblages are formed.

The redistribution of iron, and the segregation of Al and Fe, is a necessary process in bauxite formation because ferruginous minerals tend to

contaminate the ore. High quality bauxitic ores require that both Fe and Si be removed from alumina-rich rocks.

The purest bauxites are formed through a combination of processes: (1) presence of Al-rich (and Fe-poor) parent rocks such as alkali granite, syenite, tuff, or clay-rich sediment and their metamorphosed equivalents; (2) appropriate balance of temperature and rainfall (high temperatures favor Fe-rich laterites); and (3) pronounced alternation of wet and dry seasons.

As a result of these restrictions, the most important bauxite deposits in the world are located mainly in equatorial countries with tropical climates such as Guinea, Australia, Brazil, and Jamaica.

(2) *Ni laterites*

Lateritic nickel deposits are confined to laterites derived from ultramafic rocks (peridotites and serpentinites) which contain up to about 0.4 % Ni. The relatively high Ni content is attributable mainly to the substitution of Ni^{2+} for Mg^{2+} originally in olivine and its altered product, serpentine. High-temperature magmatic rocks like peridotites are particularly susceptible to extreme leaching and redistribution of elements under humid climates.

The process of laterization is directly comparable to that of bauxite formation. Nickel laterites develop when either the primary minerals of the ultramafic rocks, olivine or pyroxene, or secondary serpentine that replaces these minerals, are subjected to weathering under conditions similar to those that produce bauxite. Elements such as Si, Mg, Ca, which make up of about 90% of the parent rock, are removed and the less mobile Ni (and Co) are retained. Through this process the Ni content increases from 0.2% to 0.3% in the peridotite to 1-3% in the ores. Cobalt is also concentrated by this process and constitutes a valuable by-product.

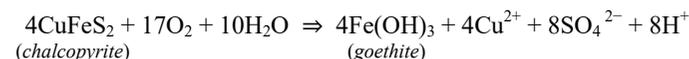
The most Ni-rich deposits of New Caledonia were developed in the lower part of the saprolithic zone of lateritic profile. Here, the main ore mineral (garnierite) occurs as a mixture of pale green or apple-green phyllosilicates with the approximate composition as $(\text{Ni}, \text{Mg})_3\text{Si}_2\text{O}_5(\text{OH})_4$. The very rich garnierite ores of New Caledonia deposit contained up to 15% Ni and averaging 2.5% Ni. But at present, the richest ores are largely exhausted and mining has turned the less Ni-rich iron oxide (goethitic) ores (1.3-1.6% Ni). Goethitic ores are predominantly confined to the lower part of the pedolithic zone (Fig. 26).

The New Caledonian deposits are thought to contain about a third of the world's resources of Ni. Other major lateritic deposits that are situated in Indonesian, Cuba and Australia comprise 50-60% of world production of nickel. The grade of most deposits being mined is from 1.5 to 2.0% Ni, but may range up to about 3% Ni or even higher.

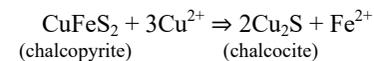
(3) *Supergene copper deposits*

When sulfide ore bodies are exposed at the surface, the sulfide minerals become oxidized and the ore metals can leach downward to become concentrated in a layer near the top of the water table (Fig. 27). For sulfide copper and silver ores (as well as iron oxides, and some uranium deposits) this process is of economic importance.

Supergene copper deposits occur in any surficial environment where oxidized, acidic groundwaters are able to destabilize sulfide minerals and leach copper. The principles involved in this process might be illustrated in terms of the following reaction:



Chalcopyrite is the major Cu-Fe sulfide mineral and its breakdown produces soluble cuprous ions that are dissolved in groundwater solutions. The soluble copper ions percolate downwards in the regolith profile and encounter progressively more reducing conditions, either as a function of the neutralization of acid solutions by the host rock, or at the water table. Copper is then precipitated as various secondary minerals, the so-called «copper-oxides» that are very complex in composition and mineralogy. Cu also replaces pre-existing sulfide minerals in more reduced (hypogene) zones. Cu typically replaces the Fe in such hypogene minerals as pyrite and chalcopyrite, to form a suite of Cu-enriched sulfide phases including chalcocite (Cu_2S), covellite (CuS), and bornite (Cu_5FeS_4). Copper is reprecipitated as chalcocite and covellite by replacement of primary sulfides according to the following reaction:



Supergene enrichment layers can contain two to five times more ore metals than the primary ore and they are conveniently located close to the surface. Here they can be easily recovered at the very beginning of the mining operations. The best-known examples of supergene enrichment ores are those that are formed over porphyry copper deposits. For example, primary ore in the Chuquicamata porphyry-type deposit contains only about 0.8% Cu but it was overlain by a thick layer of supergene enrichment in which the copper grade was 2-3%.

