# **Mineral Deposits: Types and Geology**



#### **Summary**

This chapter provides a brief introduction to the types of mineral deposits. These descriptions include both the commodities and the geology of the deposits. Previously, the evolutionary concepts about the origin of mineral deposits are established, giving a special consideration to the neptunismplutonism controversy in the nineteenth century and the influence of plate tectonics theories in the genesis of mineral deposits. Ore-forming processes (magmatic, sedimentary, hydrothermal, and metamorphic) are described before entering in the description of the main types of mineral deposits. Energy (petroleum, natural gas, tar sands, bituminous shales, coal, and uranium), metals (iron and steel, base metals, precious metals, light metals, and minor and specialty metals), and industrial minerals and rocks (aggregates, ornamental rocks, carbonate rocks for cement and lime, and clays for brick and tiles) form the main groups of mineral commodities. From a geological point of view, a simple genetic classification of mineral deposits encompasses four main groups: magmatic, hydrothermal, sedimentary, and metamorphic/metamorphosed, each of them with several types and subtypes.

# **2.1 Introduction**

Mineral deposits are concentrations in the Earth's crust of helpful elements that can be extracted at a profit. By definition, ores are somewhat unusual rocks. Like all crustal rocks, they consist of minerals formed through a variety of geological processes that collect the elements into a minor volume. One cubic meter of crustal rock contains approximately 0.15 kg of nickel, but the cost to mine and process this amount of rock clearly exceeds the value of the resulting nickel. For this reason, the existence of a concentrating geological process is crucial. The great goal of geologists is to know how the nature works to put all the elements into mineral deposits, trying to understand how these processes work. One of the most common expressions in mineral deposit is the association of specific ore types with determined host-rock assemblages; this expression is the ore-host-rock association (e.g., Stanton [1972\)](#page-70-0). In general, this association represents the geological environment and processes that formed the mineralization. Several associations have been commonly and successfully utilized for searching new deposits.

McQueen ([2005\)](#page-69-0) suggested four basic geological requirements for any ore deposit to form: «(1) a source for the ore components; (2) a mechanism that either transports these components to the ore deposit site and allows the appropriate concentration or removes non-ore components to allow residual concentration; (3) a depositional mechanism (trap) to fix the components in the ore body as ore minerals and associated gangue; and (4) a process or geological setting that allows the ore deposit to be preserved». Other requirements comprise energy to power the transport mechanism and an appropriate crustal structure to locate the ore-forming components and reach their deposition. Therefore, 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 (Jenkin et al. [2015](#page-69-1)).

Ever since Agricola ([1556\)](#page-68-0) first classified ore deposits ( $\blacksquare$  Fig. [2.1](#page-2-0)), successive writers have attempted classification of mineral deposits (Jensen and Bateman [1979\)](#page-69-2). Classifications are very useful because they mainly provide a common reference scheme. Moreover, they are utilized for both scientific communication and practical application. A classification scheme is basically a means of grouping together known geological processes, minerals, and mineral-rock association. With regard to genetic classification of mineral deposits, including geological processes of ore formation, stringent genetic classification is very difficult. In this sense, some deposits result from interplay of volcanic, intrusive, sedimentary, and diagenetic processes. However, it is necessary to remember that genetic concepts are an essential component to find new mineral deposits. Thus, the genesis must be reflected in mineral deposit classification (Jenkin et al. [2015\)](#page-69-1).

In this chapter, two main classifications of mineral resources are described: one is based on commodities, whereas the other is made

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according to the ore-forming processes and genesis. A combination of both classifications makes it possible to describe in detail the overall characteristics of mineral deposits.

# **2.2 Basic Vocabulary**

There is basic vocabulary dealing with formation of mineral deposits which is not used in other disciplines of mineral resources such as evaluation, exploitation, or environmental impact. Some terms are genetic, others are related to the geometry of the ore, and most of the following definitions are similar to those included in the *Glossary of Geology* (Bates and Jackson [1987\)](#page-68-1). Since metallogeny is the synthesis of scientific endeavors to understand ore formation (Pohl [2011](#page-70-1)), expressions such as metallogenic maps  $($ **O** Fig. [2.2](#page-3-0)), metallogenic provinces, and metallogenic epochs are usually found in the literature related to mineral deposits. 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 pronounced formation of one or more kinds of mineral deposits

(Turneaure [1955\)](#page-70-2). The size of a metallogenic province can be as large as the Superior Province (Canadian Shield), and a metallogenic epoch can be as broad as the entire Proterozoic. A detailed way to define metallogenic epoch and metallogenic province is «as those time intervals of Earth history and regions of Earth, respectively, which contain a significantly greater number of deposits or larger tonnage of a specific deposit type than would have resulted from average rates of mineralization that have occurred over Phanerozoic time» (Wilkinson and Kesler [2009](#page-70-3)). Another relevant term is metallotect, a geological, tectonic, lithological, or geochemical feature that is believed to have played a role in the concentration of one or more elements and hence is thought to have contributed to the formation of ore deposits.

The use of genetic terms is also very varied. Thus, syngenetic denotes that ore or minerals have formed at the same time as their host rock (a rock serving as a host for a mineral or ore); it is commonly but not only used for sedimentary rocks. By contrast, epigenetic means that the ore or minerals have emplaced in pre-existing rocks of any origin (e.g., veins). Both terms are essential and commonly used in genetic descriptions of mineral deposits, although they have caused intense controversies through time. Other used terms are hypogene and supergene. The former

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**D** Fig. 2.2 Part of a Spanish metallogenic map (IGME)

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. Endogenetic indicates concentrations caused by processes in the Earth's interior (e.g., magmatism), whereas exogenetic points to concentration caused by processes in the Earth's surface (e.g., sedimentation). Stratiform and stratabound are also essential terms in mineral deposits formed by sedimentary processes. Thus, a stratiform deposit means a mineral deposit related to a concrete stratigraphic bedding, while a stratabound

deposit is limited to a determined part of the stratigraphic column.

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. Veins are sheetlike zone of minerals that fill a fracture; they are formed from hydrothermal solutions and commonly composed of quartz and/or carbonates with minor sulfide minerals. A breccia is a fragmented rock in which the clasts are cemented together by minerals; it is a good host for hydrothermal mineral deposits. Other terms are disseminated

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**D** Fig. 2.3 Stockwork texture

(ore minerals dispersed through the host rock), stockwork (an interlacing network of small and narrow, close-spaced ore-bearing veinlets traversing the host rock) ( $\blacksquare$  Fig. [2.3](#page-4-0)), massive (mineralization comprising more than 50% of the host rock), tabular (an ore zone that is extensive in two dimensions but has restricted development in its third dimension), vein type (mineralization in veins, commonly discordant to the host rock layering) (Misra [2000](#page-69-3)), pipe shaped (the mineralization body has the form of a carrot and is typical of diamond deposits), and lens shaped (the mineralization body is much thicker in the center than around the edges, and it may be flat lying, dipping, or vertical).

The use of terms associated with formation temperature of ore deposits is common. Examples are epithermal (formed at less than 1500 m and temperatures between 50 and 200 °C), mesothermal (originated at intermediate depths, 1500–4500 m, and temperatures between 200 and 400 °C), and hypothermal (formed at greater than 4500 m and temperatures between 400 and  $600 °C$ ).

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 pegmatite (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.

# **2.3 Evolutionary Concepts About the Origin of Mineral Deposits**

Agricola [\(1556\)](#page-68-0) formulated the first reasonable theory of ore genesis. In his book «De Re Metallica, » he showed that «lodes originated by deposition of minerals in fissures for circulating underground waters, largely of surface origin, that had become heated within the Earth and had dissolved the minerals from the rocks.» Agricola made a clear distinction between homogeneous minerals (minerals) and heterogeneous minerals (rocks). Little progress was made in the study of ore genesis from the time of Agricola until the middle of the eighteenth century. By the 1700s, more remarkable progress was made in Germany, in the Erzgebirge mining district (Henke, Zimmerman, and Von Oppel, among others). At the end of the eighteenth century, the polarized views of either plutonist or neptunist theories were developed ( $\Box$  [Box 2.1](#page-5-0): Neptunism vs Plutonism).

At the middle of the nineteenth century, Von Cotta affirmed judiciously the various theories of mineral genesis and correctly concluded that no one theory was applicable to all ore deposits. At the end of the 1800s and starting the 1900s, different authors (e.g., Élie de Beaumont, Bischoff, Hunt, Phillips, Sandberger, Posepny, Emmons, and many others) created a new controversy related to the descensionist, ascensionist, and lateral secretionist theories. Lindgren proposed, in his book «Mineral Deposits» [\(1913](#page-69-4)), a classification of mineral deposits based on their origin,

#### <span id="page-5-0"></span> **Box 2.1**

### **Neptunism vs Plutonism**

For the origin of mineral deposits, Abraham Gottlob Werner (1749–1817), father of neptunism (denominated after the Roman God – Neptune – of the sea), discarded early theories about interior source for the metals. Although Werner was not the first to propose water as origin of the rocks, he was the most consequent supporter and divulgator of this theory. Werner was a careful mineralogist who drew up an excellent system of classification of minerals based on their properties. He became an insistent advocate of the theory that mineral veins were formed by descending percolating waters derived from the primeval universal ocean, from which not only sediments but all the igneous and metamorphic rocks were precipitated. Because of his theory that what are known today as igneous rocks originated in the sea, Werner and his followers were called neptunists.

According to Werner, by successive sedimentation onto an irregular terrestrial core, four types of formations were supposed to be deposited: (1) primitive, crystalline rocks such as granite and gneiss; (2) transitional, limestones, slates, and quartzites; (3) floetz, the layered rocks from the Permian

to the Cenozoic; and (4) alluvial, (superficial) deposits. The primitive formations would be found in the central parts of mountain ranges, from which the water would have withdrawn first. Thus, the granites were overlain by other layers of crystalline rock (metamorphic), followed by layers of sedimentary rock formed as a result of erosion of the primitive crystalline rocks and subsequent deposition. Rocks resulting from observed volcanic eruptions were attributed to the local action of «subterraneous fires. » In fact, geologists at that time had a clear understanding of the formation of many mineral ores, especially gold, which is generally formed by precipitation and fluid-induced changes. Therefore, these processes are more similar to ideas of neptunism than to plutonism.

Opposite to Werner's ideas, James Hutton (1726–1797), a prominent member of the Edinburgh scientific community (the Royal Society of Edinburgh was at that time one of the most active scientific bodies in the world), defined in his book entitled «Theory of the Earth» the true origin of magmatic and metamorphic rocks and applied his magmatic theory

not only to rocks but also to all mineral deposits. He delivered his theory in two lectures to the Royal Society of Edinburgh in the spring of 1785. Hutton claimed that ore minerals were not soluble in water but were igneous injections, being thus one of the founders of plutonism (named after the classical mythology God – Pluto – of the underworld).

He recognized the significance of the intergrowth texture between quartz and feldspar in a sample of coarse-grained graphic granite and concluded that granite might have «risen in a fused condition from subterranean regions» and that the country rock should therefore be broken, distorted, and veined. Hutton also recognized the importance of unconformities and pointed out that many igneous rocks clearly intruded surrounding rocks and therefore were younger. Because Hutton and his followers held that igneous rocks came from molten material within the Earth, they were called plutonists, being thus Hutton the founder of plutonism. The controversy between plutonism and neptunism continued into the nineteenth century, and eventually the plutonist views on the origin of rocks prevailed.

whether they were products of mechanical or chemical concentration and, if chemical, whether they were deposited from surface waters, from magmas, or inside rock bodies.

Other theories include extreme magmatic views about the origin of mineral deposits. For instance, many ore deposits have resulted from the injection and rapid freezing of highly concentrated magmatic residues (Spurr [1923](#page-70-4)). A metallurgical interpretation of the ore deposits was also proposed: during the former molten stage of the Earth, the metallic minerals sank in deep zones due to their specific gravity, and they were later brought to the surface (Brown [1948](#page-69-5)). According to this model, the upper layers first and the lower layers later moved upward in the form of vapors, from which the metals and minerals were

deposited. Simultaneously to this exotic theory, Bateman [\(1951](#page-68-2)) suggested that the formation of mineral deposits is complex, and eight diverse processes can account for their formation: magmatic concentration, sublimation, contact metamorphism, hydrothermal action, sedimentation, weathering, metamorphism, and hydrology.

The advent of plate tectonics (see next section) improved considerably the understanding of the lithotectonics of rocks and the ore occurrences. Because mineral deposit systems require a conjunction of processes to produce exceptional metal enrichment over background terrestrial concentrations that result in ore deposits, they can form only under specific conditions in particular tectonic environments. Thus, some mineral deposit types are diagnostic of given tectonic

settings and can be used to define these settings in combination with more conventional tectonic and petrogenetic evidence (Groves and Bierlein [2007\)](#page-69-6). Taking in mind this view, a logical firstorder grouping of mineral deposit types can be proposed in terms of geodynamic setting, and this is most conveniently seen in the context of plate tectonics. As an example of modern theories on mineral deposit genesis, a classification based on the different geological processes that form mineral deposits can be outlined (Kesler [1994\)](#page-69-7). Thus, ore-forming processes can be surface processes, including weathering, physical sedimentation, chemical sedimentation and organic sedimentation, and subsurface processes, involving water or magmas. This broad expression of ore-forming processes is the most used actually, and it will be explained with more detail in  $\blacktriangleright$  Sect. [2.6](#page-12-0).

# **2.4 Mineral Deposits and Plate Tectonics**

Plate tectonics is a theory of kinematic character showing that the lithosphere is divided into a finite number of plates that migrate across the surface of the Earth ( $\Box$  [Box 2.2](#page-6-0): Plate Tectonics). It has revolutionized the theories about formation of mineral deposits since plate tectonics determine the origin and distribution of many ore deposits. Thus, plate tectonics plays an essential role in the detection of geological environments with different characteristics. Consequently, the classification of mineral deposits based on plate tectonics is intensively used, particularly when discussing the broad-scale distribution of ore deposits.

Tectonic setting controls factors favorable for the formation of mineral deposits such as the

#### <span id="page-6-0"></span> **Box 2.2**

#### **Plate Tectonics**

The word tectonics derives from the Greek tektonikos, meaning «pertaining to building or construction. » In geology, tectonics concerns the formation and structure of the Earth's crust. From the late 1960s, the proposal of plate tectonics theory, supplanting the geosynclinal concept of lithotectonic associations, clearly caused a revolution in understanding the dynamic interaction of the Earth's crust and mantle as well as geological thinking. In fact, plate tectonics is one of the most important discoveries of the twentieth century. Earlier in this century, geologic paradigm was dominated by the belief that ocean basins and continental land masses were permanent and fixed on the surface of the Earth.

The theory of plate tectonics incorporates the ideas of continental drift and seafloor spreading in a unified model. Wegener [\(1912](#page-70-5)) is usually considered the first to have formulated the continental drift theory precisely, and seafloor spreading hypothesis was proposed by Harry H. Hess in 1960. The theory of plate tectonics attributes earthquakes, volcanoes, the mountain-building process,

and related geophysical phenomena to movement and interaction of the rigid plates forming the Earth's crust. Thus, plate tectonics provides a unified mechanism explaining aspects such as the distribution of earthquakes and volcanoes, the origin of continents and ocean basins, the distribution of fossil plants and animals, or the genesis and destruction of mountain chains. Two major premises of plate tectonics are: (a) the outermost layer of the Earth, known as the lithosphere, behaves as a strong, rigid substance resting on a weaker region in the mantle known as the asthenosphere; and (b) the lithosphere is broken into numerous segments or plates that are in motion with respect to one another and are continually changing in shape and size.

The Earth is composed of layers of different composition and physical properties, principally the solid central core, the fluid peripheral core, the viscous mantle, and the solid lithosph ere. The lithosphere is comprised of the upper mantle and the crust, the outer shell of the Earth. There are two types of lithosphere: oceanic and continental ( $\blacksquare$  Fig. [2.4](#page-7-0)). The oceanic lithosphere has a 5–8 km-thick oceanic crust (with a basaltic composition), while the continental lithosphere has a 30–40 km-thick graniticdioritic crust. The lithosphere is fragmented into pieces of variable shape and size, the so-called plates, and the edges of the plates are termed plate boundaries. The Earth has seven major plates (Africa, Antarctica, Australia, Eurasia, North America, South America, and Pacifica) and several minor ones (Adria, Arabia, the Caribbean, Nazca, the Philippines, and others). These plates move independently relative to one another, with a restricted independence from the seven large plates, however. The average rates of motion of the plates, in the past as well as the present, range from less than 1 to more than 15 cm per year.

The motion of lithospheric plates is a considerable consequence of thermally driven mass movements on the Earth. Thus, plates move because of the intense heat in the Earth's core, which causes molten rock in the mantle layer to move. However, the detailed mechanism by which tectonic

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#### $\blacksquare$  Fig. 2.4 Illustration of plate tectonics theory

plates move is still a subject of much debate among Earth scientists (convection cells vs slab pull). Plate tectonics, the study of such relative motions and their consequences, allows relating surface, geological, and geophysical structures with quantified movements attributed to deep processes of the Earth.

Each lithospheric plate consists of the upper roughly 80–100 km of rigid mantle rock capped by either oceanic or continental crust. Lithosphere capped by oceanic crust is often simply called oceanic lithosphere, and lithosphere capped by continental crust is referred to as continental lithosphere. Some plates, such as the Pacific Plate, consist entirely of oceanic lithosphere, but most

plates, such as the South American Plate, consist of variable amounts of both oceanic and continental lithosphere with a transition from one to the other along the margins of continents. The plates move with respect to one another on the ductile asthenosphere below. As the plates move, they interact with one another along their boundaries, producing the majority of Earth's earthquake and volcanic activity. Most plates contain both oceanic and continental crust, and a few contain only oceanic crust. Essentially, the continents are lighter and more buoyant; hence, they float higher on the Earth's mantle than the ocean's crust does.

The three basic kinds of plate boundaries are defined by the

type of relative motion between the plates: divergent, convergent, and transform. In a divergent boundary, two plates pull away or separate from each other, producing new crust. Examples are Mid-Atlantic Ridge and East Pacific Rise. In a convergent boundary, two plates move toward or collide with each other, consuming old crust. Examples are India into Asia and NW coast of the USA and SW coast of South America. In the third type of boundary (transform), two plates slide horizontally past each other. In this case, the process does not consume or create crust. Examples are North Anatolian Fault (Turkey), Dead Sea Transform Fault (Israel, Jordan), and San Andreas Fault.

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. Thus, it is not surprising that many authors have attempted to relate the distribution of mineral deposits to plate tectonics. Tectonics not only controls the architecture of a basin but

also facilitates the interaction between fluid and rock (Kyser [2007](#page-69-8)).

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) ( $\blacksquare$  Fig. [2.5](#page-8-0)), but others (e.g., Precambrian massive sulfide and Ni sulfide deposits) cannot yet be easily

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**D** Fig. 2.5 Distribution of mineral deposits in relation to the main types of tectonic plate boundaries

assigned to specific plate tectonic processes. Some plate tectonic settings, especially during the Precambrian, are still highly controversial. It is important to keep in mind the overall influence of plate tectonics in each group of mineral deposits. Since mineral deposits can be commonly separated into those originated by endogenous processes and those formed by surficial ones, Sawkins [\(1984\)](#page-70-6) proposed that: «the deposits formed by endogenous processes are invariably associated with thermal processes and, in general, can be related more readily to magmatic and tectonic events instigated by plate activity while deposits formed by surficial processes such as weathering or shallow marine sedimentation will show relationships to their tectonic environment that are more tenuous.» Moreover, since most mineral deposits are concentrated by subsurface chemical processes related to magmas and hot waters as well as by near-surface chemical and physical processes, such as erosion and evaporation, these processes are much more common on the continental crust, and their products are better preserved there because the continents are floating on the mantle. In contrast, ocean crust sinks back into the mantle at subduction zones. Thus, the oldest known ocean crust is only about 200 million years, whereas the oldest rocks on the continents are about 4 billion years old (Kesler [1994\)](#page-69-7). Consequently, the continental crust is the archive of Earth history (Cawood et al. [2013](#page-69-9)).

Initial hypotheses of the relationship between distinct classes of ore deposits and their plate tectonic locations were well established (e.g., Mitchell and Garson [1981;](#page-69-10) Sawkins [1984\)](#page-70-6). These accounted for the distribution of some ore deposit types in the Phanerozoic, but however there were limitations (Kerrich et al. [2005\)](#page-69-11): (1) at the time, genetic hypotheses for many types of ore deposit were based on syngenesis; (2) where consensus existed on a syngenetic versus epigenetic origin, the age of mineralization was not well constrained; (3) epochs, or secular cycles, of metallogenic provinces were not accounted for; and (4) extrapolation to the Precambrian met with uncertainties as to tectonic processes during that era. Other classifications and descriptions include, for example, a concise list of metallic and nonmetallic resources for each era, including their geodynamic and geological settings (Windley [1995](#page-70-7)).

During the period of plate tectonics revolution, other discoveries had a major impact on theories of ore genesis such as the observable natural concentration systems, actually active at or near the Earth's surface. For instance, modern seafloor prospection shows the great magnitude of the manganese nodules outlined by the Challenger expedition. It demonstrates not only the enormous potential resource of Cu, Co, Ni, and other associated metals but also the potential of cold seawater as a dilute-mineralizing fluid. The hot brine pools and underlying soft ferruginous muds rich in Zn, Cu, and Ag in the Red Sea deeps

<span id="page-9-0"></span>**D** Fig. 2.6 Black smoker (Image courtesy of MARUM, University of Bremen)



are also another example of this type of concentration systems. They were discovered in 1965 and show an exhalative deposit actually forming in a continental rift system. Finally, the discovery of active «black smoker» hydrothermal vents and massive sulfide deposits on the Mid-Atlantic Ridge ( $\blacksquare$  Fig. [2.6](#page-9-0)) made a dramatic impact.

