

PART I

Metalliferous Ore Deposits

Economic geology defines ore as a natural material (ore rock) from which metals or minerals can be profitably extracted. Mining professionals use the word in an identical connotation. Note that metals and minerals can also be recovered from quite exotic materials that are not ore *sensu stricto*, for example saline brines (lithium, magnesium), geothermal waters (zinc), metal-accumulating plants (nickel; “phytomining”), acid mine water (copper) and of course, recycled scrap (iron). The term ore is also applied to metalliferous minerals in a rock, for example chromite in dunite, or magnetite in gabbro (“ore minerals”). Ore rock, commonly just called ore, is typically an intergrowth of useless minerals (“gangue”) with ore minerals. Massive ore consists of ore minerals only, with little gangue, for example high-grade haematite iron ore.

Ore deposits form by geological process systems that can be viewed as a large cycle of constructive (e.g. magmatism) and destructive sectors (e.g. weathering; Figure 1.3). Within this cycling of earth materials, individual metals have specific enrichment sites that depend on chemical and physical properties of the metal or its compounds. It is very important to remember that biogeochemical fluxes mediated by life (Falkowski *et al.* 2008) control many ore forming processes.

Part I of this book is divided into two chapters. In Chapter 1, general observations, characteristics and interpretations of ore deposit formation processes, process systems and associated outstanding deposit types are presented. In Chapter 2, the economic geology of metals is systematically presented and illustrated by reference to specific mining districts and deposits.

CHAPTER 1

Geological ore formation process systems (metallogenesis)

Synopsis

Energy flow from the Earth's interior and from the sun drives geological process systems. The concentration of ore and minerals is part of these systems, which comprise intrusive and extrusive magmatism, weathering, erosion, transport and sedimentation, followed by diagenesis and metamorphism. In this chapter, we aim to acquire an overview of these systems in respect of the principles which govern the generation of ore deposits. Finally, the inspection of the different major systems is brought together in a synthetic view of global dynamics and metallogeny (i.e. the science of ore deposit formation). This chapter lays the ground for the rest of the book.

For a long time in the past, processes associated with differentiation and cooling of magmatic bodies were thought to be the main agents of ore deposit formation. Starting with mafic melt, ore minerals can form upon cooling or metal-rich melts can segregate from the silicate liquid. Because mafic silicate minerals crystallize at higher temperature, intermediate and felsic residual melts are formed with their own suite of ore deposits. Late-stage magmatic fluids collect metals and produce hydrothermal mineralization. Lindgren (1933), Niggli (1948), Schneiderhöhn (1932, 1962), Stanton (1972), Guilbert & Park (1986) and many others developed this concept of igneous ore formation. In addition, the role of weathering, erosion and sedimentation in concentrating metals was recognized. Metamorphic processes were seen to transform previ-

ously existing ore but without appreciable mass transfer.

More recently, these earlier views (here very simplified) on ore deposit formation were fundamentally expanded (Robb 2005, Evans 1998). First, the discovery of plate tectonics caused a revolution in understanding the dynamic interaction of the Earth's crust and mantle. Plate tectonics determine the origin and distribution of many ore deposits. Present ore-forming processes were investigated. Outstanding impulses brought the exploration of ocean floor hydrothermal venting that produces metal concentrations, which closely resemble long-known ore deposits (e.g. copper on Cyprus Island).

The application of new technologies of the geosciences (e.g. trace element analysis, microprobe, isotope geochemistry, fluid inclusions investigations, mathematical modelling and simulation)

guided by old and new hypotheses, led to changes in metallogenetic thinking and to the recognition of additional ore formation systems. One example is the dehydration of sedimentary basins during diagenesis: Expelled fluids cause appreciable geochemical mass-transport and formation of numerous metallic and mineral concentrations, without involvement of igneous processes. Furthermore, the role of dissolved salt, hydrocarbons, reefs and karst cavities in diagenetic ore formation was illuminated. Long after the first hypothetical considerations, metamorphism was finally proved to cause migration of aqueous fluids that transport and precipitate metals.