4.3. Sedimentary type deposits

(4) Placer deposits

Placer deposits consist of sand, gravel, or soil that host eroded particles of valuable minerals. Due to the chemical and physical properties of the minerals, they can resist and become concentrated in the surface environment. Among the most common resistant minerals that can occur in placer deposits are platinum metals; gold, present in the native or metallic form; many heavy minerals such as rutile, ilmenite, zircon, and monazite (they are sources of titanium, zirconium, niobium, and other high-technology metals); and gemstones such as diamond, garnet, or ruby. Sulfides rarely form placer deposits, because of susceptibility to decomposition by oxygenated meteoric waters.

Being products of normal surficial processes, modern placer deposits have a wide geographical distribution, although most of these deposits are small and non-economic. Placer deposits have formed throughout geologic time, but the bulk of the world's placer deposits are Tertiary (Paleogene, Neogene) and Quaternary in age. Precambrian paleoplacers, such as gold and uranium placers in South Africa and uranium in Canada, represent the most productive deposits of this

The existence of such a temporal pause in placer deposit formation (between Precambrian and Tertiary) is ascribed to possible removal by erosion of placers before their preservation by burial. It is also supposed that placer formation was favored in the Tertiary because of rapid uplift during Mesozoic-Cenozoic orogenic events and because of sea-level changes during the Quaternary time.

Based on the geologic environment of accumulation, placer deposits may be classified into several types – *eluvial* (referred to as residual), *colluvial*, *fluvial (alluvial)*, *eolian*, lacustrine, beach, and marine. Aeolian placers as well as those formed in glacial sediments do not have any economic significance. Among the most economically important examples are the fluvial and beach placers.

The main process that is common to all placer deposits (except the eluvial and colluvial placers, the formation of which is controlled by gravity) is mechanical concentration controlled by the differences in specific gravity, size, and shape of particles in a moving fluid.

Alluvial placers are composed of loose, unconsolidated sands and gravels that are commonly quite clean. The heavy mineral suites of alluvial placers vary depending on the source rock, but the most common heavy minerals are represented by magnetite and ilmenite. Economic alluvial placer deposits are mostly those of gold, uranium, diamond, platinum, and tin. Beach placers are formed by the action of waves and currents along

shorelines where a source of heavy minerals are available. Important beach placer deposits are those of ilmenite, rutile, zircon, monazite, garnet, and gemstones.

Placer deposits of gold have produced two-thirds of the gold mined over time. The fluvial placers of California, Australia, and elsewhere were mined out very rapidly in the gold rushes, usually over periods of only a few years. At present, gold placer production continues in the Witwatersrand ore bodies of South Africa, a hydrothermally reworked conglomeratic paleoplacer that is the largest gold deposit in the world. Other place deposits of economic importance are represented by tin, platinum, thorium-uranium, and diamond.

The primary source of tin is cassiterite (SnO_2), a magmatic mineral that crystallizes in so-called «tin granites» that are very rare in the Precambrian and become more abundant in later epochs. The best known examples of tin placers are on the Malayan Peninsula, Malaysia is the world's greatest producer of cassiterite, and about half of the deposits are located in placers (rivers, beach sands, and off-shore deposits. The other half of tin production is related to granites.

Among the parental sources of platinum-group elements (PGE) are ultramafic rocks such as those of the Bushveld Complex (South Africa). In certain regions, PGE nuggets released by weathering and erosion of ultramafic rocks have produced economic placer deposits.

Thorium and uranium are hosted in uraninite in the Witwatersrand ore bodies which may be of alluvial origin, and in monazite in beach sands. The beaches flanking some parts of India contain high concentrations of monazite and the country is currently developing a new type of nuclear power reactor that can use Th as a fuel.

Placer type deposits of diamond normally contain a high proportion of high-quality gems (up to 97%) because single diamond crystals that are large in size can better survive the rigorous processes of sediment transportation and deposition than smaller ones. Placer deposits provide about 34% of global diamond production.

(5) Ironstones and Banded Iron Formations

A combination of two processes produces the richest iron ores. Fe minerals first precipitate from seawater to form chemical sediment; then chemical weathering upgrades the Fe content when the deposit is exposed at the surface. There are several different types of iron deposit.

Ironstone is the iron-ore type that has been exploited throughout Europe since the start of the «Iron Age» around 800 BC.

Ironstones occur as lenticular beds commonly associated with organic-rich black shales. They contain little or no chert and the iron is present in minerals such as hematite (Fe_2O_3), goethite ($\text{FeO}(\text{OH})$) associated with carbonate (siderite, FeCO_3) and silicates such as greenalite (serpentine or clay with the composition $(\text{Fe}^{2+}, \text{Fe}^{3+})_{2-3}\text{Si}_2\text{O}_5(\text{OH})_4$), chamosite (phyllosilicate with the composition $(\text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+})\text{Al}(\text{Si}, \text{Al})\text{O}(\text{OH}, \text{O})$), and glauconite $(\text{K}, \text{Na})(\text{Fe}, \text{Al}, \text{Mg})(\text{Si}, \text{Al})(\text{O}, \text{OH})$. The iron oxides and chamosite are often oolitic.