# **2.5 Criteria for the Classification of Mineral Deposits**

Mineral deposits are found in so many different forms, and under so many varying conditions, the attempts of different writers to formulate a classification, founded upon a natural basis, have not been attended with much success (Park [1906\)](#page-70-8). This assertion made more than a century ago is actually untruth since the knowledge of the mineral deposit formation processes obviously has increased dramatically in a century, but it shows how problematic it was to create a simple classification of mineral deposits. In many cases, the difficulty to avoid the dispute between plutonist and neptunist was insurmountable. Prior to the twentieth century, models for the formation of mineral deposits were subject to the often polarized views of either plutonist (all deep igneous origins) or neptunist (all sedimentary origins) theories for the origin of rocks. It was really only in the twentieth century that modern views of mineral deposit formation emerged. Arndt and Ganino [\(2012\)](#page-68-3) observed that through the twentieth century: «many classifications were based on the types of rocks hosting the ore deposits or on the geometry of the deposit and its relation to the host rocks; thus, deposits in granites were distinguished from those in sedimentary rocks; vein-like deposits were separated from layers conformable with the stratification of the host rock; massive ores were distinguished from disseminated ores, and so on.»

Criteria used to classify mineral deposits vary widely. Since a perfect classification is utopic, a large number of items can be applied. A classification accepted implies that it has been derived by systematic application of certain principles. It must be understandable for the user and must be open so that new mineral deposit types can be added in the future. Geologists usually rank ore deposits according to the (a) commodity, (b) tectonic setting, (c) geological setting, (d) genetic model in the genesis of the mineral deposit, and (e) other aspects (e.g., form of the deposit, temperature of mineral formation, etc.). For instance, Gabelman [\(1976](#page-69-12)) shows up with different criteria to classify stratabound ore deposits such as major controlling processes, direct emplacement mechanism, host lithology, chemical reactivity, source of metals and/or transporting fluids, direction of transporting fluids, and relative age of deposit and host.

The genetic classification schemes are the most commonly used since they incorporate elements

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**D** Fig. 2.7 Genetic classification scheme for ore deposits (McQueen [2005\)](#page-69-0)

of composition, form, and association. This type of classifications allows to develop predictive models that can be used to search for geological environments in which appropriate ore-forming processes have possibly operated (McQueen [2005\)](#page-69-0). In this sense, some authors think that classifications by commodity are geologically useless; thus, uranium deposits occur in sandstone and in granites, their formation processes being radically different. However, knowledge of uranium world production, regardless of their genesis, can be essential for other purposes, such as mineral supply, world trade, etc. Other authors underline that genesis is not a good classification criterion because there is considerable controversy among geologists as to the exact mode of formation of many mineral deposits.

A sound alternative is to classify deposits based on empirical features such as type of minerals or host-rock associations, which will lead to the unique fingerprint of a particular deposit (i.e., a descriptive model). Even though no two mineral deposits are identical, empirical descriptions of deposits tend to show natural groupings into a small number of loosely definable categories or types. In turn, these categories tend to coincide with genetically derived models; so even by using purely physically descriptive classifications, there is often a close coincidence between these and models defined using genetic criteria (Herrington [2011](#page-69-13)).

The classification of mineral deposits based on major Earth process systems is very easy. Rocks are classified universally as igneous, sedimentary, and metamorphic, which express the fundamental processes active in the crust of the Earth. Likewise, since ores are rocks, they can often be associated with each type of rock. Therefore, this character (igneous, sedimentary, or metamorphic) can represent a good basis for classification as it reflects the genetic process involved in ore formation. In this sense,  $\blacksquare$  Fig. [2.7](#page-10-0) shows a genetic classification for mineral deposits showing the major clusters of ore-forming and modifying processes (McQueen [2005](#page-69-0)). The classification highlights the categories of ore-forming processes and the subsequent overprinting that can suffer the deposits.

In summary, linking deposit types directly to ore-forming processes and genesis is certainly the preferred way to classify (e.g., Herrington [\(2011\)](#page-69-13);  $\Box$  Table [2.1](#page-11-0)). It provides better criteria for

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understanding the deposits with respect to associated features such as its association with igneous rock suites, alteration patterns, etc. This will lead to more efficient exploration models for their discovery and evaluation. Nevertheless, descriptive models are needed in practical terms to aid engineers in the evaluation of particular deposits: choice of exploration tool, elements to analyze in geochemical exploration, etc. (Herrington [2011](#page-69-13)).

# <span id="page-12-0"></span>**2.6 Ore-Forming Processes**

The list of captions in ore-forming processes is much larger than the list of geological processes found in any geology text explaining the origin of rocks. Thus, some mineral deposits are formed by magmatic processes, while other mineral deposits are produced by sedimentation or surface weathering. Probably, the main difference between both lists is the secondary importance of metamorphism in the enumeration of substantial ore-forming process compared to its fundamental role in generating rocks. Another major difference is the essential function of hydrothermal fluids (hot aqueous fluids) in the genesis of ore deposits. The circulation of this kind of fluids in the crust is usually cited as a factor that modifies locally the composition and texture of previous rocks. Ore-forming processes can be classified into four main categories (Evans [1993](#page-69-14)): internal, hydrothermal, metamorphic, and surficial processes. The former three processes are related to subsurface phenomena, while the last one covers those processes occurring at the Earth's surface. Hydrothermal should be further subdivided into magmatic, metamorphic, diagenetic, and surface to refine the nature of the hydrothermal process. Therefore, the first approach to ore-forming processes can be outlined according to the next four

types described below: magmatic, metamorphic, sedimentary, and hydrothermal processes.

Whatever the ore-forming process, because of chemical and geological factors, some minerals/ metals tend to occur together in mineral deposits, while others may be found associated with a particular rock type. Examples of the former are galena with sphalerite, copper sulfides with molybdenite, gold with arsenopyrite or pyrite, and silver with galena. Regarding the association of mineralization/host rock, examples are leadzinc in carbonates, copper or copper-lead-zinc with volcanic rocks, tin and tungsten with granite intrusions, chromite in large ultramafic intrusions, and uranium in sandstone and shales.

### **2.6.1 Magmatic Processes**

In a broad sense, ore-forming processes related to the evolution of magmas emplaced at crustal levels span a continuum. The two end members of this continuum are (a) orthomagmatic processes, concentration of mineralization as a direct result of magmatic crystallization dominated by silicate melt-crystal equilibria, and (b) (magmatic) hydrothermal processes, concentration of ore minerals from magmatic hydrothermal fluids by crystallization dominated by crystal-volatile equilibria (Misra [2000\)](#page-69-3). The second possibility is considered here as totally controlled by the action of hydrothermal fluids, and, accordingly, it will be included in the group of hydrothermal processes. A large and diverse group of ore deposits originates by various processes during the formation, evolution, emplacement, and crystallization of silicate melts (magmas) in the upper mantle and in the Earth's crust. Magmatic deposits may form as a result of (1) solid phases crystallizing as a differentiate as the magma cools, (2) minerals crystallizing from the enriched residual fluids formed as magma cools and crystallizes, (3) the formation of a sulfide melt that developed by immiscibility from a coexisting silicate melt, or (4) where a magma transports xenolithic or xenocrystic phases that it has picked up on its passage through the Earth's crust (Herrington [2011\)](#page-69-13).

The processes of magmatic ore formation are related to intrinsic properties of the magmas and are linked genetically to its cooling and solidification pattern. It is recognized that different mineral deposits are hosted in igneous rocks, and these deposits display different metal associations. This must be associated somehow to the environment in which magmas are originated and the compositional characteristics generated from specific settings. In this sense, it is broadly recognized that most of the chalcophile and siderophile elements (e.g., Ni, Co, Pt, Au) more likely to be linked with mafic rocks, while concentrations of most lithophile elements (e.g., Sn, U, and W) are classically located in association with felsic or alkaline rocks (Robb [2005](#page-70-9)). Essentially, this distribution was understood because of the geochemical fate of different metals during fractional crystallization (solid-liquid fractionation) of silicate melt bodies (Pohl [2011](#page-70-1)).

Where the magma enters the crust and crystallization starts, an immiscible sulfide liquid will divide from the silicate liquid if the concentration of sulfur exceeds the solubility. Experimental studies have shown that the solubility of sulfide depends on external parameters, such as temperature and pressure, and on the composition of the melt. During fractional crystallization of magma, the temperature drops, Fe content slightly changes, and Si content increases, which lead sometimes to sulfide saturation and the separation of sulfide liquid. Many parameters influence these processes, including depth of intrusion, tectonic activity, temperature gradient in space and time, fractional crystallization, dynamics of the melt body, repeated injection of fresh melt, assimilation of country rocks, sulfur or external fluids, liquid immiscibility of ore and silicate melts, and mixing or redissolution (Kerr and Leitch [2005](#page-69-15)).

Another mechanism to explain the formation of magmatic mineral deposits is the so-called fractional crystallization ( $\blacksquare$  Fig. [2.8](#page-14-0)). In this model, dense minerals form a cooling magma chamber and settle to the bottom producing a sequence of layered rocks. The remaining liquid magma becomes saturated with sulfur, and sulfide minerals rich in some metals crystallize out of the magma and settle to the bottom. For instance, these layered rocks formed by sulfides host PGE deposits.

<span id="page-14-0"></span>



# **2.6.2 Metamorphic Processes**

Ore deposits in metamorphosed rocks can be formed before, during, or after metamorphic processes. The first category is of premetamorphic origin independent from later metamorphic overprinting, and it is the class of metamorphosed ore deposits (Pohl [2011](#page-70-1)). Metamorphic deposits owe their origin to contact or regional metamorphism and involve recrystallization, commonly accompanied by mobilization of disseminated ore constituents by metamorphic fluids (Misra [2000\)](#page-69-3). Metamorphic rocks host many ore deposits, and metamorphic fluids are thought to be a source for various mineral deposits. Thus, this type of fluids usually carries important metal content, although for chloride-complexed metals, maximum concentrations are commonly lower for magmatic fluids. For instance, gold ore is the type of mineralization usually linked to metamorphic fluids. Therefore, based on chemistry, it is possible to argue that in some circumstances, metamorphic fluids can contain high concentrations of metals and may therefore be potential ore fluids (Banks et al. [1994\)](#page-68-4). According to Yardley and Cleverley (2014), there are three situations in which ore deposits are formed from metamorphic fluid processes: (a) where relatively metal-rich metamorphic fluids provide a medium for segregation, (b) where decarbonation reactions lead to focused fluid flow and skarn formation, and (c) where rapid uplift drives dehydration reactions despite falling temperature, so that the rate of fluid production is not limited by heat flow.

Since magmatic activity is common in certain metamorphic settings, it is reasonable to consider that some mineral deposits in metamorphic rocks were formed by combined metamorphic and magmatic processes. Skarn and contact metamorphism ore deposits are intimately related to thermal aureoles of magmatic intrusions. They can be envisaged as products of contact metamorphism, but the causal agent is the interaction with magmatic fluids and not simply change by heating (Pohl [2011\)](#page-70-1). Because of the complications of describing skarns based on alteration minerals, which are a combined function of wallrock chemistry and the superimposed system, mineralized skarns are best classified in terms of component of interest. Seven major types are recognized: iron, gold, tungsten, copper, zinc, molybdenum, and tin (Herrington [2011\)](#page-69-13). The different metals found in skarn deposits are a product of the differing compositions, oxidation state, and metallogenic affinities of the igneous intrusion. For instance, Fe and Au skarn deposits are usually associated with intrusions of more mafic to intermediate compositions. Most of the large

<span id="page-15-0"></span>

..      **Fig. 2.9** Skarn tungsten mine at Los Santos (Salamanca, Spain) (Image courtesy of Daytal Resources Spain, S.L.)

and economically viable skarn deposits are associated with calcic exoskarns, a limestone (calcic) being the host rock and the metasomatic assemblage external to the intruding pluton (exo – prefix). Thus, tungsten skarns produce the bulk of the world production of tungsten ( $\blacksquare$  Fig. [2.9](#page-15-0)) and are typically associated with calco-alkaline intrusions emplaced relatively deep in the crust.

# **2.6.3 Sedimentary Processes**

Low-temperature surface processes can be responsible for the formation of economic ore deposits at or very near the Earth's surface. Under favorable conditions, sediments and sedimentary rocks become selectively enriched in some elements of potential economic value. Two main types of sedimentary processes can be outlined: sedimentation and weathering. Sedimentation may lead to the formation of mineral deposits through clastic accumulation (e.g., gold or diamond placer deposits) and chemical and/or biochemical precipitation of economically important constituents in lakes, coastal settings, or shallow to deep oceans, including evaporation processes. 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 the minerals forming the original rock, either hydraulic (water) or Aeolian (wind) being the physical processes. Examples of these deposits are the already mentioned diamond placer deposits ( $\blacksquare$  Fig. [2.10](#page-16-0)) in river sediments and deposits of heavy minerals in beach sands.

Regarding chemical and/or biochemical precipitation, metals and other valuable minerals are soluble in surface waters. They precipitate where they meet saturation levels (evaporation) or where the composition or physical conditions on the water shift. Examples of the latter are sediments enriched in iron or manganese resulting from mixing of waters with different composition or redox states. Evaporation is a surface phenomenon where dissolved salts precipitate as water is lost in an evaporating basin or by the evaporation of water from the ground's surface due to heat energy from the sun. Sedimentation is limited to the surface of the Earth, which is also the realm of life and its biochemical cycles; therefore, sedimentary ore formation will almost always show biogenic components (Southam and Saunders [2005](#page-70-10)). It is very obvious in phosphate deposits made of bones and coprolites and in lignite seams composed

<span id="page-16-0"></span>

**D** Fig. 2.10 Diamond placer deposit in river gravels (South Africa) (Image courtesy of Rockwell Diamonds Inc.)

of fallen trees. 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, ironreducing bacteria and sulfate-reducing bacteria may play important roles in low-temperature ore genesis. Thus, iron-reducing bacteria can cause reductive dissolution of Fe oxyhydroxides, such that it occurs in red beds, causing adsorbed and coprecipitated metals to be released to solution. Organic compounds produced by bacterial degradation of a more complex organic matter could enhance metal transport by formation of metalorganic complexes. Similarly, biogenic  $H_2S$  could form stable aqueous metal-sulfide complexes leading to transport of certain metals such as Ag at low temperature (Kyle and Saunders [1996](#page-69-16)).

Weathering may also lead to residual concentration of weathering-resistant minerals of the parent rock or of relatively insoluble elements reconstituted into stable minerals (Misra [2000\)](#page-69-3). In this regard, weathering is a very important ore-forming process resulting in chemical change and redistribution of components in surface rocks by migrating solutions. The differential chemical properties of minerals at the Earth's surface and in the surface-crustal interface can lead to residual upgrades or chemical dissolution and reprecipitation mechanisms to concentrate the metal/mineral of interest. 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 (Herrington [2011](#page-69-13)).

Supergene processes usually originate different types of raw materials such as iron, manganese, or aluminum ores. In supergene process, two basically different process types may lead to concentration: (1) the valued component is enriched in a residuum, while much of the rock mass is dissolved and carried away; an example are laterite deposits, in which iron or aluminum is enriched in the clayey-sandy soils of the tropics and subtropics; and (2) the valued component is dissolved, transported, and concentrated on reprecipitation; in this case, the transport distance is commonly very short, meters to ten of meters (Pohl [2011\)](#page-70-1). A special case of weathering would be the so-called supergene enrichment process, which involves the leaching of ore-forming

<span id="page-17-0"></span>**D** Fig. 2.11 Gossan at VMS deposit (Fiji) (Image courtesy of Geonomics)



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. These deposits are usually called «gossan» ( $\bullet$  Fig. [2.11](#page-17-0)). In the nineteenth and twentieth centuries, gossans were important guides used by prospectors in their quest for buried ore deposits.

# **2.6.4 Hydrothermal Processes**

A big problem dealing with the word hydrothermal is its meaning. Hydrothermal means hot water, which is an extremely lax sense of the word because hot water can range from 70 to 200 °C or even 400 °C. The former temperature can be attained in the sedimentary realm, during diagenesis, and the others are characteristic temperatures of endogenous conditions. Hydrothermal fluids generally travel along temperature or pressure gradients, from hot areas to cool areas or from high pressure to low pressure. They migrate until they reach a suitable site for metal deposition. For this deposition, the following is necessary: a rapid decrease in temperature such as where hot fluids exit at the seafloor, a rapid decrease in pressure such as where fluids enter a fault cavity, and/or a change in the

chemical composition of the fluid such as where fluids react with a rock (Stevens [2010](#page-70-11)).

Hydrothermal processes can develop in almost all geological environments. The application of new technologies in geosciences in the last 50 years (e.g., fluid inclusions, trace element analysis, isotope geochemistry, among many others) has changed many of the geological concepts, including metallogenic thinking. For instance, expelled fluids in sedimentary basins during diagenesis can produce numerous metallic concentrations, excluding the participation of endogenous processes. In the past decades, many efforts are carried out toward a better understanding of the complexity of hydrothermal processes.

Although there are several natural processes that concentrate elements within the Earth's crust and form mineral deposits, the most important of which is the hydrothermal process. Hydrothermal ore-forming processes are ubiquitous, and many mineral deposits on Earth have been originated straightly from hot aqueous solutions flowing through the crust. Direct evidence for the presence of hydrothermal fluids in the Earth's crust is surface manifestations such as hot springs and fumaroles. In this sense: «the concept of hydrothermal mineralization can be extended to deposits related to fluids derived from sources other than magmatic solutions; such fluids include those formed from metamorphic dehydration reactions, from the expulsion of pore fluids during compaction of sediment (the release of

<span id="page-18-0"></span>**D** Fig. 2.12 Yellowstone (USA) hot springs



trapped water from sedimentary basins undergoing diagenetic change), and from meteoric waters; it also considers seawater as a hydrothermal fluid with specific reference to the formation of base metal deposits on the ocean floor» (Robb [2005](#page-70-9)).

Magmatic hydrothermal fluids form as a body of magma cools and then crystallizes. In some circumstances, the magmatic system can be a passive source of heat that drives the circulation of fluids exotic to the magma through adjacent fractured crust into which the magma is intruding. In other situations, the magmas, particularly felsic magmas that form granitic rocks, include very significant amounts of miscible water, which is carried in the magma itself. As the magma cools and crystallizes, it becomes more concentrated and eventually forms an immiscible fluid phase, which in the process collects other components that prefer to partition from a silicate melt into a hydrous fluid phase. Williams-Jones et al. [\(2002](#page-70-12)) suggest that these metal-rich fluid phases can then migrate away from the magma and interact with minerals and fluids in previously crystallized magma or outside rocks, which cause these to become altered by chemical reaction and lead to precipitation of new mineral phases, including the ore minerals.

Surface or seafloor hydrothermal fluids are generated as deeply penetrating meteoric- or seawater-derived waters descend and become heated deeper in the crust. This process is particularly apparent in regions where there is elevated crustal heat flow, often where the Earth's crust is being thinned. In the case of seafloor, this phenomenon is common where a new ocean is formed by the seafloor spreading through the formation of submarine volcanoes. On land, such hydrothermal fluids can be generated in zones of crustal attenuation, often associated with subaerial volcanism. Surface manifestations of this process are the presence of hot springs on land (D Fig. [2.12](#page-18-0)) or seafloor hydrothermal vents.

The various stages of diagenesis that result in the transformation from uncompacted particles of sediment to lithified sedimentary rock produce aqueous solutions that evolve with time and depth; such type of fluids are often involved in the formation of ore deposits (Robb [2005](#page-70-9)). 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 (becoming a brine;  $\Box$  Table [2.2](#page-19-0)), which then has a greater ability to transport many cations and ligands to a point of deposition to form an ore deposit (Brimhall and Crerar [1987\)](#page-69-17). 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

<span id="page-19-0"></span>

overcome approximately 200 °C. Thus, metamorphic-hydrothermal fluids form as metamorphism results in mineral-chemical processes that may release volatiles, often dominated by water but which may include gases such as  $\mathrm{CO}_2$ . Metamorphism is induced in rocks by external heat or pressure or by a combination of both. Heat may be provided by the deep burial of a rock mass through time or alternatively by the intrusion of a magma body nearby. Pressure to cause metamorphism may be provided again during deep burial or else by tectonic processes.

# **2.7 Mineral Resources Commodities**

Mineral deposits can be classified according to the valuable raw material being extracted. This classification finds some application in a purely economic context and gives raise to three main groups: (a) energy commodities, this group is formed by petroleum, natural gas, tar sands, bituminous shales, coal, and uranium; (b) metallic commodities, a very large group that includes many metal types, related to their uses, density, monetary value, etc.; and (c) nonmetallic commodities. In turn, the latter can be subdivided into two essential categories: industrial minerals and industrial rocks. The minerals used by their specific chemical and physical properties (e.g., sodium sulfate utilized as laundry detergent) fit in the first category; the second one, developed after the Second World War and of growing commercial interest, includes a wide variety of raw materials, mainly rocks, that

are used preferably in construction (e.g., buildings, roads, or bridges). Typical examples are natural aggregates and building stone.