The classification of ore deposits by major earth process systems is in principle quite simple. Complications arise mainly because of the extreme variability of individual deposits due to manifold combinations of different processes and factors. Therefore, some authors prefer to arrange deposits into associations and types, which are related by geological setting, paragenesis and form, but not necessarily by the same genetic process (Routhier

1963, Laznicka 1985, 1993). Other authors dispense with geological environs and concentrate mainly on processes (Robb 2005). In this book, fundamental geological cycles (Figure 1.3) and ore-forming systems are to guide the reader through metallogeny.

The genetic terms of Table 1.1 provide the basic vocabulary of metallogeny. The non-genetic descriptors stratiform (layer-shaped) and strata-bound (restricted to certain strata) only denote shape and position of an orebody in relation to sedimentary features, not its origin. Comprehensive explanations of geological and mining terms can be found in the *Dictionary of Mining* (AGI 1999) and the *Glossary of Geology* by Neuendorf *et al.* (2005). Geological time nomenclature in this book follows Walker & Geissmann (2009).

1.1 MAGMATIC ORE FORMATION SYSTEMS

A very large and diverse group of ore deposits originates by various processes during formation,



Figure 1.1 (Plate 1.1) Bauxite extraction at Huntley mine, southwestern Australia. On the Darling Plateau, bauxite is part of a mature soil profile developed over Archaean gneiss and granite. The area is covered by woodland (the jarrah, or *Eucalyptus marginata* forest). Mining depends on the availability of land and its social acceptance on rapid re-establishment of the native ecosystem. Reproduced by permission of Alcoa Inc.



Figure 1.2 (Plate 1.2) Rehabilitated jarrah forest covers former extraction panels of Huntley bauxite mine in front of the lake. Reproduced by permission of Alcoa Inc.

evolution, emplacement and crystallization of silicate melts (magmas) in the upper mantle and in the Earth's crust.

Most post-Archaeon magmatic rocks can be classed according to their plate-tectonic environment. Rocks of the ophiolite association (basalt,

gabbro, ultramafic rocks) are remnants of former mid-ocean ridges, back arc basins, and of early and primitive parts of immature oceanic island arcs. Mature island arcs and active continental margins are distinguished by profuse amounts of orogenic andesites and equivalent intrusive magmatic

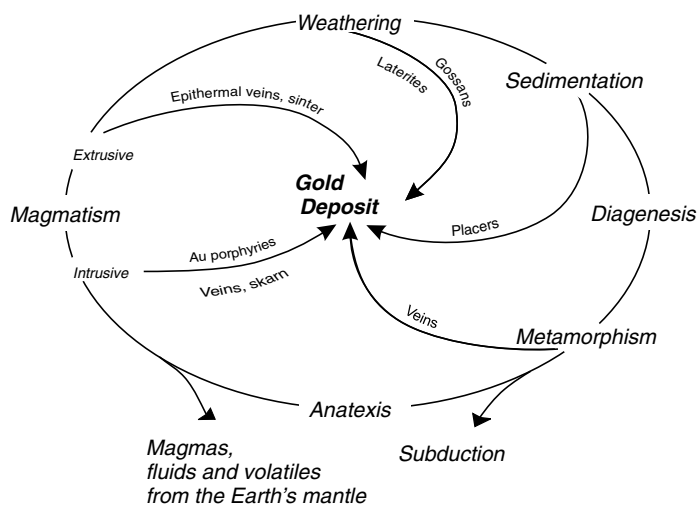


Figure 1.3 The origin of gold deposits in relation to major geological process systems within the Earth's crust, demonstrating the variety of ore-forming systems.