The ironstones were deposited within two well-defined age periods, in the Ordovician-Silurian and in the Jurassic. Ironstones are thought to form when iron on the continents is subject to deep weathering in a warm humid climate, conditions that lead to the development of lateritic soils. The initial iron enrichment and the growth of small round structures (pisolites) took place in highly oxidized surface layer in response to low-temperature and chemical and biogenic processes. The lateritic soils were then transported into shallow waters in deltas or estuaries where current and wave action sorted and concentrated the iron minerals.

Banded Iron-Formations are the dominant type of iron deposit. The term is used for bedded chemical sediments comprising alternating layers of iron minerals, usually oxides or hydroxides, and fine-grained quartz or chert. The banding is manifested at different scales: centimeter-thick beds of iron minerals and chert are internally divided into millimeter or sub-millimeter lamellae of the same minerals. Detrital components such as clays, or grains of quartz and feldspar, are usually rare.

Banded iron-formations (BIF) were deposited at three different time periods, all in the Precambrian. The oldest is 3.5-2.7 Ga; the second and far the most economically important ranges from 2.5 to 2.0 Ga; and the third, less significant, from 1,000 to 500 Ma. The tectonic setting of iron deposition and the types of associated rocks is different for each period. As a result, this has given rise the following names for each type – Algoma, Superior and Rapitan.

These three types of BIF are formed in different tectonic settings and are referred to as Algoma, Superior, and Rapitan types, respectively.

Algoma-type deposits are associated with volcanic rocks formed in volcanic arc setting, and commonly found in Archean greenstone belts. These deposits tend to be fairly small but they are mined in places as the Abitibi greenstone belt of Ontario, Canada.

The majority of *Superior-type* deposits are located on stable continental platforms where they are mainly deposited during Paleoproterozoic times. They represent the most economically important category of iron ore deposits. These deposits are named after Lake Superior that is situated

between Canada and USA and where they were first studied and mined. Since then, the similar type iron formations are also found in much larger deposits of Hamersley Basin (Western Australia), Transvaal Basin (South Africa), «Quadrilatero Ferrifero» (Brazil), Krivoy Rog (Ukraine) and Singhbhum region (India). Finally, the Rapitan type iron ores represent a rather unusual occurrence of iron ores associated with glaciogenic sediments formed during the major Neoproterozoic ice ages. The type occurrence is the Rapitan Group in the McKenzie Mountains of northwest Canada (Fig. 29).

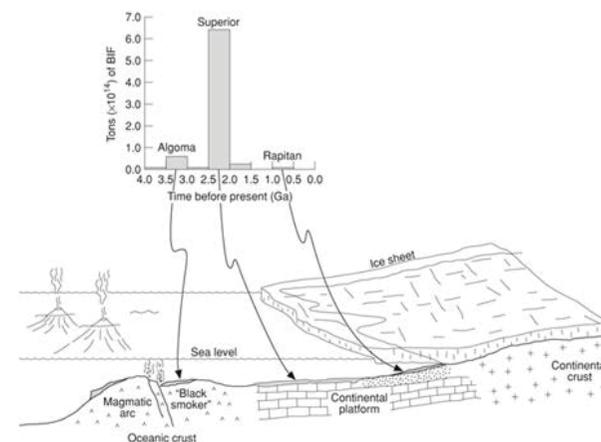


Figure 29. Depositional settings and age distribution of Algoma, Superior, and Rapitan types of BIF (after Robb, 2005).

In addition to the classification based on the tectonic setting formation, BIFs can be also classified according to the mineralogy of iron phases. Although in most BIFs the iron mineral is an oxide phase (hematite or magnetite), carbonate (siderite), silicate (greenalite and minnesotaite), and sulfide (pyrite) iron minerals also occur, together with chert or carbonaceous shale.

The different types of iron minerals are stable under contrasting conditions of Eh and pH, from relatively oxidising to highly reducing. This fact suggests that they have been deposited in different geologic environments. The oxide minerals are stable in acid solutions (hematite at high Eh and magnetite at low Eh). Pyrite and siderite are stable in near-neutral solutions at low Eh (but these fields expand at high activities of carbonate or sulfur). In alkali solutions, ferrous iron is soluble over a wide range of Eh but the field is broader under reducing conditions. It can therefore be seen that an increase in Eh, oxidation, stabilizes hematite

relative to Fe^{2+} , and this process is the key to formation of most BIF deposits.

Genetic models of banded iron-ore formation

The restriction of the Superior type BIF deposit to the Proterozoic period of 2.4-2.0 Ga, is commonly taken as evidence that the composition of the Earth's oceans and atmosphere changed markedly at this time. The Archean, pre-2.7 Ga, atmosphere was a reducing, oxygen-free mixture of nitrogen, carbon dioxide and methane. The oceans were hotter, acidic and they contained abundant dissolved Si and Fe. In the early Proterozoic, the oxygen content of the atmosphere and the oceans have risen because the appearance of abundant oxygenic cyanobacteria. It is this change that led to the precipitation of Fe and Si oxides. In reduced condition of deep oceanic basin the iron can be derived from hydrothermal exhalative volcanic source. Precipitate of iron minerals and silica occur when reduced Fe-rich deep seawater mixes with oxygenated shallow seawater.