## **2.7.1 Energy**

Energy commodities include mainly fossil energy raw materials and uranium to produce nuclear energy. Coal was the first fossil energy raw material used by man at the beginning of the Industrial Revolution, and this predominant role spanned until early in the twentieth century. Since then, oil has displaced coal to a second rank (here the terms oil and petroleum are used interchangeably, although some differences exist). In 2014, the world's primary energy supply was provided by 32.9% from oil, 23.7% natural gas, 23.8% coal, 6.8% hydroelectricity, 4.4% nuclear power, and 2.8 renewables (BP Statistical Review of World Energy [2016](#page-68-5)). Altogether they form the so-called primary energy. In the future, the Energy Outlook 2035 establishes that economic expansion in Asia will produce a continued growth in the world's demand for energy, rising by 37% from 2013 to 2035 or by an average of 1.4% a year.

# **Petroleum**

Petroleum ( $\blacksquare$  Fig. [2.13](#page-20-0)) is derived from ancient fossilized organic materials such as zooplankton and algae ( $\Box$  [Box 2.3](#page-20-1): Petroleum Formation). It is formed by hydrocarbons with the addition of some other substances. Thus, the main hydrocarbons commonly present in petroleum are the following: paraffins (15–60%), naphthenes (30–60%), and aromatics (3–30%), with asphaltics making up the remainder. The percentages for these hydrocarbons can vary greatly, depending upon the geographic region. Regarding the chemical composition, the basic components are carbon (93–97%), hydrogen (10–14%), nitrogen (up to 2%), oxygen (up to 1.5%), and sulfur (0.5– 6%), with a few trace metals making up a very small percentage of the petroleum composition. The properties of each different petroleum source are defined by the percentage of the four main hydrocarbons found within petroleum as part of the petroleum composition.

Petroleum is generally measured in volume (a barrel is equal to 159 liters). The petroleum industry classifies the different oil types by the location where the petroleum is produced (West Texas

<span id="page-20-0"></span>

**D** Fig. 2.13 Petroleum platform (Image courtesy of Pedro Cámara)

#### <span id="page-20-1"></span>**Box 2.3**

#### **Petroleum Formation**

Petroleum (also known as crude oil or simply oil) is a fossil fuel that was formed from the remains of ancient marine organisms. Coal, natural gas, and petroleum are all fossil fuels that formed under similar conditions. In fact, petroleum is frequently found in reservoirs along with natural gas. In the past, natural gas was either burned or allowed to escape into the atmosphere. Now, technology has been developed to capture the natural gas and either reinject it into the well or compress it into liquefied natural gas (LNG), which is easily transportable and has versatile uses.

Formation of naturally occurring raw petroleum takes millions of years. Large amount of the organisms sourcing the petroleum remains settled to sea or lake bottom, mixed with sediments and buried under anoxic conditions. As the microscopic algae and phytoplankton died, they sank to the bottom and accumulated in large quantities in the oxygen-free sediments. Over time, they were buried deeper and subjected to a long process of chemical conversion by bacterial decomposition followed by the effects of high temperatures. This caused the formation of liquid and gaseous hydrocarbons in the source rock (hydrocarbons are simply chemicals made up of hydrogen and carbon). Petroleum source beds are fine-grained, clayrich siliciclastic rocks (mudstones, shales) or dark-colored carbonate rocks (limestones, marlstones), which have generated and effectively expelled hydrocarbons. Most of the economically useful petroleum deposits were deposited during the Phanerozoic. This is thought to reflect the lower rate of organic carbon production and burial in the earlier eons.

Increasing heat and pressure cause the organic matter to change, first into kerogen, one of the products of anaerobic decomposition of organic matter (it is found in various oil shales around the world) and then into liquid and gaseous hydrocarbons in a process called catagenesis. Thus, catagenesis comprises all processes that act on rock matrix and organic matter after considerable burial and that result in petroleum generation; higher pressure and temperature are essential factors of change. The main result of catagenesis is the generation of oil and wet gas while kerogen «matures. » At about 60 °C, oil begins to form in the source rock due to the thermogenic breakdown (cracking) of organic matter (kerogen). There is a temperature range in which oil forms. It is called the «oil window» (often found in

the 60–120°C interval – approx. 2–4 km in depth). Below the minimum temperature, oil remains trapped in the form of kerogen, while above the maximum temperature is converted to natural gas through thermal cracking (about 160°C). The gas produced in this way is often separated from the petroleum. If temperature reaches high value (>250°C), the original biomass will be destroyed and no gas or petroleum is formed. Typically lower temperatures during petroleum formation will result in thicker, darker raw petroleum deposits, the most solid of which being a bitumen substance.

After expulsion from the source rock (<sup>o</sup> Fig. [2.14](#page-21-0)), both oil and gas, lighter than water, migrate upward through permeable rocks (e.g., sandstones) or fractures until they are stopped by a non-permeable layer of rock (e.g., shale). The production of petroleum increases pressure within the rock because oils and gases are less dense than solids and, hence, take up more volume. The overpressure fractures the source bed, enabling migration of the gas and oil into adjacent

permeable rocks. Migration occurs vertically and laterally through the fractures and faults until an impermeable barrier is reached. Oil and gas migration takes thousands or millions of years and may extend over tens of kilometers. Gravity forces the oil to move out of the source rock and upward toward the surface, looking for a reservoir. Reservoir is a rock that has the ability to store fluid such as sandstone where oil or gas can be between grains of sandstone. Porous limestone is also a good reservoir rock since many cavities can be connected with each other. Thus, reservoir rocks are porous and always saturated with water, oil, and gas in various combinations. Petroleum reservoirs can be found beneath the land or the ocean floor.

In addition, impermeable rock has to be present to stop petroleum escaping from reservoir rock. Impermeable rock that forms a seal over reservoir rocks is called cap rock. Cap rocks of most petroleum fields are fine-grained, clay-rich sediments like shales or mudstones. Due to their low permeabilities and very small-diameter

pores, capillary entry pressures are so high that they cannot be overcome by the buoyancy of a high oil or gas column. The most ideal and best sealing cap rocks are, however, evaporite strata like anhydrite or rock salt. Such goodquality cap rocks hold many of the large petroleum accumulations in the Middle East in place.

If there is a suitable combination of source rock, reservoir rock, and cap rock and a trap in an area, recoverable oil and gas deposits may be discovered there. If there is no cap rock, the oil and gas will slowly continue to migrate toward the surface. In certain geological locations, as the oil migrated and came closer to the Earth's surface, microorganisms slowly consumed the hydrocarbons, beginning with the lightest. The heavy oil and bitumen now being produced are the remnants of that migration. Heavy oil deposits (e.g., tar sands) are the world's largest known liquid hydrocarbon resources and comprise about 65% of all the liquid petroleum in the world. Very large deposits of tar sands occur in northern Canada (Athabasca tar sands) and eastern Venezuela.

<span id="page-21-0"></span>



<span id="page-22-0"></span>**D** Fig. 2.15 Oil production by region in million barrels daily (BP Statistical Review of World Energy [2016](#page-68-5))



Intermediate or Brent), the density in API gravity (if the API gravity of a crude oil is greater than 10, it floats on water; if less than 10, it sinks), and its sulfur content. The major oil-producing regions around the world are located in Kuwait and Saudi Arabia, although other countries in the Middle East region also make up a significant part of world production (e.g., Iran and Iraq) ( $\blacksquare$  Fig. [2.15](#page-22-0)). The North Sea crude oil fields are the second most influential oil field in economic terms.

The main application of petroleum is for power combustion engines (gasoline or petrol). Other applications include manufacturing of plastics and synthetics, paving road, and roofing. In general, a lighter raw petroleum composition is more useful as a fuel source, while denser petroleum composition is more suitable for plastic manufacturing and other uses. Broadly, a barrel of crude oil produce the following components: 43% gasoline, 21% diesel, 10% jet fuel, 4% fuel oil, 4% liquefied petroleum gases, and 18% other products.

### **Natural Gas**

Natural gas plays a vital role in the world's supply of energy. In its pure form, natural gas is colorless, shapeless, and odorless. Compared to other fossil fuels, natural gas is cleaner and emits lower values of harmful components to the air. Although it is a blend of different hydrocarbon gases, natural gas is formed mainly of methane (70–90%), ethane, propane, butane (all three together up to 20%), and other components (e.g., pentane, carbon dioxide, oxygen, nitrogen, or hydrogen sulfide). Temperature and pressure determine the composition of the gas phase because several higher hydrocarbons are gaseous in the reservoir but condense if the pressure is lowered. Natural gas is called «dry» if it is almost pure methane and «wet» if other hydrocarbons are present. The «dryness» of gas can be characterized by the percent methane/percent ethane ratio. Other denominations are «sour» gas if it has elevated fractions of sulfur and  $CO_2$  and «sweet» gas if it contains less than

<span id="page-23-0"></span>**D** Fig. 2.16 Natural gas reserves-to-production (R/P) ratios in 2015 by region (BP Statistical Review of World Energy [2016](#page-68-5))



2% of  $\mathrm{CO}_2$  and no H<sub>2</sub>S. Only «sweet» gas can be directly used, and the rest must be first refined.

Natural gas is found in reservoirs often associated with oil deposits. Since gas is dissolved in oil, a free gas cap forms on top of the oil pool where saturation is reached. When natural gas is formed, it rises toward the surface because it has a low density. Some of this methane will dissipate into the air, but it will also rise up into geological formations that trap the gas under the ground. These formations are mainly composed of layers of porous sedimentary rocks with an impermeable layer of sediment on top to prevent the migration of the natural gas until the surface. The obtained natural gas is then refined to remove impurities (e.g., water, other gases, or sand). After refining, the natural gas is usually transmitted through a network of pipelines to its point of use. Natural gas can be measured in cubic feet or, like other forms of energy, in British thermal units (Btu). The definition of a Btu is the following: 1 Btu is the quantity of natural gas that will generate sufficient energy to heat 1 pound of water by 1 degree at normal pressure. Regarding the production and reserves of natural gas,  $\Box$  Fig. [2.16](#page-23-0) shows the reserves-to-production ratios in 2015 by region.

<span id="page-23-1"></span>

**D** Fig. 2.17 Tar sands sample

### **Tar Sands**

Tar sands ( $\blacksquare$  Fig. [2.17](#page-23-1)), sometimes referred to as oil sands, are a combination of bitumen, water, clay, and sand, the bitumen being a heavy black viscous oil. Tar is a term for heavy and extra-heavy oils (6–12°API) that are highly viscous and sulfurrich. It is the residuum of a degradation or normal petroleum; degradation is essentially the loss of light hydrocarbons and an increase of N-S-O compounds. Deposits of tar sands may be mined to obtain the oil-rich bitumen, which is later

refined to produce oil. Because the bitumen in tar sands cannot be pumped in its natural state, tar sand deposits are commonly mined using openpit mining. In other cases, the oil is extracted by underground heating with additional upgrading. This process involves injecting steam into the ground to melt the bitumen from the sands and pumping the bitumen up to the surface.

During many decades, the oil industry clearly ignored tar sands oil since the exploitation of this energy source is much more expensive, difficult, and, more important from an environmental view point, dirty than conventional oil. Theoretically, much of the world's oil reserves (e.g., 2 trillion barrels) are in tar sands form, although obviously it is not all mineable. The largest deposits in the world of tar sands are found in Canada (Athabasca deposit) and Venezuela, although various countries in the Middle East and Russia have also important reserves. In this sense, only Canada has a large-scale commercial tar sands industry. Exploitation of tar sands produces actually a strong dispute in Canada, essentially for the environmental impacts of this kind of mining.

# **Bituminous Shales**

Oil shale or bituminous shale is a sedimentary rock that contains up to 50% of organic matter. In fact, it represents certainly an old petroleum parent rock. Once extracted from the ground, the rock can either be used directly as fuel for a power plant or be processed to produce shale oil and other chemicals and materials. With a few exceptions (e.g., fracking), these deposits are yet little exploited. Because environmental considerations and other factors make extraction of these raw materials relatively unattractive, the strategical character of oil shales as a resource of oil and gas depends on a number of criteria such as the ultimate destination of the raw material, the basic cost of extraction and processing, and the environmental costs, among many others. The heating value of bituminous shale is low and similar, for example, to that of brown coal or average forest residues and less than half of that of the average bituminous coal. This is drastically changing with the introduction of fracking or hydraulic fracture techniques ( $\Box$  [Box 2.4](#page-24-0): Hydraulic Fracking).

#### <span id="page-24-0"></span>**Box 2.4**

#### **Hydraulic Fracturing**

Natural gas produced from shale is often referred to as «unconventional gas» by contrast to «conventional gas» produced from other kinds of rock usually sandstones or limestones. Conventional gas is found in reservoirs in sandstone or limestone where gas has migrated up from source rocks. In these rocks, organic matter becomes gas or oil through the action of heat and pressure over time. According to the International Energy Agency (IEA), the volume of unconventional gas resources (including shale gas, tight gas, and coalbed methane) is currently estimated at 340 trillion cubic meters, equivalent to about 40% of global gas resources. In this statistics, shale gas accounts for the biggest share of these resources. Thus, the emergence of shale gas and shale oil has quickly changed the landscape of opportunities for energy provision and security in different regions of the world.

As the reserves of conventional natural gas and oil falling inexorably and could be nearly exhausted, the extraction of unconventional oil and gas trapped in shale appears to be an attractive alternative for several countries, especially the USA. Because shale is a finegrained, sedimentary rock, the gas and oil it contains do not easily flow and therefore must be released before it can be pumped from the ground. The technique used to extract shale gas is called hydraulic fracturing or colloquially «fracking. » It consists of injecting water, proppant (e.g., granules of sand), and chemicals at high pressure into a shale or sandstone formation. The buildup in pressure causes the formation to fracture, and the proppant fills the fractures to keep them from resealing. This allows the natural gas impounded in the formation to rush into the well for extraction. A combination

of factors, including technological advance, desire to decrease dependence from foreign energy, new geopolitical realities, and high oil prices, have made unconventional gas and subsequently hydraulic fracturing particularly attractive.

Hydraulic fracturing is most often performed in horizontally drilled wells (**a** Fig. [2.18](#page-25-0)). A typical horizontal well has an average lateral extension of 1400 m (maximum of 3000 m). After a period of vertical drilling in order to reach shale deposits (most of unconventional gas is trapped deep inside of shale formations at depths between 1500 and 3000 m), a lateral extension of up to 2000 m is drilled parallel to the rock layer containing the shale. In the next step, fracking fluids are injected into the recently bored hole in order to release the hydrocarbons that are trapped; the fluid is injected under high pressure with the intent of fracturing the soft shale. The rock is hydraulically fractured multiple

<span id="page-25-0"></span>**D** Fig. 2.18 Hydraulic fracking (Illustration courtesy of National Aeronautics and Space Administration)



times every 100 m along this horizontal extent. Occasionally, other substances such as gels, foams, compressed gases, and even air are injected. Chemical mixtures are usually included in the injection, and their objectives are to increase the permeability of the rock by dissolving various components.

Regarding the fracking fluid, it can be injected at various pressures and reach up to 100 MPa (1000 bar) with flow rates of up to 265 liters/second, the cracks

being produced typically less than 1 mm wide. The fracking fluid contains around 20 percent of sand, and this helps to open and keep open the tiny cracks, allowing gas to flow into the well. Fracturing fluid consists of about 98–99.5% water and proppant. The rest (0.5–2% by volume) is composed of a blend of chemicals, often proprietary, that enhance the fluid's properties. The concentration varies depending on the geology and other water characteristics.

These chemicals typically include acids to «clean» the shale to improve gas flow, biocides to prevent organisms from growing and clogging the shale fractures, corrosion and scale inhibitors to protect the integrity of the well, gels or gums that add viscosity to the fluid and suspend the proppant, and friction reducers that enhance flow and improve the ability of the fluid to infiltrate and carry the proppant into small fractures in the shale.

# **Coal**

Coal is a solid, black mineral made up of carbon, hydrogen, oxygen, and nitrogen in varying proportions. In addition, it contains impurities such as ash and sulfur. In the Industrial Revolution, coal was a major fuel competing with charcoal and wood. Coal is an essential fuel for steel and cement production and other industrial activities as well as to provide electricity.

Coal commonly contains altered remains of prehistoric vegetation because it is of vegetable origin, with components growing in swamps and lagoons and going through a peat stage, all with the combined effect of pressure and heat over millions of years to form coal seams. The change from

plant debris to coal involves biochemical action, preservation of the material from further decay, and pressure under accumulated plant materials and other later sediments. This caused physical and chemical changes in the organic remains transforming them into peat and then into coal. Coal formation began during the Carboniferous period, called the first coal age, which spanned 360–290 million years ago. However, coal occurs in all post-Devonian periods. For instance, Cenozoic yields most of the lignite of the world.

The types of vegetation, depth of burial, temperature and pressure and this depth, and length of the time forming the deposits are factors to define the quality of a coal deposit. The degree of change undergone by a coal deposit as it matures from peat to anthracite is known as coalification. Coalification has an important bearing on coal's physical and chemical properties and is referred to as the «rank» of the coal. Ranking is determined by the degree of transformation of the original plant material to carbon. The ranks of coals according to the carbon content are lignite, subbituminous, bituminous, and anthracite ( $\blacksquare$  Fig. [2.19](#page-26-0)).

The use of carbon as an energy source causes bad effects on both humans and the environment. Examples of these issues are acid rain, waste products, high levels of carbon dioxide, contaminated water, poisonous emissions, and increased risks of lung cancer for coal plant workers. Despite this fact, nearly 70% of China's electricity comes from coal, and around 40% of the world's electricity is produced after this energy source. Coal seam extraction can be carried out by surficial or underground mining, depending on the depth and quality of the seams and the geological and environmental factors. In addition, lignite can be broken down chemically through a process called coal gasification to create synthetic natural gas. Coal reserves in 1995, 2005, and 2015 by region are shown in  $\blacksquare$  Fig. [2.20](#page-26-1).

<span id="page-26-0"></span>

<span id="page-26-1"></span>..      **Fig. 2.20** Distribution in percentage by region of coal-proved reserves in 1995, 2005, and 2015 (BP Statistical Review of World Energy [2016](#page-68-5))

<span id="page-27-0"></span>



# **Uranium**

Uranium is the raw material for nuclear power, a radioactive metal being present on the crust of the Earth. It is important to bear in mind that nuclear power actually originates about 16% of electricity of the world. Uranium can come from mining directly uranium-rich ore bodies or as a by-product from mining other minerals such as copper, phosphate, or gold. In this sense, the uranium concentration in the mineralization can range from 0.03% up to 20%. The most important uranium-rich ore producers in the world are Kazakhstan, Canada, and Australia. There are three methods to obtain uranium in the mine: classical open-pit and/or underground methods and in situ leaching. In the latter, uranium is leached directly from the ore. It is the leading method to produce uranium today in a process called in situ leaching (ISL). The WNA (World Nuclear Association) reports that ISL mining accounted for approximately 49% of world production in 2014. ISL processing implies that mining solution is passed through the underground ore body using several bores or wells. The uranium then is brought to the surface in a dissolved state for further purification. After the chemical treatment to separate uranium, the product is the so-called yellow cake, which is a yellow powder of uranium oxide  $(U_3O_8)$  where the uranium concentration is reaching more than 80%.

Natural uranium includes mainly two isotopes: U-238 (99.3%) and U-235 (0.7%). The fission process in the nuclear reactor is carried out using preferably U-235 ( $\Box$  Fig. [2.21](#page-27-0)). Therefore, because nuclear power plants need fuel with U-235 enriched to a level of 3–5%, the material must be enriched to achieve this concentration. Since enrichment process is produced in gaseous form, the «yellow cake» is turn to uranium hexafluoride gas (UF<sub>6</sub>). Enriched uranium (UF6) cannot be directly used in reactors so that it must be converted into uranium oxide  $(UO_2)$ . Fuel pellets are formed by pressing  $UO_2$ , which is sintered (baked) at temperatures of over 1400 °C to achieve high density and stability. The pellets are packed in long metal tubes to form fuel rods, which are grouped in «fuel assemblies» for introduction into a reactor. As the spent fuel assemblies are very hot and radioactive, they must be removed from the reactor and are stored under water, which provides both cooling and radiation shielding. After a few years, spent fuel can be transferred to an interim storage facility. After 40 years in storage, the fuel's radioactivity will be about a thousand times lower than where it was removed from the reactor. Some countries chemically reprocess usable uranium and plutonium to separate them from unusable waste.

# **2.7.2 Metals**

Despite some limitations such as their low specific strength or corrosion processes, metals are still one of the most important components of our way of life. This situation will continue in the future, thanks

<span id="page-28-0"></span>**D** Fig. 2.22 Metallic mercury from Almadén (Spain)



to unique properties that make them irreplaceable. According to Lu ([2010](#page-69-19)): «metals possess much higher fracture toughness than other materials: steels are the toughest known materials; secondly, the properties of metals are uniform in all directions (their strength is the same in tension and compression and it is usually predictable), being these features critically important for predicting fracture in engineering structures; third, most metals are more conductive than ceramics and polymers; and fourth, they have the best overall mechanical properties at temperatures up to a few hundred degrees; moreover, most metals are recyclable, making them more competitive for quantity applications».

In order to separate the metals in groups, there is a general consensus that five clusters can be outlined: (1) iron and steel metals; (2) base metals, copper, lead, zinc, and tin; (3) precious metals, gold, silver, and PGM; (4) light metals, aluminum and magnesium; and (5) minor and specialty metals, this group is formed by numerous metals (e.g., mercury ( $\blacksquare$  Fig. [2.22](#page-28-0)), antimony, arsenic, bismuth, titanium, cobalt, tungsten, molybdenum, and many others).