Table 1.1 Common metallogenetic terms

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- *Syngenetic* – denotes ores and minerals that formed at the same time as their host rocks (most often applied to sedimentary rocks and ore)
 - *Epigenetic* – ores were emplaced into pre-existing rocks of any origin (e.g. veins, metasomatic ore)
 - *Hypogene* – ores that were formed by ascending solutions (e.g. Mississippi Valley type lead-zinc)
 - *Supergene* – ore formation by descending solutions (meteoric water interacting with rocks during surficial weathering processes)
 - *Lateral secretion* – concentration of metals by abstraction from surrounding rock
 - *Endogenetic* – concentration caused by processes in the Earth's interior (magmatism or metamorphism)
 - *Exogenetic* – concentration caused by processes at the Earth's surface (sedimentation, weathering).
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rocks. Continental collision causes melting of sialic crust and voluminous granitic magmatism. Continental rifts are associated with bimodal alkaline volcanism (basalt and rhyolite). Extensional deformation of continents and mantle melting result in emplacement of layered mafic intrusions, flood basalts and alkaline magmatic provinces. Most notable are subvolcanic ring complexes and kimberlite diatremes that transport diamond from 200 km depth to the surface.

The association of certain igneous rocks with specific metal ores was established long ago. Ultramafic rocks host ores of nickel, chromium and platinum, gabbro and norite copper, cobalt, nickel, iron, titanium and vanadium, andesite and intermediate intrusive rocks induce copper and gold ore, and granites are related to beryllium, lithium, tin and tungsten concentrations. Essentially, this distribution was understood as a result of the geochemical fate of different metals during fractional crystallization (solid-liquid fractionation) of silicate melt bodies (Goldschmidt 1958). Meanwhile, magmatic rocks can be further differentiated according to plate-tectonic setting, source rocks, degree of partial melting, role of volatiles and many other genetic variables. Examples are the various basalt types (N- and E-MORB, intraplate, island arc: Pearce *et al.* 1984; Pearce 1982; Winchester & Floyd 1977), or the S-, I- and A-granitoids. We shall see later in this chapter that some of these rock classes are related to specific ore deposits.

Impact magmas result from heat and high pressure caused by collision of extraterrestrial bodies with the Earth. Melting affects part of the crust and in rare cases even the upper mantle. Impact

magmas differ chemically from other melts because whole volumes of crust are liquefied, whereas normally partial melting is the rule. In addition, the impacting body may induce geochemical anomalies, especially regarding siderophile elements (e.g. platinum, iridium, cobalt and nickel). Post-impact cooling can induce hydrothermal systems that are able to redistribute matter and provoke ore deposit formation.

In conclusion, the geodynamic environment controls the formation of ores from silicate melts in several ways. At the scale of ore-forming processes caused by single magmatic bodies, the following major genetic stages are differentiated:

- Orthomagmatic ore deposits are formed before the melt cools to complete solidification, or in other terms, in the liquid stage before solidus.
- Pegmatitic ore deposits are the result of segregation of small residual melt batches from a large crystallizing magma body approaching the solid state; fertile pegmatite melt is characterized by high amounts of volatiles and of incompatible and rare elements.
- Magmatic-hydrothermal ore deposits are produced by super- or sub-critical fluids, solutions and gases that are segregated by all magmas, which had more dissolved volatiles (H₂O, CO₂, S, B, F, Cl, etc.) than the amount that could be accommodated in silicates during crystallization; because of this connection, the time of fluid phase expulsion is commonly coeval with the formation of solid phases (minerals) from the melt; a significant part of the geochemical signature of magmatic-hydrothermal ore deposits is determined by processes at the magmatic stage (Audétat *et al.* 2008).

1.1.1 Orthomagmatic ore formation

Oxide (magnetite, ilmenite, chromite), base metal sulphide (Ni, Cu), and ore of precious metals (Pt, Pd, Au) is often found in ultramafic and mafic igneous rocks. More rarely, magnetite occurs in intermediate and felsic silicate melts. Textural (and many other) observations show that these ores were formed at magmatic temperatures, while the melt was essentially liquid and before total solidification (Naldrett 2004). Therefore, this class of ore deposits is called "orthomagmatic".