Algoman-type iron formations probably result from more local mixing of reduced and oxidized fluids in restricted basins adjacent to Archean continents. An association with carbonate and sulfide facies suggests that the source of the iron were exhalative hydrothermal fluids emanating from the oceanic crust.

Rapitan-type deposits are thought to form after the periods of «Snowball Earth». This term is used to indicate Proterozoic periods during which the Earth was globally covered by ice sheets – both continents and oceans. Seawater became reducing, rather as in Archean times and was able to dissolve ferrous (Fe^{2+}) iron. During interglacial periods the reduced seawater mixed with oxidized surface waters, leading to the deposition of iron formations with iron as ferric (Fe^{3+}) oxides.

Primary iron formations (those formed in water environment) commonly contain 20-30% Fe, whereas the most ores mined contain 55-65% Fe. Such enrichment occur a result of BIF exposure at the Earth's surface (air environment). Exposure under hot and humid climate conditions with circulating groundwater leaches silica from the rock and replaces it by iron oxides that result in formation economic iron-ore grades.

(6) Manganese deposits

Manganese deposits may be classified into two broad genetic groups: (a) strata-bound and vein deposits of hydrothermal origin; and (b) bedded (stratiform) deposits of sedimentary origin.

Most of the sedimentary manganese deposits are formed in environments similar to those in which BIF occur. The geochemical behavior of manganese, like iron, is mostly controlled by redox potential.

Mn^{2+} is soluble under reducing and acidic conditions whereas Mn^{3+} and Mn^{4+} are less soluble and can be stabilized (precipitated) as manganese oxides under relatively oxidizing and alkaline conditions. Pyrolusite (MnO_2) the dominant oxide phase at high Eh and over wide range of pH.

Comparison of the manganese with the iron phase has shown that higher oxidation potentials are required to stabilize pyrolusite than hematite. The fact that Fe^{2+} oxidizes more readily than Mn^{2+} means that iron can precipitate while Mn remains in solution, and provides a possible explanation for the observation that iron ores may be spatially (or stratigraphically) separated from manganese ores.

Manganese deposits can occur in sediments ranging in age from the Paleoproterozoic to Recent. The best analogue of the Recent sedimentary manganese ores formation is provided by the Black Sea.

The Black Sea is stratified in terms of water density and composition – waters below 200 m depth are euxinic (highly reduced by presence of H_2S). Pyritic muds accumulate on the sea floor and this effectively depletes the entire water column of iron. Mn is concentrated in the deeper waters (as soluble Mn^{2+}), but is depleted in the upper oxidized 200 m where it can precipitate (as insoluble Mn^{3+}).

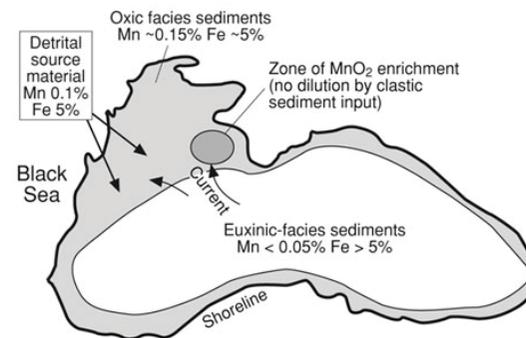


Figure 30. Mn ores in the sea floor sediments of Black Sea (after Robb, 2005).

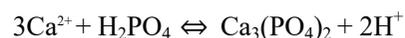
Just below the redox interface where mixing between high-Mn reduced euxinic and oxidized surface waters occurs. At the interface Mn^{2+} is oxidized to Mn^{3+} and then settles at deeper levels where it can redissolve. However, where the enriched mixing zone intersects shallow sea floor, accumulation of either MnO_2 or MnCO_3 (depending on the local oxidation potential) takes place. Mineralization is further enhanced if the sites of accumulation are protected from dilution by clastic sediment input, as shown for the north-central portion of the Black Sea (Fig. 30).

Most of the world's manganese production comes from a few giant sedimentary deposits. Two such deposits, Chiatura in Georgia and Nikopol in Ukraine, contain 75-80% of the world's present onshore reserves of manganese.

(7) Phosphorites

Phosphorites generally form along continental shelves and in shallow marginal marine settings such as lagoons and deltas. The processes of formation involve the upwelling of cold ocean water containing high phosphorus concentrations with its subsequent precipitation onto the continental shelves.