# **Iron and Steel Metals**

Iron ore is destined to the production of pig iron in the blast furnace. High iron concentration in ore, low content of  $SiO_2$  and alumina, and coarse grain size are favorable properties. The basic materials for pig iron production are iron ore, coal and

coke (also used as energy input to the process), and alternative reducing agents such as limestone and dolomite. The main application of this raw material is to produce steel, the toughest of all construction materials, which is an alloy made of low-carbon iron (steel production requires iron, steel scrap, and lime). Non-metallurgical uses of iron ore, such as chemical applications, pigments, and abrasives, consume a very small share of total iron ore production. Steel is obtained by blowing oxygen through molten iron, thereby reducing its carbon content up to 2%. The properties of steel can be adapted by alloying it with other metals such as manganese, chromium, nickel, cobalt, molybdenum, tungsten, and vanadium, the so-called steel metals.

The most famous and used alloy steel is stainless steel. Iron and the most common iron alloy, steel, are relatively poor materials from a corrosion viewpoint. In spite of this, there is a group of ironbase alloys, the iron-chromium (Fe-Cr) alloys, often with nickel (Ni) additions, known as stainless steels, which do not rust in seawater, which are resistant to concentrated acids, and which do not scale at temperatures up to 1100 °C. The combined effect of the alloying elements, heat treatment and, to some extent, the impurities, establishes the property profile of a certain steel type (Outokumpu [2013](#page-70-13)). Applications of stainless steel include food handling/processing, medical instruments, and structural/architectural uses, among many others  $\left( \square$  Fig. [2.23](#page-29-0)).

<span id="page-29-0"></span>

**D** Fig. 2.23 Santander (Spain) Sport Hall; the external cover is made with stainless steel

### **Base Metals**

Base metals such as copper and zinc are widely used in communication and information technology. Copper and its alloys exhibit many desirable properties. It is ductile, malleable, hard, tough, strong, wear, and corrosion resistant. It also has high-tensile strength, fatigue strength, and thermal and electrical conductivity. The production of copper is mainly utilized by the wire and cable markets, taking advantage of properties such as the electrical conductivity, corrosion resistance, and thermal conductivity. Excellent malleability, ductility, and resistance against atmospheric attack distinguish copper metal and its alloys (e.g., tin or zinc); copper shows also strong antibacterial properties. Other applications include structural and aesthetic uses.

With regard to zinc and lead, there are few ore deposits that contain only lead or zinc, and most mines produced both metals. Zinc is used predominantly in galvanizing and alloys. Steel coated with zinc (galvanized steel) exhibits high levels of corrosion resistance. This application is responsible for around 50% of total demand. Zinc-based alloys are also used in die casting, ranging from automotive components to toys and models. Lead is a heavy metal, soft, and malleable. Lead is commonly utilized in alloyed form, which increases its low-tensile strength. When added to metal alloy, lead improves their machinability. Regarding tin, it is a soft, weak, malleable, and ductile metal and has many important uses as an alloy. It can be alloyed with lead and with copper to produce bronze. The most

<span id="page-29-1"></span>

**D** Fig. 2.24 Nickel briquettes (Image courtesy of Sherritt International Corporation)

important properties of tin-based alloys are their high resistance to corrosion, low-fatigue strength, and compressive strength. For its part, nickel, also a base metal, is hard and ductile ( $\blacksquare$  Fig. [2.24](#page-29-1)), and the main application is in steel alloys.

### **Precious Metals**

Apart from copper, gold is one of the earliest metals intentionally looked for by humans. Gold was always a metal valued for wealth, adornment, and strong currency. There is little difference today, and only 10% are consumed by industry (e.g., electronics and dental applications). For the future, an increasing role of nano-sized gold particles as catalysts in chemical production, in pollution control, and in medical applications is predicted (Pohl [2011\)](#page-70-1). In respect of silver, it is

obtained mainly as a by-product from copper, lead, zinc, and gold ores. In fact, the economic viability of many base metal and gold deposits relies on by-product silver. The use of silver is basically in industrial applications, but nearly 40% is consumed in jewelry, coins, and silverware.

The platinum group metals (PGM) are used in several industrial applications as well as in jewelry. The six chemical elements normally referred to as the platinum group elements (PGE) are ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt). Platinum and palladium are actually the most commercially important of the PGM with largest utilization in the automotive industry where they are applied to decrease harmful emissions from vehicle systems (Gunn [2014\)](#page-69-20). Rhodium is the third more important PGM. It is also used in autocatalysts, although its consumption is an order of magnitude less than platinum and palladium.

### **Light Metals**

Aluminum is the most important of the noniron metals, and it is commonly produced from bauxite, which is a loose soil or a hard rock with 30–65%  $\mathrm{Al}_2\mathrm{O}_3$ . About 95% of bauxite produced is processed into aluminum metal. The remaining 5% serves as an industrial raw material for numerous special products such as abrasives, Portland cement, technical ceramics, glass, chemicals, paints, and refractories. Favorable attributes of aluminum metal such as lightweight, strength, and excellent corrosion resistance (Lu [2010\)](#page-69-19) allow its use in many applications from building air frames to food packaging.

The other light metal is magnesium. Very diverse raw materials, natural and industrial brines, and seawater are used for the production of magnesium and magnesium compounds. For instance, harvesting salts on the shores of the Great Salt Lake is a source of magnesium. Applications of the extremely light magnesium metal (density  $1.74$  g/cm<sup>3</sup>) employ the pure metal or aluminum alloys. Magnesium-aluminum alloys are mainly consumed for beverage container making. About 40% of magnesium is used for die casting in the car industry in order to reduce weight and fuel consumption. Other sectors include the space, aircraft, and chemical industry. Magnesium is mainly utilized as magnesium oxide in applications such as refractory material (e.g., furnace linings for the production of iron and steel), glass, and cement.

### **Minor and Specialty Metals**

The term minor metals encompasses a vast array of metals, including tungsten, titanium, cobalt, and molybdenum, to name just a few. These metals are crucial to the global economy, and many of them are by-products of the major exchange metals. Only the precious metals are more valuable than many of the minor and specialty metals. Minor metals show relatively low annual production volume, compared to base metals, and they have commonly high-technology applications. Uses include filaments in lightbulbs, electronic pastes, components in mobile phones and tablet Pc's, agriculture, and flat panel screens as well as alloying agents in specialist steels for the automotive and aerospace sectors, among many others; as technology progresses, new applications are found which will create new supply and demand patterns, as demonstrated by the growth in renewables technology (Minor Metals Trade Association – MMTA).

Nowadays, one of the most important groups of these metals is rare earth elements (REE) because their chemical properties make them indispensable and non-replaceable in many high-technology applications. For this reason, REE consumption is growing due to their daily contribution to our lives in products like hybrid cars, catalytic converters, wind power generators, household appliances, industrial motors, MRI machines, iPods and computer hard drives, and green energy technology.

### **2.7.3 Industrial Minerals**

The use of the term «industrial minerals and rocks» is very common in the literature (e.g., Kuzvart [1984](#page-69-21); Carr and Herz [1989;](#page-69-22) Jeffrey [2006](#page-69-23)), and it cover both types of raw materials. In this section, industrial minerals are described separately from industrial rocks because the characteristics of the materials and applications are wholly different. The economically usable minerals automatically classify themselves into four broad groups based on the stages of processing required for conversion to finally usable products (Chatterjee [2009\)](#page-69-24): (1) those that are mainly used directly in consumer product industries, (2) those that are not used without first extracting metals from them, (3) those that are used in both ways but mainly valued for their metal content, and (4)

those that are used in both ways, but their direct uses are of importance and their metal values are of minor significance. It has become a convention to refer to the first and fourth groups as «industrial minerals» (earlier called «nonmetallic minerals»), while the second and third groups are considered as «metallic minerals. »

Industrial minerals are valuable economic raw materials that are not used in the production of metals or energy. Compared with metals and other nonmetallic resources, they are mainly processed by physical methods. Both definitions, however, are not without exceptions, and some attributions to the group are rather by tradition (Pohl [2011\)](#page-70-1). Typical examples of industrial minerals are talc ( $\blacksquare$  Fig. [2.25](#page-31-0)), mica, and fluorite. Several ore minerals such as chromite, bauxite, and rutile also have industrial applications, but the bulk of production feeds metallurgy. Because of multiple and even changing uses and a wide genetic variety, the most common classification of industrial minerals is based in the alphabetical order. Occasionally, final applications of the industrial minerals are used as a basis for their classification.

Although the industrial mineral deposits are generally exploited for single minerals, a significant number are worked together as by-products such as fluorite and barite from Mississippi Valley-type lead-zinc deposits or quartz, feldspar, and mica from pegmatites. Most industrial minerals and rock commodities also have multiple uses. For instance, a pure limestone deposit could supply material for lime, aggregate, and cement production, in granular form for flue gas desulfurization, and in a range of powders for fillers, soil stabilization, and agricultural uses. Each of these applications can command very different prices per ton, so evaluating the overall value of the deposit is difficult and involves assessing for multiple quality requirements and variable product splits. In many cases, the evaluation process for an industrial mineral resource is considerably more technically complex than that for metal deposits (Jeffrey [2006\)](#page-69-23).

Globalization is an important economic driver in the industrial mineral sector. Large international corporations (e.g., Sibelco in Belgium) have formed by consolidation and acquisition of smaller companies. In some cases, this process has led to one or two corporations having dominant control over individual mineral commodities such as borates, nepheline syenite, garnet, and talc. As the technical demands on specific minerals increase or supplies are restricted, companies explore the possibilities of making synthetic mineral products. This is especially true for gemstones, but

<span id="page-31-0"></span>

**D** Fig. 2.25 Talc mine at León (Spain)

In some applications, the boundaries with material science become blurred such as in industries making synthetic corundum and silica for laser, military, and electronic applications. Here the mineral structure has been perfected to a point not found in nature. Some of these synthetic minerals are also produced as by-products of upgrading other mineral products, but all affect the demand for primary industrial minerals from new or existing deposits. More often, a shortage of suitable mineral supplies, or the possibility of cost savings, leads to substitution by function. Other minerals that can perform the same role in a product are then used instead. The increased use of fine-ground or precipitated calcium carbonate at the expense of kaolin in paper coating is a good example.

As a tool to assist in teaching about industrial minerals, a classification that defined seven groups of commodities based on the relative importance of physical and chemical applications or a combination of the two can be established (Smith [1999\)](#page-70-14). The classification is constructed using a matrix of commodities and uses that are grouped according to applications. Clustering of commodities reveals the following groupings: (1) principal abrasives (diamond, alumina, garnet, and pumice), (2) principal refractories (pyrophyllite, sillimanite group, magnesite, and graphite), (3) principal fillers (wollastonite, titanium minerals, mica, barite, and iron oxide), (4) principal physical and chemical minerals (feldspar and zeolite), (5) mixed-application physical minerals (silica, perlite, clay ( $\blacksquare$  Fig. [2.26](#page-32-0)), and talc), (6) principal chemical minerals (phosphate, salt, and sulfur), and (7) mixed-application physical and chemical minerals (olivine, chromite, fluorspar, gypsum, and limestone).

Regarding the trade value of industrial minerals, most of them are essentially high-volume, lowvalue commodities, while metals are the opposite, mainly precious metals. Beyond the difference in scale of value between the two groups of commodities, a key issue is the fact that industrial minerals do not have markets whose prices are set by an exchange system (e.g., London Metal Exchange in metals). Some attempts have been made by various organizations in recent years, especially with

<span id="page-32-0"></span>

**D** Fig. 2.26 Clay (bentonite) quarry from Milos (Greece) (Image courtesy of José Pedro Calvo)

the advent of the Internet and e-commerce. For the reasons outlined here, it is unlikely that any kind of industrial mineral pricing exchange will be created in the foreseeable future.

### **Industrial Mineral Applications**

The industries in which industrial minerals are utilized are cover paint, electronic, metal casting, paper, plastic, glass, ceramic, detergent, pharmaceutical and cosmetic, environmental engineering, and construction (IMA Europe). For instance, glass in buildings is manufactured with industrial minerals, mainly silica. The following descriptions are a brief resume of the application of industrial minerals in these sectors.

The glazes that cover ceramics are largely composed of minerals, mainly borates, silicates, and metallic pigments. Ceramics and refractory articles are indispensable in buildings: pipes, tiles, and refractory bricks are all 100% industrial minerals. Even if some ceramics are being replaced by resins, these also contain important amounts of industrial minerals. Technological developments in the ceramic sector represent an area in which industrial minerals are at the forefront of progress. For instance, ceramic tiles protect space shuttles in order to support the high temperatures of the Earth's atmosphere.

Industrial minerals such as clays, sand, feldspar, kaolin, and other minerals are basic to all construction materials, from bricks to tiles and from cement to limes and plastics. Apart from the basic structure, industrial minerals are also present in all parts of the building as a constituent or during their manufacturing. For instance, all ceramic compounds of a house (e.g., tiles, tubing, etc.) include industrial minerals. Even the wallpaper, paints, and carpet lining contain important amounts of industrial minerals.

Detergents such as the powder ones utilized for laundry and dishwashers include a «bleaching system. » Two systems are currently in use: perborate and percarbonate. Both rely on industrial minerals, borates, or calcium carbonate, respectively, which are chemically processed up to the required properties. Detergents are a major consumer of silica, which makes a whole family of detergents based on sodium silicate. Other industrial minerals (e.g., bentonite and sepiolite) are also used in detergent applications because of their adsorption properties. In this sense, sepiolite is the main component in making cat litter ( $\blacksquare$  Fig. [2.27](#page-33-0)).

The nervous system of a computer is made of silicon, this component being extracted from silica sand or massive quartz rocks. This quartz crystals also pace actually the functioning of most of clocks. After extraction, the silicon is delivered to the electronic manufacturers in the form of «wafers» a few centimeters wide.

Industrial minerals are crucial in water management, whether considering drinking water preparation or wastewater treatment. Thus, silica sands are used as filters, perlite, zeolites, or talc as flocculants or adsorbents, bentonite as

<span id="page-33-0"></span>**D** Fig. 2.27 Cat litter manufactured with sepiolite (Image courtesy of SAMCA)



a degreasing agent, and calcium carbonate as a neutralizing agent, to mention but a few. Industrial mineral-based liners and geosynthetic liners, either basal or superficial, are increasingly used to avoid escape of leachate from landfill sites. Air treatment of industrial effluents also largely relies on minerals. Activated carbon is the best-known technique, but other minerals are used as well. For instance, flue gas desulfurization of power station

The glass industry is one of the primary consuming markets for industrial minerals with the highest demand in terms of volume for silica sand, limestone, feldspar, and soda ash. Fiberglass and glass wool are also members of this group.

fumes is achieved with calcium carbonate.

The mineral blend is a determinant to the glass properties during manufacture and use.

Historically, fillers and extenders were used to furnish low-cost bulk to paint solid content. Today, the range of extenders available is extremely wide and determines many of the paint's properties: gloss, opacity, flow, film toughness, permeability, rheology, resistance, etc. Waterborne systems, low solvent paints, powder coatings, high-solid coatings, and industrial minerals are crucial to all the environment-friendly developments of paint technology. The paper industry, particularly printing and writing paper, is by far the largest volume user of industrial minerals ( $\Box$  [Box 2.5](#page-34-0): Papermaking Additives).

#### <span id="page-34-0"></span>**Box 2.5**

#### **Papermaking Additives**

Papermaking starts with the production of the most important raw material: wood. The pulping process then converts the wood into the most appropriate type of pulp. Pulping of wood can be done in two ways: mechanically or chemically. In the case of mechanical pulp, the wood is processed into fiber form by grinding it against a quickly rotating stone under addition of water. In chemical pulp, the pure fiber has to be set free, the wood chips being cooked in a chemical solution. The next step is pulp bleaching. It is a complex process consisting of several chemical process steps with washing taking place between the various chemical treatments. The paper machine then converts the pulp into a thin base paper, which, at the end of the production process, is coated to give it a superb flat surface and bright shade. Coating a paper enhances its optical and tactile characteristics (whiteness and shade, gloss, and smoothness), but it also improves its printing behavior, allowing the use of very fine screens, yielding more color in thinner ink layers, and producing more contrast in printed images.

In all the previous processes, many types of additives (fillers, binders, and many others) are used to improve the efficiency and quality of the final product. In papermaking, minerals are used either as fillers or as a coating on paper. Some minerals, like talc, are also used in pitch control (absorption of wood resins that tend to obstruct the machines). The use of minerals in paper production increases the speed of the machine performance and fluidity. The final characteristics of the paper (strength, whiteness, gloss, ink retention, etc.) are largely determined by the blend of minerals used. High-quality, glossy paper is obtained by applying a thin layer of industrial minerals on the surface of the paper. As for fillers, the final characteristics of the coating and its fitness for use are governed by the nature of the mineral blend.

The list of minerals used as additives in papermaking is impressive. Soda ash dissolves out the noncellulose parts without weakening the finished paper. Titanium dioxide is a strong white pigment which makes paper whiter and more opaque, acting as a filler and giving a smoother surface to the paper. The filling effect is much stronger than with calcium carbonate, but it does not have the ability to neutralize paper acids. Titanium dioxide is also used to tint-colored pulps. China clay is a fine white powder, also known as opal gamma kaolin, which is used to make paper more opaque and smooth and reduce shrinkage. It is

especially useful in paper casting and will appeal to papermakers and model makers alike. Calcium carbonate provides an alkaline reserve in paper which promotes acid-free archival qualities, being also used as filler and in coating. It retards shrinkage in paper castings and makes a smoother surface. In paper sheets, it improves opacity and whiteness. Talc gives paper a greasy or soapy feel and enables it to take a high finish. Kaolin is one of the most used filler. Lime is used in alkaline pulping process. Magnesite is a common component of cigarette paper as filler, being also considered as an excellent ingredient for harmless smoking; hydromagnesite and huntite are used to control the burning rate of cigarette papers. Sodium silicate is utilized in waste paper deinking for wetting, ink dispersion, and peroxide stabilization. Finally, many pigments and dyes used in papermaking come from industrial minerals such as iron oxide, titanium oxide, zinc compounds (e.g., zinc sulfide or zinc oxide), lead compounds, cadmium sulfide, etc. A type of mixture containing coprecipitates of titanium and mica (or other minerals) is used to make a pearlescent, which is transparent and highly light refractive, imparting to the ink film the luster characteristic of motherof-pearl.

The role of industrial minerals in pharmaceuticals falls into one of two main categories: excipient or active substances. The excipients have no intrinsic health benefit on their own; they are used solely as carriers, allowing the intake of minute amount of active substances. pH regulation or adsorbents are the kind of applications for which some minerals are used as active ingredients. Thus, antacid pills are composed mainly of calcium carbonate, lithium used in antidepressants is derived from industrial minerals, and many excipients are minerals such as talc, magnesium carbonate, or silica. Many cosmetics incorporate important amount of industrial minerals such as talc, although others like mica, silica, or borates are utilized for their abrasive, visual, or stabilizing properties. It is necessary to remember that earliest civilizations (e.g., the Romans) already made use of earth pigments for body painting.

Finally, polymeric resins such as PVC and PP are generally filled and/or reinforced with industrial minerals (e.g., talc and calcium carbonate). They are also used in polyamide, unsaturated polyesters, HDPE (high-density polyethylene), and LDPE (low-density polyethylene). Small amounts of minerals, particularly talc and silica, are used in the compounding and manufacturing of rubber goods. Thus, the new-generation car tire relies its energy saving on the silica content of the polymer.

# **2.7.4 Industrial Rocks**

This term encompass a group of rocks (single mineral species are excluded of this group) whose main application is addressed to construction market. Industrial rocks typically comprise of multi-mineral hard and unconsolidated rocks and sediments. Aggregates (sand and gravel) for road construction, limestone for cement, and dimensional stone (granite, marble or slate) for building material are all well-known examples of industrial rocks.

The main characteristics of industrial rocks can be outlined as follows. Firstly, the price of the raw material is low to very low, and sometimes the price of the finished product is low as well. One of the principal industrial rocks, namely, aggregates, displays the lowest price for a raw material in the industry (e.g., 7 dollars per ton of concrete sand). For this reason, exploration, exploitation, and mineral processing costs must be very low. Secondly, the very high prices of transport resulted in

a proximity to consumption center. Consequently, the markets for the product are commonly local markets, especially in aggregate industry. Finally, resources and reserves of industrial rocks are almost infinite. Moreover, one particular type can be substituted by another one, for example, if the price of the product suddenly increases, and even a finished product can also be replaced by another one of similar specifications. According to the main markets of construction, industrial rocks can be grouped in to five main types: (1) aggregates, (2) ornamental rocks, (3) limestone for cement and lime, (4) gypsum, and (5) clay for bricks and tiles.

### **Aggregates**

Aggregates are granular materials used in construction formed of natural or crushed, hard, sound, and durable particles of nonreactive minerals. Sand, gravel, and crushed rock are typically the most common natural aggregates in the market. While aggregate is used primarily in asphalt and concrete (asphalt pavement includes 94% aggregate and concrete is formed by 80% aggregate), all construction worldwide involves the use of this raw material. In fact, aggregates are the second natural resource more used by the humankind, after water. Aggregates are mainly obtained by mining quarries and gravel pits and in some countries from sea-dredged materials (marine aggregates). Recycled aggregates (see  $\blacktriangleright$  Chap. [1](http://dx.doi.org/10.1007/978-3-319-58760-8_1)) are derived from reprocessing materials previously used in construction such as demolition debris.

The production and consumption of this raw material are impressive. According to the Union Européenne des Producteurs de Granulats (UEPG – European Aggregates Association), the European aggregate consumption is 2.8 billion tons per year, the average aggregate consumption being 5.2 tons per person per year; about 90% of all aggregate produced are from quarries and pits (25,000 quarries and pits in Europe) and the remaining 10% from recycled aggregates (6%) and marine and manufactured aggregates (2% each). US aggregate consumption includes approximately 1 billion tons of sand and gravel in 2016 and similar amount of crushed rock (USGS).