Phosphorus can be dissolved in sea water as either PO_4^{3-} (alkaline conditions), HPO_4^{2-} (anionic complex), or H_2PO_4^- (acidic conditions) complexes. These anionic complexes are absorbed by the organisms living in shallow marine environments to form their shells, bones, and teeth. Therefore accumulation of phosphorus on the sea floor is not related to a chemical redox reaction, but occurs after the host organism dies and settles to the ocean floor. Phosphorus is released from the decaying organism to form a calcium phosphate compound, which then converts to an impure, cryptocrystalline form of apatite ($\text{Ca}_5(\text{PO}_4)_3[\text{F},\text{OH}]$) or collophane (carbonate-apatite). The concentration of calcium phosphate on the sea floor might occur according to following reaction:



Genetic models of phosphorite formation:

Possible formation of apatite/collophane in phosphatic sediments is still a problem under considerable debate. Some geologists suppose that it is developed as a primary precipitate resulted from a decay of organic material of living marine organisms, while the others treat it as a product of diagenesis during later compaction and dewatering of the sediment.

The most recent studies of phosphorites formed along western and southern continental margins of South Africa and Namibia have revealed two different phosphorite varieties. One variety developed mainly along the Namibian coastline and comprises oolitic apatite/collophane ores derived by accretionary growth arising from the direct precipitation of phosphate from sea water. The other type, formed mainly along the South African coastline, consists of phosphatic replacement of fossiliferous limestone and is diagenetic in origin.

Phosphorus is a very important element that is essential for the growth and development of most living organisms. Plants also require it for growth and it is for this reason that phosphate is such an important ingredient of

fertilizer. In order to sustain global food requirements the manufacture of artificial fertilizers has become an enormous industry that requires approximately 150 million tons of phosphate per year, the raw material for which comes predominantly from phosphorus-rich (more than 15-20% P_2O_5) sediments or phosphorites.

(8) Evaporites and Li-brines

Evaporites are chemical precipitates that form as a result of evaporation of a brine, usually from sea water.

There are two main geological settings where evaporites can form. The first and most important represents marginal marine basins formed in large lagoons or embayments which are periodically recharged with sea water. This type of deposit are referred as «saline giants» because they may be laterally extensive and thick. For example, Permian Zechstein Formation covers large areas of the United Kingdom, The Netherlands, Germany, and Poland. The second setting is represented by intracontinental and lacustrine basins where much smaller and thinner deposits can occur. Examples of intracontinental lacustrine deposits include the dry lakes of Chile and Great Salt Lake of Utah (USA).

The formation of evaporite deposits is considered to be relatively simple. As sea water (or brine) evaporates, i.e. water vapor is removed into the atmosphere, the salinity of the residual solution increases and individual salts precipitate. The order (sequence) of precipitation reflects the scale of increasing solubility at a given temperature, such that the salts with the lower solubilities precipitate first. The relative quantities of precipitated products are also constrained by the solubility limits of the various salts. These considerations seem to suggest a relatively simple precipitation process. In fact the chemistry of brine solutions is very complex and such basal factors as convection dynamics and post-precipitation diagenesis can result in considerable diversity of evaporite deposits.

Marine evaporites are commonly characterized by constant composition dominated by the same assemblage of major mineral precipitates, namely halite (NaCl), gypsum/anhydrite ($\text{CaSO}_4/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and sylvite (KCl). At the same time, evaporites can also contain minor accumulations of other salts, especially those representing the late stage precipitations. They typically comprise Mg, Br, Sr, K chlorides and borates that are called bitterns.

Evaporites ensure the world's bulk production of rock salt (halite), as well as potash, borates, and nitrates that are used for agricultural fertilizers. Among typical products that are commonly mined from «saline giants» are halite, potash, and sulfates.

Lithium

Currently two main types of Li ore are mined. The first consist of deposits of the mineral spodumene, a Li silicate with a pyroxene-like composition ($\text{LiAlSi}_2\text{O}_6$), that occur in pegmatites. The second is Li carbonate which occurs in evaporitic sediments and in the waters of high-altitude lakes. Past production has been mainly from spodumene, but this has been largely supplanted by the second source. At present about 75% of the world's Li reserves are treated to be localized in South America – in the Andean «*altiplano*», the high flat plain that extends through three countries, Bolivia, Chile and Argentina. Here, such geological factors as the presence of siliceous volcanic rocks (Li source) and climatic conditions favor the concentration of Li in the altiplano lakes. The high altitude, strong winds and arid climate promote rapid evaporation of closed basins where Li accumulates in lake waters and sediments.



Figure 31. Evaporation of Li-brine in closed pen (after Arndt, 2012).

Lithium extraction includes two stages. At first, lithium is separated by evaporation of the brine in closed pens (Fig. 31). Then, Li is extracted from the concentrated brine and separated from other salts by a series of chemical reactions. The process is slightly long and 1-2 years are required for the initial evaporation stage. But it is relatively much cheaper than process of lithium extraction from pegmatites.

4.4. Fossil fuels

(1) Oil and gas

All organisms living on the Earths are made up of relatively few organic molecular building blocks:

- 1) *Carbohydrates* – mono- and polysaccharide polymers represented by the sugars, chitin and lignin.
- 2) *Proteins* – amino acid polymers of high molecular weight.
- 3) *Lipids* – occur in animal fats and vegetable oils.
- 4) *Resins and pigments* – occur in both plant and animal matter.

Plants comprise mainly carbohydrates (40-70%), although the higher, woody forms also contain substantial lignin for strength. Phytoplankton contains around 20% protein. Animals are made up mainly of proteins (55-70%) with lesser carbohydrates and lipids but no lignin.

As the organic constituents are buried, they are subjected to increases in pressure and temperature, resulting into changes which are divided into three stages – diagenesis, catagenesis, and metamorphism.

Diagenesis refers to the early changes that occur in organic-rich sediments at low temperatures (less than 50°C). At this stage the biopolymers of living organisms are either oxidized or attacked by microbes and converted into less complex molecules. These molecules, in turn, can react and condense to form more complex, high molecular weight geopolymers that are the precursors to kerogen. Biogenic reactions that occur during diagenesis produce significant amounts of gas – biogenic gas. But, it escapes into the atmosphere or ocean water and is not retained in the sediment.

Catagenesis stage occurs between about 50 and 150°C and is the most important stage as far as petroleum generation is concerned. During this stage temperature plays an important role in catalyzing reactions, the majority of which result in the formation of light hydrocarbons from high molecular weight kerogen by the breaking of carbon-carbon bonds.

In this process, known as *thermal cracking*, a complex organic molecule such as a paraffin or alkane will split and form two smaller molecules (alkene or olefin). *Catalytic cracking* is known as alternative process of organic molecule distraction. For example, alkanes subjected to catalytic cracking could yield gaseous products such as ethane or butane. Catalytic cracking tends to be the dominant process in petroleum generation up to about 120°C , but at higher temperatures thermal cracking becomes increasingly important.

Such parameters as time and temperature are very important for petroleum generation. They are inversely related in terms of petroleum productivity so that, a given quantity of oil formed at 110°C over 25 million

years would require 100 million years to form at 90°C. The time-temperature evolution of sedimentary basins is, therefore, a critical factor in petroleum origin. Oil would not be formed in a young basin with low geothermal gradient because the threshold for efficient hydrocarbon generation might not yet have been reached. Likewise, little oil could be preserved in an old, hot basin as it would all have been destroyed during metamorphism. As a general rule, oil resources are sought to be formed either in young, hot basins or in old, cold ones.

Petroleum sources

Most of the organic matter on Earth can be classified into two major types, namely *sapropelic*, which refers to the decomposition products of microscopic plants such as phytoplankton, and *humic*, which refers essentially to the maturation products of macroscopic land plants. Sapropelic organic matter has H/C ratios in the range 1.3-1.7, whereas humic matter has a lower H/C ratio of about 0.9. These compositional differences were used for classification of kerogen types that has relevance to the generation of fossil fuels. A more recent classification uses a plot of hydrogen index versus oxygen index. These indexes, being analogous of H/C and O/C in general, but they can be directly measured with using spectrometric analysis (Fig. 32).

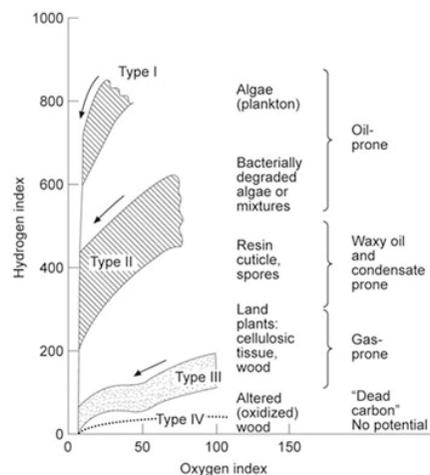


Figure 32. Kerogen types (after Robb, 2005).

According to the classification scheme four main kerogen types can be distinguished:

- 1) Type I kerogen – is derived from algal material and, on maturation, yields mainly oil.

- 2) Type II kerogen – is obtained from the breakdown of plant spores, pollens, exines, and resins, but it may also comprise bacterially degraded algal (Type I) organic matter.
- 3) Type III kerogen – is derived from humic land plants rich in lignin and cellulosic tissue and on maturation yields only gas..
- 4) Type IV kerogen – is obtained from oxidized woody material and has no hydrocarbon potential.

Oil-prone kerogens of Type I and II will yield not only oil, but also gas fraction that can be «wet» (ethane, propane, butane as high condensable fraction) and «dry» (mainly methane). Gas-prone kerogen of Type III produce mainly dry gas.

Petroleum migration

Petroleum originates in a fine grained source rock and then migrates into more permeable, coarser grained, reservoir sediments. Petroleum migration can be subdivided into *primary migration*, which accounts for the movement of oil and gas out of the source rock during compaction, and *secondary migration*, which describes petroleum flow within the permeable reservoir, as well as the segregation of oil and gas. Primary migration can occur over short distances (hundreds of meters), with secondary migration being apparent over tens and hundreds kilometers.