Aggregates are indeed the main component in all homes, offices, social buildings, and infrastructures. For instance, the construction of a common new home uses up to 400 tons of aggregates, from the foundations through to the roof tiles. Other

<span id="page-36-0"></span>



examples are roads or railways: the construction of 1 km of motorway consumes up to 25,000 tons of aggregates, and the construction of 1 m of railway for a high-speed train (TGV) uses up to 10 tons of aggregates. Drainage, dams, and breakwaters ( $\blacksquare$  Fig. [2.28](#page-36-0)) are a few more of other important construction items involving aggregate.

Specifications for the most important applications of aggregates such as concrete and ballast are closely regulated and subject to industrial standards (e.g., ASTM in the USA, EN in Europe, ISO worldwide) and concern petrographical composition, geometrical properties such as particle size and grain shape, mechanical and physical properties (e.g., resistance to wear or resistance to fragmentation), thermal and weathering properties (e.g., boiling test for Sonnenbrand basalt), and chemical properties (e.g., determination of acid-soluble chloride salts).

# **Ornamental Rocks**

For centuries, natural stone has been used by nearly all civilizations, being applied mainly in architecture. Ornamental rocks are the main economic component of the natural stone industry. The market is shaped by three rock types: granites ( $\Box$  Fig. [2.29](#page-37-0)), marbles, and shales ( $\Box$  Fig. [2.30](#page-37-1)), although they do not always represent the same typology of geological rock. Thus, limestone is a marble in natural stone industry, although obviously the limestones need a metamorphism to become a marble. Other example is basalt, which is defined as granite in natural stone industry, although the former is a volcanic rock and the latter a plutonic one.

Ornamental rock blocks are exploited in quarries. Currently, the most common method to extract the blocks is by using diamond wire. Diamond wires are cutting tools for rocks (marble, granite, or slates). The wires are composed of a stainless steel cable over which are assembled diamond-sintered pearls, 10–12 mm in diameter and spaced 25 mm along the wire. The utilization of this slabbing technology has expanded all over the world due to its advantages facing other techniques such as explosives or thermal lance. After extraction in quarries, the blocks are manufactured using different techniques, which depend on the size of the products and the type of rock. Marble or granite is commonly polished to perform products for interior paving. Granite is also processed to obtain flamed granite, most used in pavements.

# **Carbonate Rocks for Cement and Lime**

Carbonate rocks are extremely important raw materials for industry, construction, agriculture, forestry, and environmental engineering. The most representative application of these rocks is in cement and lime industry. Cement is a fine powder that sets after a few hours when mixed with water. It then hardens in a few days into a solid and strong

<span id="page-37-0"></span>

**D** Fig. 2.29 Granite quarry for ornamental rock at Cadalso de los Vidrios (Spain) (Image courtesy of Marcelino Martínez)

<span id="page-37-1"></span>

**D** Fig. 2.30 Underground shale quarry for ornamental rock (roofing) (León, Spain)

material. The so-called Portland cement is the most classical type of cement although there are many types of common cement. This product is manufactured in a controlled chemical combination of mainly calcium, silicon, aluminum, and iron ( $\Box$  [Box 2.6](#page-38-0): Manufacture of Cement). The main use of cement is to make concrete, the most important construction material in the last century.

#### <span id="page-38-0"></span>**Manufacture of Cement**

Cement is a fine gray powder that, when reacted with water, hardens to form a rigid chemical mineral structure that gives concrete its high strengths. The credit for its discovery is given to the Romans, who mixed lime (CaCO<sub>2</sub>) with volcanic ash, producing a cement mortar that was used during construction of such impressive structures as the Colosseum. When the Roman Empire fell, information on how to make cement was lost and not rediscovered until many centuries later. Roman cement was not improved upon until 1758, when Smeaton noticed that using a limestone that was 20–25% clay and heating the mixture resulted in a cement that could harden under water.

Portland cement (the most common type of cement in common use today) is manufactured in a four-step process: (a) quarrying, (b) raw material preparation, (c) clinkering, and (d) cement milling and mixing. The name Portland was given owing to the resemblance of this hardened cement paste to the natural stone available at a place called Portland in England. Most common way to manufacture Portland cement is through the so-called dry method. The raw material for cement manufacture is a rock mixture of about 80% limestone (which is rich in CaCO<sub>3</sub>) and 20% clay or shale (a source of  $SiO<sub>2</sub>$ , Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>). Lime and silica provide the main strength of the cement, while iron reduces the reaction temperature and gives the cement its characteristic gray color.

Raw material preparation includes a variety of blending and sizing operations that are designed to provide a feed with appropriate chemical and physical properties. Thus, quarried clay and limestone are crushed separately, and samples of both rocks are then sent off to the laboratory for mineral analysis. If necessary, minerals are then added to either the clay or the limestone to ensure that the correct amounts of aluminum, iron, etc. are present. Since the four basic oxides must be present in exact proportions (calcium oxide, 65%; silicon oxide, 20%; alumina oxide, 10%; and iron oxide, 5%), limestone and clay are mixed together with many other raw materials such as slate, marl, blast furnace slag, silica sand, iron

ore, and much more. These are called correctors because they must define the final proportions of all oxides. The clay and limestone and correctors are then fed together into a mill where the rock is ground until the material is less than 100–200 μm in diameter.

In the third step of manufacturing, the fine-grained raw materials are then dried, heated, and fed into a rotating kiln (D Fig. [2.31\)](#page-38-1). Here the raw materials react at very high temperatures to form 3CaO·SiO<sub>2</sub> (tricalcium silicate), 2CaO·SiO<sub>2</sub> (dicalcium silicate), 3CaO·Al<sub>2</sub>O<sub>3</sub> (tricalcium aluminate), and  $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (tetracalcium aluminoferrite). Minor compounds such as MgO, TiO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, and Na<sub>2</sub>O are also present in clinker. The cement kiln heats all the raw materials to about 1500 °C in huge cylindrical steel rotary kilns (60 m long). The materials are continuously and slowly moved to the lower end by rotation of the kiln. A burner is located at one end of the kiln, and the ground raw materials are introduced at the other end. As the material moves through the kiln, some elements are driven off

<span id="page-38-1"></span>



in the form of gases. The remaining elements are joined to form a new substance called clinker and formed by gray balls. They are discharged red-hot from the lower end of the kiln and commonly are brought down to handling temperature in various types of coolers.

The final step includes clinker milling and mixing with other components to obtain the socalled Portland cement. Thus, after the clinker is cooled, cement plants grind it in large ball mills to obtain a very fine powder (e.g., 20 μm). Finally, it is then mixed with small amount of either gypsum or anhydrite, both of which are

forms of calcium sulfate (as setting retardant) and other materials. It is essential to note that cement manufacture is an energy-intensive process.

One of the most significant challenges facing the industry into the twenty-first century is a requirement to reduce CO<sub>2</sub> emissions. CO<sub>2</sub> is produced during the calcination phase of the manufacturing process and also as a result of burning fossil fuels. Opportunity to reduce emissions through increased energy efficiency is only possible on the latter of the CO<sub>2</sub> emissions. In this sense, due to the characteristics of the

Regarding the other main product obtained from carbonate rocks, lime is a term specifically used to refer high-quality products such as quicklime (CaO) and calcium hydroxide, also known as hydrated lime  ${\rm (Ca(OH)_2)}$ . The raw material for all this type of products is limestone, commonly formed by almost exclusively calcium carbonate  $(CaCO<sub>3</sub>)$ . Limestone is processed to form lime, being heated in a specially designed kiln to over 900 °C. In this process, called calcination, a chemical reaction occurs and creates calcium oxide. The applications of lime are huge, but those in environmental engineering are the most widely consumed (e.g., soil conditioning or to neutralize the acidic effluents).

#### **Clays for Bricks and Tiles**

Clay rocks are cohesive unconsolidated or indurated clastic sedimentary rocks where size fraction lower than 0.002 mm is dominant. They vary considerably in physical properties, color, and mineralogical content. Clay rocks mainly consist of clay minerals such as kaolinite, illite, montmorillonite, chlorite, and mixed-layer clay minerals. Besides clay minerals, clay and claystone contain fine-grained clastic silicates (quartz, mica, and feldspar), biogenic matter (carbonate microfossils, kerogen, and coaly particles), and diagenetic minerals (marcasite, pyrite, carbonate, and phosphate). These clays are mainly used for the production of bricks, roof tiles, ceramic tiles, and other fired and sintered products. Ceramic materials are one of the most important

production process, the cement industry is capable of coprocessing (a) alternative fuels, which have significant calorific value (e.g., waste oils); (b) alternative raw materials, the mineral components of which mean they are suitable for the production of clinker or cement (e.g., contaminated soil); and (c) materials that have both a calorific value and provide mineral components (e.g., paper sludge, used tires). Without coprocessing, the wastes and by-products that make up these materials would have to be incinerated or landfilled with corresponding greenhouse gas emissions.

components of the construction industries, and they are primarily utilized as building materials. These include two big groups: (a) bricks and roof tiles and (b) ceramic tiles. Clay for bricks and roof tiles is used in a wide range of buildings from housing to factories as well as in the construction of tunnels, bridges, etc. In brick- and roof tile-making terms, clay includes a range of naturally occurring raw materials. In manufacturing process, clay must possess some specific properties and characteristics. It usually shows the most important property to obtain these products: plasticity. This property permits clay to be shaped and molded when mixed with water.

All types of clays used for bricks and roof tiles contain some percentage of silica and alumina sand, silt, and clay with varying amount of metallic oxides. Metallic oxides act as fluxes promoting fusion of the particles at lower temperatures (950 °C). In geological terms, the key in the manufacturing process is the mineral content of the raw material. Due to variances in the age of the deposits, depositional conditions, and impurities involved, there are variations between different clay types even in the same deposit. These variations may affect the brickmaking process and the properties of the finished product.

Regarding the second group, ceramic (wall and floor) tiles ( $\blacksquare$  Fig. [2.32](#page-40-0)), they are made from clay and other inorganic raw materials that are ground and/or mixed and then molded before drying and firing at sufficiently high temperatures (1400 °C)

<span id="page-40-0"></span>

**D** Fig. 2.32 Glazed ceramic tiles (Image courtesy of José Pedro Calvo)

to acquire the necessary stable properties. The raw materials that make up the ceramic tile are essentially clays, feldspars, sand, carbonates, and kaolin. From a glazed point of view, ceramic tiles can be unglazed or glazed. The former is fired only once, whereas glazed tiles include a vitrified coating between the firing. The manufacturing of glaze and frit is a complex process involving many different raw materials, such as carbonates, silicates, borates, and many others.

# **2.8 Genetic Classification of Mineral Deposits**

According to the main ore-forming processes, a simple genetic classification of mineral deposits encompasses four main groups: (1) magmatic, (2) hydrothermal, (3) sedimentary, and (4) metamorphic/metamorphosed. The following is a description of the main classes included in these groups. However, it is not obviously an exhaustive overview of all types of mineral deposits existing in the Earth's crust.

# **2.8.1 Magmatic Ore Deposits**

A magmatic ore deposit is formed by an accumulation of magmatic minerals. Some of them are extremely rare and almost never encountered in common rocks (e.g., alloys of the platinum metals). However, other minerals such as magnetite are common. A very large and diverse group of ore deposits originates by magmatic processes. According to Ardnt and Ganino (2012), many magmatic ore deposits are hosted by granites, but the ore results from precipitation of ore minerals from aqueous fluids and not from the granitic magma itself. The type of ore mineral in magmatic deposits is directly linked to the composition of the host rock. For instance, deposits of nickel, chromium, and platinum group elements are founded in mafic-ultramafic hosts. By contrast, felsic rocks generate ores from the elements confined that concentrate in evolved magmatic liquids. Some of these elements are present in late-crystallizing phases such as ilmenite, which contains Ti and cassiterite; the ore of Sn and others enter the water-rich fluid that separates from

the silicate liquid to be redeposited in pegmatites or in hydrothermal ore bodies. Pegmatites are also an important source of rare but increasingly important metals such as lithium and beryllium.

Crystallization of economic minerals normally occurs from mafic to ultramafic magmas that are low in viscosity and have important content of nickel, copper, and platinum group elements. Magmatic ore deposits associated with ultramafic and mafic rocks span most of the history of the Earth, being well represented in all continents. «Currently, these deposits are estimated to account for approximately 7% of the total value of annual global metal and mineral mining and they include the world's greatest concentration of metals: the Bushveld Complex, which has an estimated total metal endowment value, representing past production and current reserves and resources, of US \$3.6 trillion» (Peck y Huminicki [2016\)](#page-70-15).

The description of magmatic deposits can be carried out according to the host rock association or related to the commodity. The latter is easier and allows to summarize the main groups of deposits present in the Earth's crust from a magmatic viewpoint. On this basis, four types of magmatic ore deposits can be defined: (1) chromite deposits, (2) nickel (copper) sulfide deposits, (3) platinum group element (PGE) deposits, and (4) diamond deposits. Since the four types can be considered as orthomagmatic deposits, a fifth type related to granitic pegmatites can be added.

#### **Chromite Deposits**

Chromite (Mg, Fe<sup>2+</sup>) (Cr<sup>3+</sup>, Al, Fe<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> is the only commercial source of chromium. The source to obtain this metal comes mainly from four different mineral deposit types: podiform deposits, stratiform deposits, placer deposits, and laterites. The latter are derived from weathering of ultramafic rocks that contain chromite. In particular, most of the world's resources are located in stratiform chromite deposits such as the Bushveld Complex (South Africa) ( $\blacksquare$  Fig. [2.33](#page-41-0)) and the Great Dyke (Zimbabwe). The Bushveld Complex contains the main type examples of ore deposits in a large layered intrusion. Important podiform chromite deposits are located in Kazakhstan, Turkey, the Philippines, New Caledonia, and Russia. Known resources of alluvial and eluvial placer deposits derived by erosion of such rocks are low in grade and of very minor importance (Misra [2000\)](#page-69-3). The major stratiform chromite deposits also contain important contents of platinum, palladium, rhodium, osmium, iridium, and ruthenium.

Regarding the genesis of the deposits, little consensus has been reached about the magma chamber processes responsible for chromite segregation and crystallization although extensive studies have been carried out. In general, the most widely accepted explanation involves the mixing of primitive and fractionated magmas. Thus, the commonly cited hypotheses include: «(1) mixing of a parent magma with a more primitive magma during magma

<span id="page-41-0"></span>

**D** Fig. 2.33 Stratiform chromite at South Africa (Image courtesy of Roland Oberhänsli)

chamber recharge; and (2) contamination of the parent magma by localized assimilation of country rock at the roof of the magma chamber; the mixing of magmas would produce a partially differentiated magma, which could then be forced into the chromite stability field and result in the massive chromitite layers found in stratiform complexes» (Schulte et al. [2012](#page-70-16)). In this sense, chromitite is a term used for massive chromite containing 50% to more than 95% of cumulus chromite.

The sequences of massive chromitite layers (>90% chromite) or seams of disseminated chromite (>60% chromite) are commonly found in the lower ultramafic parts of the layered intrusions. These intrusions were emplaced in stable cratonic settings or during rift-related events throughout the Archean or early Proterozoic, although a few younger deposits exist. The intrusions extend anywhere from 2 to 180 km in diameter and can reach thicknesses of as much as 15 km. As a rule, the individual seams included in the intrusions range from less than 1 cm to 5–8 m thick. The mineral occurs in layers that reach a meter or more in thickness alternating with layers composed of other magmatic minerals (Arndt and Ganino [2012](#page-68-3)). In some cases, the chromite deposit is not economic due to the low grade of the mineralization or the low tonnage of chromite available for mining.

Podiform chromite deposits, another important source for chromite, are small magmatic chromite mineralization originated in the ultramafic part of an ophiolite complex in the oceanic crust. Most podiform chromite deposits are located in dunite or peridotite close to the contact of the cumulate and tectonite zones in ophiolites (Mosier et al. [2012\)](#page-70-17). Accordingly, 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.

### **Nickel (Copper) Deposits**

These deposits are referred as magmatic sulfiderich Ni-Cu ± 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 Montana (USA). Nickel sulfide deposits can be classified into two principal classes based on the petrology of the host rocks: peridotite-dunite class (komatiitic association) and gabbroid class (tholeiitic association)  $\left( \blacksquare$  Fig. [2.34](#page-43-0)).

According to Schulz et al. ([2014](#page-70-18)): «sulfide deposits containing nickel and copper with or without (±) platinum-group elements (PGE) account for approximately 60% of the world's nickel production and they form where mantlederived, sulfur-undersaturated picrite or tholeiitic basalt magma becomes sulfide-saturated, commonly following interaction with continental crustal rocks; sulfur saturation results in formation of an immiscible sulfide liquid, which tends to segregate into physical depressions in the lower parts of dike- and/or sill-like intrusions because of changes in the magma flow dynamics; such dynamic systems appear to promote the interaction of sulfide liquid with a sufficiently large amount of silicate magma to concentrate chalcophile elements to economic levels». The ore metals nickel, copper, and the PGE are all chalcophile and show a tendency to partition more or less strongly 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 PGEs 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 (Arndt and Ganino [2012\)](#page-68-3).

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. For this explanation, sulfur-bearing crustal rocks such as black shales, evaporites, or paragneisses are near to many deposits and a potential source of sulfur. These deposits range in age from Archean to Cenozoic, but the largest number of deposits are Archean and Paleoproterozoic. Although the

<span id="page-43-0"></span>

**D** Fig. 2.34 Aguablanca mine (Spain), a gabbroid class sulfide-rich nickel-copper deposit (Image courtesy of Lundin Mining Corporation)

deposits occur in most continents, the biggest ones are located in Russia, China, Australia, Canada, and Southern Africa. The major Ni-Cu sulfide mineralogy typically consists of an intergrowth of pyrrhotite, pentlandite, and chalcopyrite. In most cases, the massive and matrix ore is zoned, with copperrich 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. The compositional zonation is attributed to fractionation of monosulfide solid solution from a sulfide liquid. Cobalt, PGE, and gold are extracted from most magmatic Ni-Cu ores as by-products, although such elements can have a significant impact on the economics in some deposits, the Noril'sk-Talnakh deposits being a good example, which produce much of the world's palladium; in addition, these deposits may contain between 1 and 15% magnetite associated with the sulfides (Schulz et al. [2014\)](#page-70-18).

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 ≥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. Three other Ni-Cu sulfide deposits in the world are also important: Voisey's Bay in Newfoundland, Kambalda in Australia, and Jinchuan in China.

### **PGE Deposits**

The concentration of PGE in terrestrial environments ranges from sub-ppb 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 PGE and involve concentration factors in the order of

1000, similar to those for gold deposits. Anomalous concentrations of PGE are known from high-temperature magmatic to low-temperature hydrothermal and sedimentary environments, but significant concentrations of PGE are virtually restricted to ultramafic rocks. Two types of deposits, both intimately associated with Ni-Cu sulfides, account for about 98% of the world's identified PGE resources: (a) stratabound deposits in large, layered complexes (e.g., Bushveld, Stillwater, and Great Dyke) mined primarily for PGE and (b) Ni-Cu sulfide deposits mined primarily for Ni-Cu sulfides, but containing recoverable amounts of PGE as by-products (e.g., Sudbury, Noril'sk-Talnakh, Jinchuan, and Karnbalda deposits) (Misra [2000](#page-69-3)). The large layered intrusions contain about 90% of the world's PGE resources, with the Bushveld Complex accounting for about 80%.

In general, the deposits generally occur as sparsely dispersed sulfide minerals in basal units or stratabound layers or reefs in very large- to medium-sized, typically layered mafic and/or ultramafic intrusions. In the Bushveld Complex, there are in the lower part important deposits of the platinum group elements mainly at two specific horizons. The upper layer is the Merensky Reef, a thin (1–10 m) layer of pegmatoid pyroxenite. The second principal mineralized layer, termed UG2, is a group of thick chromite reefs that, in addition to high PGE concentration, are also extracted for their chromium contents (Arndt and Ganino [2012](#page-68-3)). 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. Arndt and Ganino [\(2012](#page-68-3)) also said that: «in the first case, a plume of primitive magmatic liquid was injected into the base of the chamber and then mixed with evolved liquid to produce a hybrid magma that became saturated in sulfide. The other view propose that volatilerich fluids migrated up through the cumulus pile, leaching out the PGE from the cumulus minerals then redepositing them at favorable horizons.»

### **Diamond Deposits**

Diamonds form under extreme high pressures and temperatures at depths greater than 150 km below the surface, predominantly though not exclusively, in the Earth's lithospheric upper mantle. They are transported into the crust either rapidly in explosively emplaced volatile-rich kimberlite, lamproite, or related magmas or more slowly by tectonic processes in rocks that have undergone ultrahigh-pressure metamorphism ( $\blacksquare$  Fig. [2.35](#page-44-0)).

<span id="page-44-0"></span>

**D** Fig. 2.35 Origin of diamonds (Illustration courtesy of De Beers)

Diamond ore deposits are confined to a minority of the volcanic sources and to secondary deposits derived from them (Gurney et al. [2010](#page-69-25)). Since diamonds only form beneath old, stable, and thick parts of the Earth's crust, this greatly restricts the global distribution of primary deposits.

Although diamond deposits are often very low grade, the value of the individual diamonds makes the overall deposit highly valuable. Thus, diamond deposits represent some of the highest value mines globally. Grade values in diamond deposits commonly range from 0.25 to 1.5 carats/t, carat being the measurement of weight in diamonds (1 carat equals 0.2 g). 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 (Stevens [2010](#page-70-11)). Diamond in kimberlite is probably the best-known type of magmatic mineral deposit ( $\blacksquare$  [Box 2.7](#page-45-0): Diamond in Kimberlite).