As the organic source rock is lithified during diagenesis, water (salinity brine) is expelled from the sediment to form a connate fluid. In the early catagenic stages oil and gas migrate in the presence of water. Oil is unlikely to migrate in aqueous solution since hydrocarbons generally have low solubilities in water. However, small hydrocarbon molecules (methane, CH₄) can readily dissolve, with methane being fairly soluble in water as pressure increases. Moreover, it is hydrocarbon gases that can dissolve hydrocarbon liquids (oils) and, as a result, primary migration can be promoted by gas phase dissolution.

At the same time, two other mechanisms are treated to be more important for hydrocarbon primary migration, namely – *migration* and *diffusion*. Petroleum source rocks usually contain a relatively high proportion of pore water that prevents oil migration. Oil globules that float in the water-dominated pore spaces cannot generate the capillary forces required to initiate migration. As compaction progresses the the pore water is constantly removed. In such a case, oil occupies enough of the pore space to be subjected to capillary forces and start flowing through the rock. Once «oil-saturated» pathways are established (water do not prevent rock permeability), *oil migration* becomes feasible mechanism. Another possible way of hydrocarbon movement is the *diffusion*. Hydrocarbon and water can form clathrate compounds in the sediment pore space, with diffusional

energy gradient being responsible of hydrocarbon clathrates migration towards lower free energy environment. This diffusion can cause oil movement from fine-grained shales towards coarse-grained sands.

It should be noted, that exactly water plays a very important role as transporting agent in primary migration. In the case of low-organic source rocks when gas phase is predominantly generated, hydrocarbon migration would occur by diffusion in aqueous solution or as gas phase dissolution. At high-organic content of source rocks, hydrocarbons would migrate predominantly as the oil phase. Intermediate situations might be possible over the entire range of migration processes.

At more large geological scale, where oil and gas migrates over tens to hundreds of kilometers, the main factor that controls hydrocarbon migration are *pressure gradient* and *overpressured fluids*. In case of low permeability of source rocks (fine-grained shale) the removal of pore water will be impeded and, then, compaction will caused fluid pressures increased to values above normal hydrostatic pressures. Fine and coarse sediment will expel pore waters at different rates during burial and will compact along different pressure gradients. Overpressured fluids show will tend to exist in the finer grained sediments. Among several factors that can cause hydrostatic fluid overpressures in rocks are rapid sediment deposition, thermal expansion of fluids, tectonic compression, and others.

Secondary petroleum migration can occur at the advanced stages of catagenesis. At such temperatures and pressures many hydrocarbons exist close to their critical points – low density contrasts between liquid and vapor phase. The progressive separation of liquid and vapor phases into a low dense, buoyant gas and more dense, viscous oil is a process that generally accompanies secondary migration. At the same time, the segregation of oil from gas mainly reflects the decline in temperatures that accompanies migration of petroleum products into reservoirs that occur far away from the sites of oil and gas generation.

Petroleum entrapment

Hydrocarbon traps are critical to the formation of oil and gas fields, because they can reduce permeability or occur as barrier that impedes migration of hydrocarbon fluids. Evaporite layers may be good hydrocarbon traps as they are laterally extensive and have low permeability because of the ability of halite to flow plastically at elevated temperatures. Many giant oil fields are capped by evaporite sequences. Besides sandstones, carbonates represent important reservoirs because the high solubility of minerals such as calcite promotes secondary porosity and migration of hydrocarbons. For example, limestone reefs occur as important trap sites in carbonate sequences.

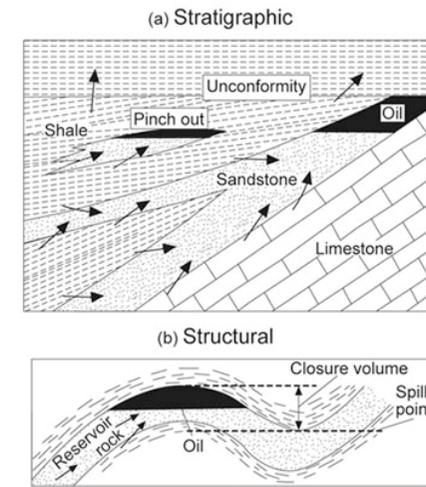


Figure 33. Petroleum traps: a) stratigraphic; b) structural (after Robb, 2005).

All know hydrocarbon trap sites can be classified into three categories – stratigraphic, structural, and asphalt (hydrodynamic) traps. Among them, such structural types as faults and anticlines are considered to be the dominant hydrocarbon trap sites (Fig. 33).

Stratigraphic traps are represented by sediment pinch-out zones, where permeability is reduced as one sediment facies grades into another, or unconformities that can reduce flow capability. Structural traps are formed as result of sediment deformation and provide physical barriers which prevent the fluid flow along an aquifer. Fault structures might juxtapose permeable sediment against unpermeable shales and, in such a way, can act as barrier behind which hydrocarbons will accumulate. Since most hydrocarbons show a tendency to flow into up crustal levels, the anticline or dome-like folding also provides a very efficient trap site.

Other important structurally related trap sites are linked to the deformation that accompanies salt diapirism. When salt beds underlie more dense rock strata rising salt diapires can pierce the overlying permeable sediments with formation of hydrocarbon traps.

Hydrodynamic traps are known as trap sites where oil migration is diverted by a strong groundwater flow which affect sediment pore spaces and impede the flow of hydrocarbons. In addition, groundwaters can interact chemically with reservoir oil that results in oxidation, biodegradation, and formation of bituminous asphalt layer. This layer (asphalt trap) can also act as possible barrier beneath which hydrocarbons may accumulate.

(2) Peat and coal

Coal is derived from a peat through burial or coalification, when it can be progressively transformed to a series of products ranging from lignite and sub-bituminous coal (brown coals) to bituminous coal and finally anthracite (hard coals). The formation of peat is an essential initial step that involves biochemical degradation of plant matter without oxidation and bacterial decay. It can occur in an environment represented by a well vegetated land surface that is saturated with water, which is commonly termed as «swamp». Swampy environments commonly contain waters that are both anaerobic and acidic, which promotes the preservation of organic material by minimizing oxidation and destroying bacteria.

Tropical rain forests seldom form peat accumulations because the high temperatures promote rapid oxidation and decay of organic material. The best conditions for peat accumulation reflect a balance between organic productivity and decay. Many peat and coals have accumulated in cold climates at mid- to high latitudes. The greatest concentrations of peat are accumulating in Russia (about 60% of the world's resources) at latitudes of around 50-70°N. Coalification stage follows once peat is covered by overburden and subjected to an increase in temperature with progressive burial.

Coal is a heterogeneous sedimentary rock that contains more than 50 % of carbonaceous material. Most coal is derived from kerogen and generally represents the sedimentary type accumulations of land-derived vegetation subjected to alteration and compaction. Peat deposits are known to have formed in many settings including lacustrine, fluvial, deltaic, and beach-related. Coals that form by compaction of peat can also exhibit marked variations in composition.

Coal is made up of «macerals» (similarly rocks that are made up of minerals), which are components of plant tissue, altered during compaction and diagenesis. Macerals can be mainly classified into three groups:

- a) *vitrinite* (huminite in brown coals) – made up of woody material (branches, roots, leaves)
- b) *exinite* (liptinite) – comprises spores, cuticles, waxes, resins, and algae.
- c) *inertinite* – comprises mainly the remains of oxidized plant material and fungal remains.

Different combinations of maceral groups identify the coal lithotypes, that is similar to that of rock type classification. The majority of coals are humic (made up of macroscopic plant parts) and formed after peat. These coals can be subdivided into four lithotypes – vitrain, clarain, durain, and fusain. Coal lithotypes are important in determining economic properties of

coal, such as calorific value and liquefaction potential. The highly reflective, more combustive coals are made up of vitrain, whereas the duller, less combustive coals comprise essentially durains. Small proportion of coals is sapropelic in origin and formed largely from microscopic plant remains such as spores and algae (exinite).

The sapropelic lithotypes (cannel and boghead) do not form from peat. They can be found as overlying humic coals that are formed in muddy environments – when the swamp was flooded and buried.

Coals can also be subdivided based on their chemical composition – contents of carbon, hydrogen, and oxygen. As peat is progressively compacted and became altered through coalification, the carbon content increases noticeably, whereas contents of hydrogen remains constant and oxygen decreases. Hydrogen only starts to diminish noticeably once the hard coals start to develop. The chemical changes that accompany coalification are also accompanied by the production of gaseous fractions (CO₂ and CH₄).

Ash content is another important property of coal. As peat forms it can incorporate inorganic, clastic detritus. During coalification this detritus is diagenetically altered to form authigenic minerals – quartz, carbonate, sulfide, and clay minerals. These components are responsible for ash content once the coal is burned and processed (crushing, grinding, etc.). Low ash content of coals results in much higher calorific values, better grindability, and less environmental deterioration by harmful constituents such as sulfur emissions. Such a quality parameter as coal rank is used for separation of low calorific value brown coals from high heat capacity hard coals.

The majority of the world's energy requirements is still obtained from the burning of coal and lignite. The two largest producers of coal in the world are China and the USA, although Australia ranks top as an exporter of high quality coal.

Questions for self-testing:

1. *Describe the main features of surficial and sedimentary ore-forming processes with detailed explanation of ore formation at weathering.*
2. *Describe the main features of surficial and sedimentary ore-forming processes with detailed explanation of ore formation at sedimentation.*
3. *Describe the main features of surficial and sedimentary ore-forming processes with detailed explanation of fossil fuels formation.*
4. *Classify surficial and sedimentary type deposits.*
5. *Analyze typical features of bauxite deposits.*
6. *Describe the main features favorable for formation of laterite type deposits.*
7. *Phosphorites and the main theories of their formation.*

8. *Evaporites and Li-brines; setting favorable for their formation.*
9. *Fossil fuels; features favorable for peat and coal formation.*
10. *Fossil fuels; features favorable for oil and gas formation.*

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