#### <span id="page-45-0"></span>**Box 2.7**

### **Diamond in Kimberlite**

Diamond is one of the most sought-after gemstones on Earth. They 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 alkaline igneous rocks. Following the discovery of diamonds in river deposits in central South Africa in the mid-nineteenth century, it was at Kimberley where the volcanic origin of diamonds was first recognized. These volcanic rocks, that were named «kimberlite,» were to become the cornerstone of the economic and industrial development of Southern Africa. Thus, the name of the rock comes from the town of Kimberley in South Africa, where the discovery of a diamond called «the Star of South Africa» in 1869 spawned a diamond rush and creating the Big Hole ( $\bullet$  Fig. [2.36\)](#page-46-0). It is claimed to be the largest hole excavated by hand. Early mining of the kimberlites around Kimberley was a chaotic business with many claim holders digging small individual claims of 10 by 10 m. Later, as mining reached deeper levels and became more difficult, claims were consolidated into numerous companies. In 1888 De Beers Consolidated Mining Company was created, and this company consolidated all mining operations under the one company, thereby creating the leading diamond producer in the world for the next 90 years.

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. 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 ages of kimberlites range from Proterozoic to Tertiary). Diamonds in economic deposits are estimated to be mainly (99%) derived from subcontinental lithospheric mantle (Gurney et al. 2010). In both kimberlites and lamproites, diamonds range in size from microcrystals smaller than 50 microns to macrocrystals occasionally over l cm in size. It is important to remember that most kimberlites and lamproites contain no diamonds. In fact, diamonds are a very minor xenocryst component (<5 ppm) in even the richest ore bodies. 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. The presence and quality of diamonds in a kimberlite can only be determined with confidence by the collection and processing of a large and representative sample.

The typical diamond deposit is pipe- or carrot-shaped with a circular surface diameter of 50–500 m and a depth extent of several hundred to one thousand meters or more. The distribution of the diamond xenocrysts is variable in the whole host rocks, and the concentration has a level of less than 0.01–2.0 ppm. Strictly speaking, diamonds in kimberlites are not truly magmatic. Kimberlite magma is merely a vehicle that transports the diamonds rapidly to the surface under conditions that prevent them from reverting to graphite, their unattractive low-pressure polymorph. Diamonds remain hidden, unless they are picked up by «younger» kimberlites, lamproites, or other magmatic rocks originated either within or below the mantle source region and intruding 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.

<span id="page-46-0"></span>

**D.** Fig. 2.36 Kimberley mine in South Africa (The Big Hole) (Image courtesy of De Beers)

The famous diamond deposits at India and Borneo were the only diamond producers until the eighteenth century. Some big and famous diamonds such as Koh-i-Noor or the Great Mogul Diamond were obtained from these countries. Several decades ago, almost all diamond mines were located in Southern Africa, but large and important deposits have been found and mined in Russia, Australia, and Canada. Examples of these deposits are the Mir pipe in Yakutia (Russia), perhaps the most diamond-bearing kimberlite pipe in the world, which contains only one part of diamond per every one and half million parts of kimberlite; the diamond-bearing kimberlites of Africa (Angola, Botswana, Lesotho, Sierra Leone, South Africa, Swaziland, Tanzania); the diamond deposits in Australia (Western Australia); and the kimberlite pipes in Canada (NWT). Secondary diamond deposits such as placer deposits are formed from these primary source kimberlite rocks by weathering and transportation. The resulting deposits are commonly very rich in high-quality diamonds. Examples include those of the Ural Mountains, the marine deposits of Namibia, and the alluvial deposits of West Africa, Brazil, and Venezuela. These deposits have supplied about 90% of the world's diamond output.

<span id="page-47-0"></span>**D** Fig. 2.37 Lithium pegmatites (Salamanca) (Image courtesy of Carlos Villaseca)



# **Pegmatite Deposits**

Another type of magmatic ore deposit is found in pegmatites. In these rocks, metals like lithium, beryllium, boron, tin, niobium, thallium, and the rare earth elements are mined. Pegmatites are formed by the crystallization of melts expelled from granitic magmas. Pegmatitic rocks are very coarse-grained basement rocks abundant in quartz, feldspar, and/or mica, in places endowed either with megacrystals of the aforementioned rock-forming minerals or rare-element minerals. «Apart from the size of their crystals, it is the varied spectrum of rare elements and the significant number of extraordinary minerals resultant from these elements, which renders these crystalline rocks so different from granitic rocks» (Dill [2015\)](#page-69-26).

Most pegmatites show a paragenesis of orthoclase, microcline, albite, mica, quartz, and common minor minerals including topaz, tourmaline, cassiterite, beryl, and lithium. Granite pegmatites occur in the form of dikes, oval, and lenticular bodies, being homogeneous (without a change of mineralogy or texture from wall to wall) and isotropic or strikingly inhomogeneous and anisotropic (zoned or complex pegmatites). Most pegmatite bodies are relatively small with a thickness that rarely surpass tens of meters and a length of a few hundred meters (Pohl [2011\)](#page-70-1), but with increasing industrial request for high-technology metals such as lithium and the rare earth elements (Arndt and Ganino [2012\)](#page-68-3).

Pegmatites may host many useful raw materials: ores of Be, Li ( $\blacksquare$  Fig. [2.37](#page-47-0)), Rb, Cs, Ta > Nb, U, Th, REE, Mo, Bi, Sn, and W; the industrial minerals muscovite, feldspar, kaolin, quartz, spodumene, fluorite, and gemstones; as well as rare mineral specimens (emerald, topaz, tourmaline, ruby, etc.) (Linnen et al. [2012\)](#page-69-27), the complex-type pegmatites of the lithium-cesium-thallium (LCT) family being an important class of rare-element pegmatites. The NYF pegmatites are a different family of pegmatites and are enriched in niobium, yttrium, and fluoride. Their current economic importance 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.

Pegmatites of the LCT family were emplaced in orogenic hinterlands intruding metasedimentary rocks, typically at low-pressure amphibolite to upper greenschist facies, the largest deposits being Archean in age. Giant deposits of these pegmatites include Tanco in Canada (2.1 Mt at 0.215% Ta<sub>2</sub>O<sub>5</sub>), Greenbushes in Australia (70.4 Mt at 2.6%  $\rm Li_2O$ ), and Bikita in Zimbabwe (12 Mt at 1.4% Li<sub>2</sub>O) (Bradley and McCauley [2013\)](#page-68-6). On the other hand, NYF pegmatites are also sometimes REE-enriched pegmatites. Traditionally, the vast majority of this kind of pegmatites has been exploited for their major mineral content: feldspar, quartz, and muscovite. Studies of REE-enriched granitic pegmatites as a whole

lag severely behind those of LCT pegmatites in terms of classification, numbers and detail of field descriptions, and mineral compositional data (Ercit [2005\)](#page-69-28).

# **2.8.2 Hydrothermal Ore Deposits**

They represent an essential group of ore deposits 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 quite different, being located in a broad rank of geological and tectonic settings: some of them are closely linked with granitic rocks, 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 (Arndt and Ganino [2012\)](#page-68-3). The main examples of hydrothermal ore deposits include (1) porphyry deposits, (2) volcanogenic massive sulfide (VMS) deposits, (3) sedimentary exhalative (SEDEX) deposits, (4) iron oxide-copper-gold deposits, and (5) gold deposits.

# **Porphyry Deposits**

Porphyry copper deposits (PCD) are large, lowto medium-grade,  $Cu \pm Au \pm Mo$  hydrothermal deposits related to igneous intrusions, being the largest source of the world in copper and a major source of molybdenum, gold, and silver. Despite relatively low grades, PCDs have significant economic impact due to their large size (commonly hundreds of millions to billions of metric tons), long mine lives (decades), and high production rates (billions of kilograms of copper per year). With incrementing molybdenum/copper ratio, these deposits are transitional to low fluorine (quartz monzonite type) porphyry molybdenum deposits; with incrementing gold/copper ratio, they are transitional to porphyry gold deposits (John et al. [2010](#page-69-29)). Thus, it is common to describe several subtypes of porphyry deposits according to the dominant metal: porphyry Cu, porphyry Cu-Au, and porphyry Cu-Mo.

Porphyry copper deposits are constituted by disseminated copper minerals in veins and breccias and form high tonnage (greater than 100 million tons) and low- to moderate-grade (0.3–2.0% copper) mineral deposits. In contrast to VMS deposits (see next section), which normally are small (1–5 Mt) but of high grade (3–10% ore metals), porphyry deposits are enormous but of low grade. These deposits were the first group of metallic mineral deposits mined by large-scale, open-pit methods in the early twentieth century. The best-known deposits are in the cordilleras of North and South America, the Bingham mine in the USA (2.7 billion tons of ore grading, 0.7% Cu and 0.05% Mo), and the Chuquicamata mine in Chile (11 billion tons of 0.56% Cu and 0.06% Mo) (Arndt and Ganino [2012\)](#page-68-3) ( $\Box$  [Box 2.8](#page-48-0): Chuquicamata Copper Mine (Chile)).

#### <span id="page-48-0"></span>**Box 2.8**

#### **Chuquicamata Copper Mine (Chile)**

Chile is known worldwide as the site of one of the largest copper concentrations on Earth. Thus, Chuquicamata mine ( $\Box$  Fig. [2.38](#page-49-0)), property of Codelco, is one of the largest open-pit copper mines and the second deepest open-pit mine in the world (popularly known as Chuqui). The name comes from indigenous communities, «Chuquis, » who lived in the area and obtained native copper. The openpit measures are 5 km large, 3 km width, and 1 km deep forming an ellipse. Chuquicamata mine began open-pit mining in the year 1915

although its mining properties had been known for centuries by the pre-Hispanic cultures. In 1971, the mine was nationalized, and management and operation were taken over by the Corporación Nacional del Cobre-Chile (Codelco). At the end of the year 2005, it had mined out about 2.6 billion tons of copper ore with a mean grade of 1.53%, reaching a pit depth of 850 m. The Chuquicamata mine complex is located 1650 km north of the Chilean Capital city (Santiago), at 2870 m above sea level. Chuquicamata produces electrorefined

and electrowon cathodes having a purity of 99.99% copper. It also produces fine molybdenum, as well as other by-products, such as anode slimes and sulfuric acid.

The Chilean cordillera contains 9 of the 16 giant porphyries along the circum-Pacific belt. Chuquicamata lies in the Precordillera of northern Chile, which is parallel and west of the volcanoes that form the modern continental arc of the Andean Cordillera. The Chuquicamata mine lies on the Chuqui porphyry complex, a north-northeast trending, elongated, tabular, intrusive complex

<span id="page-49-0"></span>

#### **D** Fig. 2.38 Chuquicamata mine (Image courtesy of Codelco)

that measures 14 km  $\times$  1.5 km. Virtually the entire ore deposit at Chuquicamata is hosted by and related to this 36–33 Ma porphyry complex that comprises a number of phases, many of which do not have well-defined contacts. The porphyry copper ore body is rectangular in plan and dips vertically, being the zone's porphyries largely affected by potassic alteration. The great majority of the mineralization at Chuquicamata occurs in veins and veinlets, the earliest of which are quartz and K-feldspar veinlets with little or no sulfides. These are cut by more continuous quartz veins ranging up to 5 cm in width with molybdenite and traces of chalcopyrite. The next generation is the pyritic main stage veins which carry pyrite,

chalcopyrite, bornite, and digenite. The final phase of mineralization is represented by a partly preserved leached cap and extensive oxide ore that replaces an upper chalcocite blanket which overlies a high-grade supergene blanket that persists to nearly 800 m below surface in the zone of fault brecciation and pervasive pyritic main stage quartzsericite alteration.

Finally, Chuquicamata underground mine is a structural and strategic project that represents an important part of Codelco's future and which considers transforming the world's largest open-pit mine into a gigantic underground operation. This new underground mine is being developed to access the ore body situated beneath the

present open-pit mine because currently the mine is producing 400,000 tons of waste rock, and since it increases the cost and distance that must be reached to find mineralization, it generates higher costs. The geological data from drillholes indicate that below the final pit bottom, there are about 2.3 billion tons of ore with a mean copper grade of 0.81%. The project involves ore extraction by macro blocks and block caving in an underground mine at depths of 1300–1800 m. The underground mine, scheduled to begin operations in 2020, will comprise four production levels, a 7.5 km main access tunnel, five clean air injection ramps, and two air-extraction shafts.

The mineralization in the porphyry deposits consists of disseminated small concentrations of sulfide minerals in the highly altered upper portions of the intrusion and in surrounding rocks. Closely associated with the mineralization is a moderate to intense alteration that shows a zoning concentric about the intrusion. This alteration also

span outside the zone of mineralization, and it is commonly utilized as a guide during the exploration of this type of deposits. Most PCD deposits are located within felsic to intermediate igneous intrusions and in the country rocks that surround the intrusion. Original sulfide minerals are pyrite, chalcopyrite, bornite, chalcocite, 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. Molybdenite distribution is variable, and radial fracture zones outside the pyrite halo may contain lead-zinc veins with significant gold and silver contents. In deposits with an extensive supergene enrichment zone developed in the upper parts of the deposit, copper oxide minerals and native copper may be present.

In many districts, plutons and batholiths that host the mineralization are older and not related to the ore-forming system, although they can be part of long-lived magmatic successions. In other districts, they are only slightly older and range from multiple large stocks to composite batholiths (John et al. [2010\)](#page-69-29). The regional, deposit-scale, and local-scale environments of porphyry copper can be very varied. They are widespread but mostly localized in time and space through the evolution of magmatic arcs along convergent plate margins where subduction of oceanic crust and arc-type magmatism generates hydrous, oxidized upper crustal granitoids genetically related to ores. It is possible that many porphyry copper deposits are formed during unusual periods of subduction. Deposits have formed throughout most of Earth's history, but because they generally form in the upper crust (less than 5–10 km depth) in tectonically unstable convergent plate margins and are prone to erosion, more than 90% of known deposits are Cenozoic or Mesozoic in age.

PCDs are thought to derive from hydrothermal fluids generated near the top of a cooling magma body at depths between 1 and 5 km (Stevens [2010\)](#page-70-11). 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. 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 the characteristic stockwork texture of this type of deposits. 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. Thus, formation of porphyry copper deposits, as John et al. published in 2010, «involves a complex series of processes including magma generation, differentiation, emplacement, crystallization and degassing, high-temperature reactions between degassed fluids and meteoric and other non-magmatic waters, and near-surface reactions between low-temperature meteoric water and earlier formed, high-temperature minerals; external saline waters such as sedimentary brines were probably involved in the earlier stages of evolution of some porphyry copper systems, resulting in sodic and sodic-calcic alteration».

# **Volcanogenic Massive Sulfide (VMS) Deposits**

This type of deposits is referred to as volcanogenic massive sulfide (VMS) although similar terms have been used: volcanic massive sulfide, submarine exhalative massive sulfide, and volcanic-hosted massive sulfide, among many others. More recently, the term polymetallic massive sulfide deposit has been also applied by many authors to VMS mineralization on the modern seafloor that contains significant quantities of base metals. Volcanic massive sulfide deposits are small- to medium-sized, moderate- to high-grade  $Cu \pm Zn \pm Pb \pm Au \pm Ag$ 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 sometimes high-grade character of the deposits make them a preferential target for exploration. As in the case of the porphyry deposits, there are several subtypes of VMS deposits depending on the dominant metal and host rocks.

VMSs are among the best understood of all ore deposits due to the ore bodies that are relatively simple, both in their structure and their composition and mineralogy, and they have been studied intensively over the last decades. They are one of very few deposits whose formation, by way of precipitation of sulfides at or just below the ocean floor, can be observed directly - black smokers. VMS 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 Roman centurions. The old Rio Tinto mine in southwestern Spain has one of the world's longest known mining histories with copper having been mined there even before Roman times ( $\Box$  [Box 2.9](#page-51-0): Rio Tinto Copper Mine (Spain)). This mine was the foundation stone for the mega mining company that still bears its name. Rio Tinto has subsequently gone on to become one of the world's biggest diversified mining companies.

#### <span id="page-51-0"></span>**Box 2.9**

#### **Rio Tinto Copper Mine (Spain)**

The Iberian Pyrite Belt is located in the SW of the Iberian Peninsula, comprising part of Portugal and of the provinces of Huelva and Sevilla in Spain, being one of the most important volcanogenic massive sulfide districts in the world. Río Tinto mine is located at the eastern end of the Iberian Pyrite Belt. Within the Pyrite Belt, there are eight major mining areas, each thought to contain more than 100 million tons or ore. These are from east to the west: Aznalcóllar-Los Frailes, Río Tinto, Sotiel-Migollas, La Zarza, Tharsis, Masa Valverde, Neves Corvo, and Aljustrel. Río Tinto mining area is the largest of these and includes two big open-pit mines: Cerro Colorado ( $\blacksquare$  Fig. [2.39](#page-51-1)) and Corta Atalaya. The high geological interest of this mining district is because it is most probably the biggest sulfur anomaly on the Earth's crust, with original tonnages around the 2500 million tons of mineralized rock in different degrees. In fact, the Cerro Colorado deposit contained one of the largest known concentrations of sulfides in the world. The name of Río Tinto mines comes from Río Tinto river; in turn, it takes the name from its red color.

Río Tinto mines have a very long history, dating back to pre- Iberian times; then came the Iberians, including Tartessian, the Phoenicians, the Carthaginians, the Romans, the Moors, the Spaniards, and the British. It is believed that copper was first recovered from the ores in the third millennium BC and that silver was mined in the late Bronze Age, ninth to twelfth centuries BC onward. From Tartessian to Romans, mineralizations were mined actively, but little mining was done after the departure of Romans. After several centuries of some mining activities in the region, the British arrived to Río Tinto at 1873 (The Rio Tinto Company Limited was registered in London in March of this year). It seems that the purchase price of the mines was 92,800,000 pesetas equal to 3,600,000 sterling pounds. The Rio Tinto Company continued mining and smelting in Spain through two world wars and a civil war, until 20 June 1954 when twothirds of its Spanish assets were sold to a Spanish group of bankers. Then, different owners lead Río Mines to closure, and in the last 10 years different efforts have been made to reopen the mines. Thus, open-pit mine and processing facilities have been on care and maintenance since mining ceased in 2000 due to low copper prices of less than \$1.00/lb at the time. EMED Mining (actually Atalaya Mining) was granted an option to acquire

the operation in May 2007, and it was subsequently acquired in October 2008. New commercial production will begin shortly. In summary, few mines in the world have such a history as Río Tinto mines.

Most of the mineral deposits in this area consist of massive sulfides within the Volcano-Sedimentary Complex. The Río Tinto massive sulfide (pyrite-chalcopyrite) deposit occurs on the transitional contact between a lower mafic volcanic unit composed of andesitic and spilitic pillow lavas and dolerite sills intercalated with bands of slate and chert of Lower Carboniferous age and the overlying felsic volcanic unit. It is composed of rhyolite lavas and pyroclastic rocks formed by submarine volcanic activity in the Lower Carboniferous period about 320 million years ago. Río Tinto is a textbook example of the volcanogenic massive sulfide (VMS) type of deposits.

Overall, massive sulfides display the typical structure of volcanogenic massive sulfide deposits: a lens of massive sulfides overlays a wide zone with rocks affected by an important hydrothermal alteration. In its core, there is a network («stockwork») of sulfide-rich veins considered as the zone that channeled hydrothermal fluids on their way out to exhalation at the

<span id="page-51-1"></span>



sea bottom or a favorable level. The mineralization in Río Tinto is found either as dissemination or small veins in the stockwork areas within volcanic rocks and slates, or as massive sulfide lenses lying atop or included in the stockwork zones, or in gossan areas representing the supergenic alteration of massive sulfides, sometimes up to 70 m thick. What makes Rio Tinto different from other districts in the Pyrite Belt is the fact that the massive sulfides seem to be formed in two different environments. On one side, the mineralizations in Southern Lode and Planes – San Antonio – are hosted in slates and have sedimentary structures, suggesting they were formed by exhalative processes in the sea bottom. However, the mineralizations in the Northern Vein hosted by dacite have a

coarser grain and always display replacement structures with the hosting dacite. The mineralization was supergenically altered and eroded during the Cenozoic. Originally, there was a gossan (Cerro Colorado) of 10–70 m deep mined between 1974 and 2002 together with the copper of the underlying stockwork. The gossan was rich in Au, Ag, Pb, Sb, and Bi and poor in Cu and Zn.

Volcanogenic massive sulfide deposits are stratabound concentrations of sulfide minerals precipitated from hydrothermal fluids in extensional seafloor environments. The term volcanogenic implies a genetic link between mineralization and volcanic activity, but siliciclastic rocks dominate the stratigraphic assemblage in some settings. Relation to volcanoes ranges from proximity to quite tenuous connections to volcanism, as in parts of the Southern Iberian Pyrite Belt (Pohl [2011\)](#page-70-1). VMS deposits are hosted in volcanic rocks dominated by basalt. There are usually important felsic volcanic and sedimentary rock layers closely associated with the deposit, and small intrusive igneous rock bodies are often located beneath the deposits (Stevens [2010](#page-70-11)).

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 deposits are characterized by abundant Fe sulfides (pyrite or pyrrhotite normally comprises more than 80% of the minerals in the massive sulfide bodies).

VMS deposits are derived from hydrothermal fluids that circulate through a sequence of volcanic rocks and exit on the seafloor as a plume of metal-rich fluids. They encompass a wide variety of geodynamic and more local genetic settings. Thus, «the main tectonic settings include midoceanic ridges, volcanic arcs (intraoceanic and continental margin), back-arc basins, rifted continental margins, and pull-apart basins; the composition of volcanic rocks hosting individual sulfide deposits range from felsic to mafic, but bimodal mixtures are not uncommon and the volcanic strata consist of massive and pillow lavas, sheet flows, hyaloclastites, lava breccias, pyroclastic deposits, and volcaniclastic sediments; a zonation of metals within the massive sulfide body from Fe + Cu at the base to  $Zn$  + Fe  $\pm$  Pb  $\pm$  Ba at the top and margins characterizes many deposits» (Koski and Mosier [2012\)](#page-69-30). Deposits range in age from Early Archean (3.55 Ga) to the present, and significant occurrences of VMS mineralization are found in greenstone belts of almost all Precambrian shield areas. 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 (e.g., Kuroko sulfide deposits) (Misra [2000](#page-69-3)).

# **Sedimentary Exhalative (SEDEX) Deposits**

Almost 100 million tons of sediment containing 2% Zn, 0.5% Cu, and significant amount of Au and Ag have precipitated from hot dense brine that accumulated in the «Atlantis II Deep, » a 10 km diameter depression on the floor of the Red Sea. It would constitute a very attractive ore body of the type referred to as a SEDEX or sedimentary exhalative deposit. SEDEX deposits are medium to large sizes, moderate to high grade,  $Zn \pm Pb \pm Ag$ 

<span id="page-53-0"></span>

**D** Fig. 2.40 McArthur River Mine (Australia) (Image courtesy of Glencore)

hydrothermal deposits hosted in sequences of sedimentary rocks. Another example is the Salton Sea, a big and shallow lake in southern California that originated in 1905 where a canal transporting water from the Colorado River breached and flooded a salt pan (Arndt and Ganino [2012](#page-68-3)). The two processes recorded in Red Sea and Salton Sea examples are essential elements to understand the formation of SEDEX deposits.

The term SEDEX, derived from «sedimentary exhalative» (Carne and Cathro [1982\)](#page-69-31), is based on the interpretation that the finely laminated or bedded sulfide ores represent chemical sediments precipitated from hydrothermal fluids exhaled onto the seafloor. Examples of SEDEX deposits are Broken Hill, Mount Isa, and McArthur River in Australia ( $\Box$  Fig. [2.40](#page-53-0)), Sullivan in Canada, and Navan in Ireland. These types of deposits are the world's largest source of zinc and a major source of lead. SEDEX deposits are on average an order of magnitude bigger than VMS deposits (Stevens [2010\)](#page-70-11). The dominant economic minerals are sphalerite and galena, and in some deposits chalcopyrite, with silver primarily contained with galena. SEDEX deposits range in age from 2

billion to 300 million years old, deposits younger than 300 million years not being documented. The deposits are characterized by moderate to high grades of zinc and lead, and copper is an important by-product in some deposits.

SEDEX Pb-Zn-Ag deposits are hosted in marine sedimentary rocks in intracratonic or epicratonic rift basins. The distinguishing features of an idealized, unmetamorphosed, or mildly metamorphosed SEDEX deposit may be summarized as follows: (a) mineralization hosted mostly either by marine, clastic sediments of continental derivation, typically pyritic and carbonaceous shales, or by platform carbonate rocks, with thin (1–10 cm thick) tuff horizons in the sedimentary sequence in some cases; (b) a zone of stratiform mineralization consisting of stacked lens-like, concordant, tabular bodies of low-Cu massive sulfide ore; (c) a footwall zone of minor stockwork and vein-type sulfide mineralization associated with hydrothermal alteration (predominantly silicification); (d) a distinct (Cu)-Pb-Zn-(Ba) lateral zoning of hydrothermally precipitated minerals and a less systematic (Cu)-Zn-Pb-(Ba) vertical zoning; (e) spatial association with a synsedimentary fault

system that was active at the time of mineralization and may have been reactivated during later deformation; and (f) a general lack of demonstrable magmatic affiliation of the host rocks or of mineralization (Misra, [2000\)](#page-69-3).

The main ore minerals of SEDEX deposits, sphalerite and galena: «were probably precipitated on or just below the sea floor from warm 100–200 °C, saline -10–30% total dissolved solids- basin brines that ascended along basincontrolling synsedimentary faults; deposition and sequestration of metals occurred by precipitation of sulfide minerals as a result of mixing of metal-transporting brine and locally derived  $\rm H_2S$ produced by bacterial and perhaps thermochemical reduction of local seawater sulfate» (Emsbo [2009\)](#page-69-32). They are formed in a similar manner to VMS deposits, although there is little if any involvement of igneous rocks in their formation.

# **Iron Oxide-Copper-Gold (IOCG) Deposits**

An iron oxide-copper-gold deposit can be defined as a breccia-hosted polymetallic mineral deposit in which mineralization is spatially and temporally associated with granite and with iron oxide alteration. The Olympic Dam deposit in Australia is probably the best example in the world for this group of deposits; other typical examples are Kiruna in Sweden and Bayan Obo in China. IOCG deposits range in age from recent to Precambrian, and such deposits commonly show (1) Cu, with or without Au, as economic metals; (2) hydrothermal ore styles and strong structural controls; (3) abundant magnetite and/or hematite; (4) Fe oxides with Fe/Ti greater than those in most igneous rocks and bulk crust; and (5) no clear spatial associations with igneous intrusions as, for example, displayed by porphyry and skarn ore deposits (Williams et al. [2005\)](#page-70-19). IOCG deposits are found in a wide range of rock types (sedimentary, volcanic, and igneous), and common forms of mineralization include breccia zones, tabular bodies, veins, stockworks, volcanic pipes, and disseminated mineralization. Hydrothermal iron oxide-coppergold deposits can include mainly various combinations of metals such as Fe, Cu, Au, Ag, U, Th, F, Co, Bi, W, and rare earth elements (REE).

The supergiant Olympic Dam Cu-U-Au-Ag ore deposit of South Australia has the largest uranium resource and the fourth largest copper and gold resource in the world. The tectonic setting includes a hydrothermal breccia complex surrounded by Mesoproterozoic granite, the breccia being composed mainly of granite clasts and minor amount of Mesoproterozoic volcanic clasts. Very thick (>350 m) sections of bedded sedimentary facies occurring in the breccia complex include laminated to very thin planar mudstone beds, thin to medium internally graded sandstone beds, and thick conglomerate beds. Lateral continuity, provenance characteristics, great thickness, below-wave-base lithofacies, and intracontinental setting suggest that these bedded sedimentary facies are remnants of a sedimentary basin that was present at Olympic Dam prior to formation of the breccia complex (McPhie et al. [2011\)](#page-69-33).

Due to the very recent discovery of the deposit type, theories of ore formation are subject to continual revision. According to Williams et al. [\(2005\)](#page-70-19): «most theories call on large-scale magmatic events that 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 fluids or brines is commonly invoked as the ore-forming process and brines and metals may be sourced directly from underlying magmas, indirectly by interaction of magmatic fluids with country rocks or other fluids, or independently through modification of basinal or metamorphic fluids». However, although the Olympic Dam breccia complex and ore body are primarily hydrothermal in origin, the Olympic Dam hydrothermal system would have had access to and interacted with the overlying sedimentary succession, so this succession should be considered as an additional source of both fluids and metals (McPhie et al. [2011\)](#page-69-33).

### **Gold Deposits**

Trace amounts of gold are present in a wide variety of mineral deposits, ranging from <0.01 ppm Au in Mississippi Valley-type deposits to concentrations in some sulfide deposits high enough to be recoverable as a by-product; main types of ores that routinely produce by-product gold are Ni-Cu sulfide ores associated with mafic and ultramafic rocks, VMS ores, and Cu ores of porphyry copper deposits. However, most of the important gold deposits belong to one of the following seven types: (a) young placer deposits, (b) deposits hosted by quartz-pebble conglomerates (Witwatersrand type), (c) volcanic-associated epithermal deposits, (d) sediment-hosted, disseminated

deposits (Carlin type), (e) deposits hosted by banded iron formations, (f) intrusion-related deposits, and (g) lode deposits (Misra [2000\)](#page-69-3). Type (c) is possibly the most important gold type deposit of hydrothermal affiliation. Other essential types for gold extraction (e.g., Witwatersrand type) are also described below.

Volcanic-associated epithermal gold deposits got the name «epithermal» according to the classification of Lindgren ([1913\)](#page-69-4), who coined this term for deposits that form from hydrothermal fluids at shallow crustal levels, occurring in a variety of structural settings. They are commonly associated with subduction-related calc-alkaline to alkaline arc magmatism as well as back-arc continental rift magmatism. Because of their relatively higher grades and amenability to cheaper open-pit mining and heap-leach extraction of gold, epithermal deposits have been a favored target of exploration since the early 1970s.

The main distinguishing characteristics of epithermal gold deposits are the following:

- 1. Andesitic volcanic and pyroclastic rocks are the more common host to ore (early to late Tertiary).
- 2. The deposits formed in extensional tectonic settings, in zones with well-developed tension fracture systems, and in normal faults that could channel hydrothermal fluids and localize mineralization.
- 3. (c) The mineralization is epigenetic and occurs commonly in the form of quartz veins.
- 4. Ore and associated minerals occur dominantly as open-space fillings, producing characteristic banded and crustiform textures.
- 5. Gold and silver are the principal economic metals; main ore minerals in the veins are native gold and silver, electrum, argentite, Ag-bearing As-Sb sulfosalts, and Au-bearing pyrite; associated base metal sulfides, which are generally concentrated below the precious metal horizon, include sphalerite, galena, and chalcopyrite.
- 6. Quartz and calcite are the most abundant gangue minerals in the veins.
- 7. Hydrothermal alteration of wall rock is a characteristic feature of all epithermal precious metal deposits (Misra [2000](#page-69-3)).

### **Vein Deposits**

The most convincing examples of hydrothermal deposits are vein systems discordant to stratification or lithologic boundaries in host rocks (O Box 2.10: Panasqueira Tungsten Mine (Portugal)). They represent dominantly openspace filling of structurally controlled fractures and faults. Some vein-type deposits are believed to be genetically related to exposed or buried igneous (especially felsic) intrusions because fluid inclusion and isotopic data provide evidence for a major contribution of magmatic water in the oreforming fluids. Ore fluids for other types of vein deposits may have been dominated by magmatic water, meteoric water, or basinal brines.

#### <span id="page-55-0"></span>**Box 2.10**

#### **Panasqueira Tungsten Mine (Portugal)**

The first prospecting license was granted in 1886 and the first reference to wolframite mineralization in the Panasqueira area reportedly dated to 1888, but probably Panasqueira mines were first worked for tin by the Romans and next by the Moors. The mining company was founded in 1896 to mine tungsten at Panasqueira as the industrial uses of the commodity were first being developed throughout the world. All the individual concessions were grouped into one single mining area known as the «Couto

Mineiro da Panasqueira. » During the period 1947–2014, a total of approximately 31 million tons of rock have been mined that has produced approximately 111,123 tons of tungsten concentrate, 5383 tons of tin concentrate, and 31,702 tons of copper concentrate. Today Panasqueira is still one of the biggest tungsten mines in the world. Mining at the Panasqueira mine has evolved from labor-intensive hand operations in the early 1900s through mechanized longwall methods to the mechanized room and pillar operation currently

used and based on an analysis of geological and geomechanical characteristics of the rock mass. This mining method is possible in part due to the very competent host rock, and underground rock support is rare.

Panasqueira mine is a worldclass W-Sn-Cu vein-type deposit, located in the Central Iberian Zone of the Palaeozoic Iberian Massif (Portugal), which is one of the most important metallogenic provinces of Europe. The Central Iberian Zone is composed of a thick sequence of flysch-type

units primarily composed of graywackes, shales, and schists of late Precambrian to Cambrian age. Intruding this flysch sequence are the Epi-Hercynian synmetamorphic muscovite-biotite granites or post-metamorphic biotite-rich granites. The Panasqueira deposit consists of a series of stacked, subhorizontal, hydrothermal quartz veins intruding into the Beira schists and shales. A second set of non-wolframite-bearing quartz veins (veins contain minor chalcopyrite, galena, and pyrite) also exists at the Panasqueira deposit and is aligned with the vertical foliation and cut by the later tungsten-bearing hydrothermal vein

system. Intrusives are an important component of the mineralizing events at Panasqueira. The most dominant and important structural feature at the Panasqueira mine is a flat open joint system prevalent throughout the mine workings. The remobilized ore-bearing fluids migrated from the intrusive to these flat joints to form the stacked quartz vein system.

The dimensions of ore body are 2500 m (length), 400–2200 m (width), and 500 m (depth). The principal tungsten-bearing mineral is wolframite, and byproducts include tin (cassiterite), copper (chalcopyrite), and silver. The mineralization is generally

coarse grained and very erratically distributed in the quartz veins. Wolframite mineralization occurs as very large nugget-like crystals or large crystal aggregates, usually concentrated toward the margins of the quartz veins or, occasionally, close to the central portion of the quartz veins ( $\blacksquare$  Fig. [2.41](#page-56-0)). The Panasqueira mine is renowned throughout the world for the extraordinary size and quality of the minerals wolframite, apatite, arsenopyrite, cassiterite, and quartz crystals that occur in cavities in the quartz veins. Wolframite crystals of this size are reportedly rare in other tin-tungsten occurrences.

<span id="page-56-0"></span>

**.** Fig. 2.41 Pillar with a quartz vein in Panasqueira tungsten deposit

Many veins in this type of deposit are developed upward into a fan of thinner veins and veinlets, which resemble a branching tree. Thickness, vertical extent, and horizontal length of veins vary widely. Less than 0.5 m in thickness may allow profitable mining of high-grade gold and silver ore veins ( $\blacksquare$  Fig. [2.42](#page-57-0)), whereas tin and tungsten require a width of 1 m and barite and fluorite a minimum of 2 m width. The distribution of veins in space ranges from horizontal to vertical, although steeply dipping veins are the majority. From a tectonic viewpoint, many veins are associated with large-scale tensional tectonics including rifting and late-orogenic relaxation of orogens. However, veins may also originate during convergent tectonics (Pohl [2011](#page-70-1)).

<span id="page-57-0"></span>**D** Fig. 2.42 Ore sample with visible gold (Image courtesy of Petropavlovsk)



The most important control on vein formation is related to the mechanical properties of the host rocks. Fractures form more readily in competent rocks than in ductile materials. Very brittle rocks such as dolomite or quartzite use to create a network of short fractures instead of spatially separated longer ones. In that case, hydrothermal activity may result in stockwork ore. Stockwork ore bodies consist of numerous short veins of three-dimensional orientation, which are so closely spaced (e.g., 30 veins/m) that the whole rock mass can be mined.

The distribution of ore in veins is usually inhomogeneous, and only a small part of the total vein fill is exploitable. Veins commonly consist of quartz (sometimes of several varieties, e.g., chalcedony). This quartz commonly occurs as interlocking crystals with a great variety of sizes or as finely laminated bands parallel to the walls of the vein. Minor amount of sulfide and other gangue minerals such as calcite and various clay minerals occur. Typical mineral associations in vein deposits are gold with pyrrhotite, gold with arsenopyrite, gold with pyrite, gold with chalcopyrite, gold with minor sulfides (free gold), silver with galena and galena-sphalerite, silver with tetrahedrite, or antimony or copperarsenic sulfides.

# **2.8.3 Sedimentary Ore Deposits**

Sedimentary mineral deposits are those that form by sedimentary processes. They include placers originated by erosion, transportation, and sedimentation processes as well as deposits related to water infiltration, supergene alteration, and diagenetic processes. The boundary between sedimentation and diagenesis is subtle. Moreover, diagenetic ore deposits can be many times considered as diagenetic/hydrothermal mineral deposits.

# **Supergene Enrichment Deposits**

If the sulfide mineralizations are exposed at the surface of the Earth, it is very common that these minerals become oxidized, the ore metals being leached downward and usually concentrated at the top of the water table. Thus, supergene enrichment is a consequence of near-surface oxidation caused by meteoric water seeping downward through the unsaturated zone. This oxidation process can be very useful if the previous mineralization has a low-grade character. In some cases, the copper grade can increase from 0.8% Cu in the primary ore to 2–3% in the thick layer of supergene enrichment. Consequently, these layers of supergene enrichment contain two to five times more ore metals than the primary ore, and

<span id="page-58-0"></span>

**D** Fig. 2.43 Ambatovy (Madagascar) nickel-cobalt laterite deposit (Image courtesy of Sherritt International Corporation)

they are conveniently located close to the surface where they can be recovered at the start of the mining operation. For sulfide copper and silver ores, iron oxides, and some uranium ore deposits, this process is of economic significance (Pohl [2011\)](#page-70-1). The best-known examples of supergene enrichment zones are perhaps those overlying porphyry copper deposits.

Other example of supergene enrichment deposits is lateritic nickel ore deposits. Nickelcobalt laterites ( $\blacksquare$  Fig. [2.43](#page-58-0)), an important source of nickel, are supergene deposits of Ni ± Co formed from pervasive chemical and mechanical (tropical) weathering of ultramafic rocks, which contain as much as 0.3 percent nickel. Marsh and Anderson ([2011\)](#page-69-34) suggest that: «the extreme weathering removes all elements except the least soluble ones from the protolith and the residual material can average as much as 5% nickel and 0.06% cobalt; thus, the enrichment of nickel in the weathering profile is controlled by several interplaying factors that include parent rock, climate, chemistry/rates of chemical weathering, drainage, and tectonics.» In some cases, these deposits can be later subsequently weathered, redeposited, reconcentrated, and probably covered by new sediments.

# **Residual Deposits**

In this type of deposits, the economically interesting component is concentrated in situ while weathering removes diluting parts of the rock. Examples are residual and eluvial placers, bauxite, lateritic gold, platinum, iron and nickel ores, residual enrichment of subeconomic iron and manganese ores, and industrial minerals such as phosphate, magnesite, and kaolin (Pohl [2011\)](#page-70-1). The fundamental geochemical principle of the enrichment is the steady activity of a reaction front in soil while the land surface is lowered by weathering and erosion. At the reaction front, the valuable component is immobilized, and the enrichment is due to retention and accumulation of the component of interest contained in the removed rock and soil volume. An example of this process is eluvial enrichment of phosphate from carbonatites by leaching of carbonate whereas apatite remains in place.

Probably, one of the most characteristic ores of this group is bauxite ( $\blacksquare$  Fig. [2.44](#page-59-0)). The purest bauxites form through a combination of processes: (1) the presence of Al-rich (and Fe-poor) parent rocks such as alkali granite, syenite, tuff, or clayrich sediment and their metamorphosed equivalents; (2) an appropriate balance of temperature

<span id="page-59-0"></span>**D** Fig. 2.44 McCoy bauxite mine (Australia) (Image courtesy of Alcoa)



and rainfall (high temperatures favor Fe-rich laterites); and (3) a pronounced alternation of wet and dry seasons (Arndt and Ganino [2012\)](#page-68-3). 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. In parts of Africa, South and Central America, and Australia, the concentration of  $\text{Al}_2\text{O}_3$  increases from about 15% in the source rock to close to 60%, the level in rich Al ore (Ardnt and Ganino [2012\)](#page-68-3).

### **Infiltration Deposits**

Infiltration mineral deposits are formed where meteoric water takes up a substance that is dissolved by weathering and it is concentrated after considerable transport by infiltration in a different geological setting. The so-called «roll-front» uranium deposits are the most typical example of this

type of deposits. In this deposit, uranium is quickly dissolved from rocks such as granite, gneiss, and felsic tuff and then transported during hundreds of kilometers by rivers, until infiltrating into an aquifer where reduced conditions produce the precipitation and concentration of uranium minerals (uraninite  $(UO_2)$  or pitchblende,  $UO_3$ ,  $U_2O_5$ ). The critical aspect to the formation of uranium deposits is the great different solubility of uranium in oxidized and reduced fluids. Uranium occurs in two valence states, the reduced form  $U^{4+}$  and the oxidized form  $U^{6+}$ . The latter is highly soluble in oxidized fluids where it forms stable complexes with fluoride, phosphate, or carbonate ligands; under these conditions, uranium is readily transported in the fluids that circulate along sedimentary basins. Some deposits of metal such as copper, iron, vanadium, silver, and Pb-Z-Ba-F could have a similar genesis (Pohl [2011\)](#page-70-1).

<span id="page-60-0"></span>

**D** Fig. 2.45 Illustration of roll-front formation

From a geological viewpoint, roll-front uranium deposits host in coarse-grained permeable sandstones, which at depth contain a reduced array of pyrite, calcite, and organic matter. The age of this host sediment ranges from Upper Paleozoic to Cenozoic. In many cases, the sandstone bed is confined above and below by shale or other impermeable rocks ( $\blacksquare$  Fig. [2.45](#page-60-0)). This forces the groundwater to flow through the sandstone and provides a better opportunity to form an economic deposit. The Colorado Plateau region in the USA is the most famous place showing this type of uranium deposit.

### **Placer Deposits**

A placer ore body is a deposit of sand, gravel, or soil containing 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. Classical minerals 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.

Moreover, in this type of deposit the valuable minerals are clearly denser than other minerals that are transported at the Earth's surface. This allows minerals to be separated from detrital minerals or rock fragments that constitute the overall sediment load and finally to become concentrated in ore bodies. Therefore, a simple washing in a gold pan easily separates light minerals of valuable ones. There are many classifications of placer deposits of economic importance, but the most useful separate them as residual, eluvial, colluvial, fluviatile, and coastal; marine and beach placers are also terms used for coastal placer deposits. Other types include Aeolian placers and placers in glacial sediments, but they commonly have no economic significance.

Placer gold deposits 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, production continues in the Witwatersrand ore bodies of South Africa, a hydrothermally reworked conglomeratic paleoplacer deposit that is the largest gold deposit in the

<span id="page-61-0"></span>

 $\Box$  Fig. 2.46 Features commonly used to describe shoreline (strandline) depositional environments associated with deposits of heavy-mineral sands (not to scale) (Van Gosen et al. [2014\)](#page-70-20)

world. An example of placer exploitation in the past is Las Médulas in Spain, mined by the Romans (see  $\blacksquare$  Box 3).

The processes that form coastal deposits of heavy-mineral sands usually begin inland and can be described in the following sequence (Van Gosen et al. [2014\)](#page-70-20): high-grade metamorphic and igneous rocks that contain heavy minerals are weathered and eroded, contributing detritus composed of sand, silt, clay, and heavy minerals to fluvial systems; streams and rivers carry the detritus to the coast, where they are deposited in a variety of coastal environments such as deltas, the beach face (foreshore), the nearshore, the barrier islands or dunes, and the tidal lagoons as well as the channels and floodplains of streams and rivers in the coastal plain ( $\blacksquare$  Fig. [2.46](#page-61-0)); the sediments are later reworked by waves, tides, longshore currents, and wind, which are effective mechanisms for sorting the mineral grains on the basis of differences in their size and density. Regarding the age, most economic deposits of heavy-mineral sands are Paleogene, Neogene, and Quaternary in age.

Famous placer deposits also include diamond placers, which are the source of about 34% of global diamond production. The first diamonds discovered in South Africa were in gravels of the Orange River and its tributaries, and tracing these rivers back to their sources led first to the discovery of the primary diamond sources in kimberlites around the town of Kimberley in the center of South Africa and then to huge beach placers at the western coast of the continent in countries such as South Africa and Namibia ( $\Box$  Fig. [2.47](#page-61-1)). Other interesting examples of placer deposits are those related to tin, platinum, and thorium-uranium metals. Regarding the tin placer deposits, Malaysia is the world's greatest producer of cassiterite, and

<span id="page-61-1"></span>

**D** Fig. 2.47 The Debmar Atlantic is one of five deepwater mining vessels operating off the Namibian coast to extract diamonds (Image courtesy of De Beers)

about half of the deposits are located in placers in rivers, beach sands, and offshore deposits (the other half is related to granites). The same pattern can be applied to the platinum group elements.

### **Autochthonous Deposits**

This type of deposits includes a large number of sedimentary ore deposits of varied characteristics. Sulfide deposits, mainly in black shales, conform the first group. Deposits focused in two metals, iron and manganese, form the second group, and phosphate and different types of salt deposits shape the third group. Autochthonous sulfide

deposits are the second most important sources of copper in the world behind porphyry copper deposits and the most important sources of cobalt (Hayes et al. [2015\)](#page-69-35).

Stratiform sediment-hosted copper deposits are hosted in black, gray, green, or white (reduced) sedimentary strata within or above a thick section of red (oxidized) beds. Mineralization consists of fine-grained copper and copper-iron-sulfide minerals that occur as stratabound to stratiform disseminations in siliciclastic or dolomitic sedimentary rocks. Regarding their tectonic setting, they are found in intracontinental rift-related sedimentary sequences and vary considerably in size, grade, and metal association. These deposits are characterized by zoning of ore minerals laterally along and across bedding, from pyrite and chalcopyrite to bornite and chalcocite.

Most famous deposits of this type are the Kupferschiefer in Central Europe and the Central African Copperbelt. The models proposed for the formation of these deposits fall under two main groups: synsedimentary (syngenetic) and diagenetic (syndiagenetic). According to the syngenetic model, sulfides precipitated in an anoxic water column containing  $H_2S$  from bacterial sulfate reduction as in the present Black Sea. In the diagenetic model, the ore emplacement occurred during early diagenesis or late diagenesis of the host sediments, which is a difficult question to answer, especially for deposits that have been subjected to metamorphism and deformation (Misra [2000\)](#page-69-3). Taylor et al. ([2013\)](#page-70-21) and Hayes et al. ([2015](#page-69-35)) suggested that sediment-hosted stratabound copper mineralization is derived from hydrothermal fluids generated during diagenesis and lithification in sedimentary basins.

With regard to iron and manganese, autochthonous ores are chemical, partly biogenic marine sediments. Although manganese nodules and crusts of the deep oceans may become an essential source of these metals, actually the most important raw materials of this group are enriched parts of marine-banded iron formations and manganese formations (predominantly formed in the Paleoproterozoic) and ooidal or massive iron and manganese ore beds that are of Phanerozoic in age. The so-called banded iron formations (BIF) constitute by far the most abundant and economically the most important iron-rich sediments.

The term BIF means bedded chemical sediments, which comprise alternating layers of iron minerals, commonly oxides or hydroxides, and fine-grained quartz (e.g., chert). The banding is manifested at different scales, not only centimeter-thick beds but also millimeter or submillimeter lamellae. In the major iron formations, the bedding has an impressive continuity: a single 2.5 cm-thick band has been traced over an area of 50,000 km2 , and varves at a microscopic scale are continuous for 300 km. Banded iron formations were deposited at three different time periods, all in the Precambrian, receiving different names for each type: Algoman, Superior, and Rapitan, respectively. Algoman-type deposits are usually small and are found in Archean greenstone belts in association with volcanic rocks. Superior-type deposits were the first iron-rich deposits mined, being located in marine shelf sediments. Finally, the Rapitan-type deposits are a relatively minor type, occurring in association with Neoproterozoic glacial deposits.

Oxides such as hematite or magnetite are the main phase in most banded iron formations although carbonate, silicates, or sulfide are the main minerals in other BIFs. Primary iron formations contain 20–30% Fe, but the ores mined in most countries contain grades ranging from 55% to 65% Fe. This is because enrichment processes act on the iron formations as they are exposed at or near the surface. Exposure under hot, humid climate conditions to circulating groundwater leaches silica from the rock and replaces it by iron oxides.

More autochthonous sedimentary deposits include manganese deposits  $($ **O** Fig. [2.48](#page-63-0)), phosphate deposits, and sodium and potassium nitrates and sulfates ( $\Box$  Fig. [2.49](#page-63-1)). Regarding bedded manganese deposits, they are formed in a similar manner to iron formations, and the mineralogy assemblage is formed by pyrolusite  $(MnO<sub>2</sub>)$  and rhodochrosite ( $MnCO<sub>3</sub>$ ), which precipitate from seawater as bedded sedimentary rocks. Manganese deposits occur in rocks of all ages, the largest deposits occurring in Proterozoic ore bodies of the Kalahari in South Africa. Phosphorites, which are mined to be used as fertilizers, form on shallow continent shelves either through direct precipitation from seawater or by diagenetic replacement of limestone.

<span id="page-63-0"></span>**D** Fig. 2.48 GEMCO sedimentary manganese oxide mine (Australia) (Image courtesy of BHP Billiton)



<span id="page-63-1"></span>

**D** Fig. 2.49 Potassium sulfate underground mine (Brazil) (Image courtesy of Vale)

### **Brine Deposits**

Although current global production and resources of potash are dominated by stratabound potashbearing salt deposits, in some areas of the world, closed-basin potash-bearing brines are the main source for production of potash and potash-bearing brine resources. These brines may be alkaline or enriched in chloride, sulfate, or calcium, depending on the geological features of the drainage basin and the resultant chemistry of the inflows into the

basin. Potash-bearing brines form in salt lakes and salars or playas in closed basins in arid environments, where high rates of near-surface evaporation concentrated the brine. The duration of this process is very variable, but it can range from hundreds of years to tens of thousands of years, even over a million years. From acidic to intermediate volcanic rocks and sometimes saline and continental sedimentary rocks are the main source rocks for this type of deposit (Orris [2011\)](#page-70-22).

<span id="page-64-0"></span>

**D** Fig. 2.50 Evaporation of brines to obtain common salt (Spain) (Image courtesy of José Pedro Calvo)

The evaporation of brines  $($ **O** Fig [2.50](#page-64-0)) produces chemical precipitates that are extracted to obtain common salt, sylvite (KCl), gypsum, and anhydrite. Evaporites including halite or gypsum can also form from seawater evaporation in broad inland seas where there are extensive water evaporations. Sodium and potassium nitrates and sodium sulfates are also evaporation deposits. In this sense, one of the driest regions in the world, the Atacama Desert of Chile, includes the world's largest natural deposits of sodium nitrate.

On the other hand, the process of evaporation can be induced artificially, as occurs in some lithium brine deposits. These deposits account for about three-fourths of the world's lithium production. Lithium brine deposits are accumulations of saline groundwater enriched in dissolved lithium. All producing lithium brine deposits share a number of first-order characteristics such as arid climate, closed basin including a playa or salar, tectonically driven subsidence, associated igneous or geothermal activity, adequate lithium source rocks, one or more suitable aquifers, and enough time to concentrate a brine (Bradley et al. [2013\)](#page-69-36). All closed-basin lithium-brine deposits that are of present economic interest are of Quaternary age (e.g., Atacama Salar; **D** Fig. [2.51](#page-65-0)). Brine, typically carrying 200–1400 milligrams per liter (mg/l) of lithium, is pumped to the surface and concentrated by evaporation in a succession of artificial ponds, each one in the chain having a greater lithium concentration. After a few months to about a year, a concentrate of 1–2% lithium is further processed in a chemical plant to yield various end products, such as lithium carbonate and lithium metal.

### **Diagenetic Deposits**

As aforementioned, diagenetic deposits form a complex group of mineral deposits where the qualification of the ore-forming fluid as diagenetic or hydrothermal is almost impossible, since both are sometimes the same. The previous described stratiform sediment-hosted copper deposits are a good example of this controversy. The Mississippi Valley-type Pb-Zn-F-Ba deposits hosted in marine carbonates are probably the most representative mineral deposit type of this group **(**. [Box 2.11](#page-65-1): Reocín Pb-Zn Mine (Spain)).

<span id="page-65-0"></span>..      **Fig. 2.51** Atacama Salar (Chile) (Image courtesy of SQM)



#### <span id="page-65-1"></span>**Box 2.11**

### **Reocín Pb-Zn Mine (Spain)**

Mesozoic basins in the north Iberian Peninsula contain Zn-Pb Mississippi Valley-type mineralization mainly in the Basque-Cantabrian basin. Thus, the Reocín zinc-lead (Zn-Pb) deposit in the Basque-Cantabrian basin of northern Spain is the largest known stratabound carbonatehosted Zn-Pb deposit in Spain and one of the world's largest known Mississippi Valley-type (MVT) deposits. Prior to closure in 2003, the deposit yielded approximately 62 Mt of ore grading, 8.7% Zn and 1.0% Pb after 150 years of exploitation. This is a stratabound ore deposit 3300 m long and 800 m wide, formed by different mineralized and overlapped bodies with variable richness, locally reaching thicknesses up to 100 m included in barren intermediate zones. Previous geologic investigations on the genesis of this deposit have generated the typical confrontation between proponents of a syngenetic origin and supporters of an epigenetic origin, very common in Mississippi Valley-type deposits. The stratigraphic and structural setting, timing of epigenetic mineralization, mineralogy, and isotopic geochemistry of sulfide and gangue minerals of the Reocín deposit are consistent with the features of most of Mississippi Valley-type ore deposits.

Reocín was discovered in 1856 and first mined by the Compagnie Royale Asturienne des Mines and, since 1981, by its affiliated company, Asturiana de Zinc, S.A. Miners began the extraction of «calamines» (oxides, hydroxides, and carbonates of Zn, Pb, and Fe) in Reocín, and at the beginning of the twentieth century, as the exploitation got deeper, the sulfides started appearing, forcing a change in the calcination treatment and the installation of the first European plant of sulfide flotation (1922). Between 1943 and 1965, mining work focused in the interior, but a collapse caused the reactivation of open-pit mining. Since 1976, a mixed system was developed with both open-pit mining and interior works (Santa Amelia well). Peak production was reached between 1990 and 1995. The exhaustion of the deposit and the lack of new reserves caused the closure of Reocín in 2003.

The mineralization occurs within Lower Cretaceousdolomitized Urgonian limestones (116  $\pm$  1 Ma) on the southeastern flank of the Santillana syncline.

The Urgonian Complex reaches a thickness of 4000 m of marine sediments. It is limited at the base by siliciclastic formations of saline and freshwater environments and, at the top, by a sandy complex. Its most characteristic facies are limestone with rudists and dolostones, the Reocín ores being always located in the dolostones. The geometry of the mineralized bodies is highly variable (stratabound), conditioned by synsedimentary faults contributing as paths for the circulation of dolomitizing and mineralizing fluids, which formed deposits along bedding planes and fractures. The Reocín ore bodies appear only slightly deformed, and few faults are observed in the mine. The most important mineralized level in Reocín, for its extension and grades (>25% Zn), is the so-called Southern Layer, mostly hosted in dolomite and even replacing it locally.

The mineralogic and paragenetic sequence of the ore minerals is simple and includes, in order of abundance, sphalerite; wurtzite; galena; marcasite; pyrite, accompanied by dolomite; and rare calcite as gangue minerals. Sphalerite is usually the major sulfide, commonly precipitating as colloform and banded growths ( $\blacksquare$  Fig. [2.52\)](#page-66-0).

Galena is present as skeletal or dendritic growths, evidence of rapid precipitation. Carbonate gangue is usually dolomite; at Reocín, several precipitation stages of this carbonate have been recognized. Marcasite is locally

very abundant in this deposit. The following minerals are found in the open-pit showing supergenic alteration: smithsonite (ZnCO<sub>2</sub>), hydrozincite  $(\text{Zn}_5({(\text{OH})}_3\text{CO}_3)_2)$ , goethite (FeOOH), hemimorphite  $(Zn_4(Si_2O_7) (OH), H_2O)$ , etc. It is

important to bear in mind that the deposit was discovered in the eighteenth century due to the presence of a pervasive gossan, although there are evidences for the extraction of the oxidation area since Roman times.



<span id="page-66-0"></span>**D** Fig. 2.52 Typical mineralization from Reocín (Santander, Spain)

Mississippi Valley-type (MVT) deposits are a large and heterogeneous group that contains a substantial amount of the reserves of zinc and lead in the world. They are the main source of these metals in the USA and contribute significantly to the production of lead and zinc in Canada and Europe, usually occurring in districts (clusters) that may extend over hundreds of square kilometers and contain up to 500 million tons of ore. These deposits constituted a wide group of lead-zinc mineral deposits that occur mainly in carbonates of any age from the Proterozoic to the Cretaceous (no MVT deposits have been reported from the Archean). In spite of the abundance of appropriate carbonate rocks, the Proterozoic contains only a few MVT deposits. MVT deposits display their maximum presence from Devonian to Carboniferous. By that time, vast and permeable carbonate platforms and abundant evaporites are formed. According to Leach et al. [\(2010](#page-69-37)), the intense orogenic activity during the assembly of Pangea in relatively low latitudes created abundant opportunities for the migration of sedimentary brines into the interior carbonate platforms and within extensional domains landward of the orogenic belts to form MVT deposits.

This type of deposit is typically stratabound and takes place in dolostones, although limestone or sandstone can also include this mineralization, and always at shallow depths along the flanks of sedimentary basins. The most common depositional setting is represented by platform carbonate sequences, commonly reef facies, located in fairly undeformed foredeeps or in foreland thrust belts. MVT deposits are mineralogically simple, although considerable variation exists among districts in terms of the total ore-gangue assemblage. Thus, the most typical mineralogy includes sphalerite and galena as dominant minerals and lesser amount of pyrite, marcasite, dolomite, calcite, and quartz. The textures of the sulfide minerals are very varied, and examples are coarse and crystalline to fine-grained textures and/or massive to disseminated ones. One of the most characteristic structures in this type of deposit is banded and colloform structure, which is common as a result of deposition in open spaces. Other recognizable processes consist mainly of dolomitization,

brecciation (mineralization in breccias is one of the most characteristic features of Mississippi Valley-type deposits), and host-rock dissolution.

Fluid inclusion studies invoke lowmineralization deposition temperatures ranging from 50 to 200 °C. However, these temperatures are higher than those attributable to normal thermal gradients within the sedimentary pile. Regarding the composition of the ore fluids, they were dense basinal brines, commonly containing 10–30 wt. % dissolved salts. Classical examples of this type of deposit are Viburnum Trend (Southeast Missouri, USA) and Pine Point (Canada). Regarding the origin, the general framework of genetic models for typical MVT deposits is constrained by two important common factors: the ore fluids were moderately hot, highly saline brines, and the mineralization was epigenetic. Controversies are centered in the origin and migration of ore fluids, the source(s) of the mineralization constituents, and the mechanisms of mineral precipitation.

# **2.8.4 Metamorphic and Metamorphosed Mineral Deposits**

As commented previously, mineral deposits in metamorphosed rocks can have been originated before, during, or after metamorphic processes. The first category, which is of premetamorphic origin independent from later metamorphic overprinting, is the class of metamorphosed ore deposits. Some authors consider that the skarntype deposits can be included in the magmatic domain but here are considered as metamorphic ore deposits because they are a product of contact metamorphism. On the other hand, the formation of ore deposits by regional metamorphism is now generally accepted (Pohl [2011](#page-70-1)), and examples of these deposits are orogenic gold, graphite veins, and several large talc deposits, among others.

The most important ore deposit type is undoubtedly the skarn deposits. They represent a very diverse class in terms of geological setting and ore metals, which range from Precambrian to late Cenozoic in age, and constitute the world's premier source of tungsten and important sources of copper, iron, molybdenum, and zinc. A continuum exists between the porphyry-type and the skarn-type ore deposits, and at least some skarn deposits appear to be mineralized in carbonate wall rocks within porphyry systems. Nevertheless,

skarn deposits do possess enough special characteristics to be treated as a distinct class (Misra [2000](#page-69-3)).

The term skarn, an old Swedish mining term, encompasses a large variety of generally coarsegrained calc-silicate rocks enriched in calcium, iron, magnesium, aluminum, and manganese, regardless of their association with minerals of potential economic value. They were formed by replacement of originally carbonate-rich rocks by metasomatic processes (Einaudi et al. [1981](#page-69-38)). Carbonate rocks such as limestone and dolostone are by far the most common protoliths of skarns, although occurrences of skarns in shales, quartzite, and igneous rocks have been reported. A diagnostic feature of typical skarns is their mineral assemblages; the primary assemblage varies with the compositions of the skarn-forming fluids and the invaded rocks but is characterized by anhydrous Ca-Fe-Mg silicates and pyroxenes (including pyroxenoids), and garnets are of special importance.

Skarn deposits can be classified on the basis of the dominant economic metal(s): iron, copper, molybdenum, gold, tungsten, tin, and zinc-lead. The main ore minerals of these skarn types are, respectively, magnetite  $\left( \square$  Fig. [2.53](#page-68-7)), chalcopyrite ± bornite, molybdenite, electrum, scheelite, cassiterite, and sphalerite-galena (e.g., Misra [2000](#page-69-3)). In addition to distinctive metal associations, the skarn deposits exhibit a systematic variation in skarn mineralogy, especially in terms of pyroxene and garnet compositions, for instance, a decrease in diopside component of pyroxenes through the sequence Cu  $\ge$  Fe  $\ge$  W $\ge$  Zn-Pb skarn deposits. From an economic point of view, seven major skarn types can be distinguished: iron (calcic), iron (magnesian), copper (calcic), molybdenum (calcic), tungsten (calcic), tin (calcic), and zinclead (calcic). Skarn ore bodies are also a major source of many industrial minerals, including wollastonite, graphite, asbestos, magnesite, talc, boron, and fluorite.

As an example of this type of deposits, skarn gold deposits «consist of disseminated to massive sulfide lenses and crosscutting veins in carbonate platform sequences superimposed by volcanic and/or plutonic arcs; mineralization is associated with Al-rich garnet-pyroxene skarn assemblages replacing limestone, calcareous siltstone, and carbonatized volcanic rocks adjacent to diorite or granodiorite stocks, dykes, or sills» (Robert

<span id="page-68-7"></span>..      **Fig. 2.53** Mineralization of magnetite and sulfides in Cala mine (Spain) (Image courtesy of César Casquet)



et al. [1997\)](#page-70-23). Sometimes, the deposits occur in districts along with porphyry Cu-Mo mineralization, tending to be linked with more mafic, hotter intrusions. Mineralogy includes the following minerals: pyrrhotite, pyrite, arsenopyrite, and lesser amount of telluride minerals, presenting also wide variations in their gold-to-silver ratios  $(Au/Ag = 1:10 \text{ to } 10:1).$ 

# **2.9 Questions**

### ?**Short Questions**

- 5 List the four basic geological requirements for any ore deposit to form.
- 5 What is a metallogenic province?
- 5 List several criteria used to classify mineral deposits.
- 5 What are the main ore-forming processes?
- 5 What «gossan» means? Explain its importance.
- 5 What is the definition of a Btu?
- 5 Explain the term «tar sands.» What are they used for?
- 5 What is the hydraulic fracturing?
- 5 List the rank of coals according to the carbon content.
- 5 What are the industrial rocks? List some examples.
- 5 List the four main types of magmatic ore deposits related to the commodities.
- 5 What are the main examples of hydrothermal ore deposits?
- $\blacksquare$  Describe very briefly the genesis of the so-called «roll-front» uranium deposits.
- 5 Explain why Mississippi Valley-type deposits are typically stratabound.

### ?**Long Questions**

- 5 Identify relationship between mineral deposits and plate tectonic settings.
- 5 Explain the industrial minerals applications.

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