Numerous observations suggest that enrichment processes concentrate ("segregate") low metal traces from a large mass of silicate melt into small volumes. A common evolution is that the parent melt evolves towards saturation so that either a solid (e.g. chromite) or a liquid (e.g. sulphide melt) accumulates the metal in question. At some stage, residual fluids may intervene. Many parameters influence these processes, including the depth of intrusion, tectonic activities, the temperature gradient in space and time, fractional crystallization, dynamics of the melt body (e.g. convective flow), repeated injection of fresh melt, assimilation of country rocks, sulphur or external fluids, liquid immiscibility of ore and silicate melts and mixing or redissolution (Kerr & Leitch 2005). Because of their higher density compared to silicate liquids, ore melt droplets or solid ore phases typically accumulate above or within floor rocks, which may be cumulates below still liquid magma (gravitational accumulation; Sparks *et al.* 1993). Consolidation of cumulate minerals can lead to expulsion of intercumulus liquid ("filter pressing"). As the system cools, ore melts themselves may then separate into cumulates (e.g. Fe-sulphides) and residual liquids (Cu-rich sulphide melt).

Various mathematical models have been proposed that describe the orthomagmatic enrichment process. Concentration of metals such as PGM (platinum group metals), Au, Ni and Cu in sulphide melt is controlled by the Nernst partition coefficient (D) between sulphide and silicate liquids, and by kinetic factors. Disequilibrium is exposed by calculating the silicate/sulphide liquid mass ratio ("R-factor"; Robb 2005, Campbell & Naldrett 1979). A zone refining model is appropriate when,

for example, sulphide droplets sink through a magma chamber and collect chalcophile metals. Limited base metal content but very high PGM enrichment can be explained by resorption of iron sulphide liquid in undersaturated magma (Kerr & Leitch 2005). In this process, the residual sulphide retains the precious metals, which it may bequeath to a later batch of undersaturated mafic melt.

Most orthomagmatic ore deposits are found in intrusive rocks. Eruptive equivalents are also notable, such as the Ni-Cu-Fe sulphides in komatiitic lava flows of Archaean greenstone belts, or the magnetite and haematite lavas and tuffs in andesitic-rhyolitic volcanoes in Chile, Mexico and Pakistan.

Basic shapes of orthomagmatic orebodies are layers in stratified magmatic rocks (often formed as cumulates), lenses or cross-cutting dykes and veins. This depends on the morphology of the segregation (sedimentation) surface and on dynamic factors. Massive ore is the product of highly efficient unmixing of ore particles or melt droplets and silicates, whereas disseminated mineralization reflects lower efficiency. Highly complex orebody shapes can be found in flow channels and pipes of mafic lavas and intrusions, for example when widening or curvature of flow tubes induce lower flow velocity of silicate melt that carries chromite crystals or sulphide melt droplets (Naldrett 1200, 1199; e.g. Voisey's Bay, Canada).

Textbook examples of orthomagmatic deposits are sulphide Fe-Ni-(Cu-PGE) ores hosted by Archaean komatiitic lavas of the Yilgarn Craton in Western Australia (Box 1.1; Barnes *et al.* 2007, Barnes 2004, Hoatson *et al.* 2006).

Gravitational settling can also explain many features of ore formation in layered mafic intrusions (Naldrett 2004, Cawthorn 1996, Irvine 1982). Other contributing processes include flowage differentiation and convective scavenging (Rice & Von Gruenewaldt 1994), *in-situ* crystallization on the floor of the melt body, mixing of two different melts, and uptake of material from outside (e.g. by melting siliceous or sulphur-rich host rocks). Often, the formation and segregation of a sulphide melt is the key to enrichment of exploitable metals (Barnes *et al.* 2009). Layered melt bodies (in respect of composition, temperature and density)

BOX 1.1 Orthomagmatic nickel sulphide ore in komatiites

Komatiites are ultramafic volcanic rocks with melting temperatures of $\sim 1700^{\circ}\text{C}$ containing >18 wt.% MgO (Arndt *et al.* 2008). Their formation is the consequence of mantle temperatures $\sim 100^{\circ}\text{C}$ higher than today (Naldrett 2010). Komatiitic melts originated by 30–50% partial melting of mantle. Normally, these melts remained sulphide-undersaturated from extraction through ascent and eruption to emplacement. Liquid komatiite lavas had a very high temperature and very low viscosity (similar to water), resulting in high flow velocities. Komatiite lavas are capable of eroding and melting most volcanic and sedimentary footwall rocks (“ground melting” or “thermochemical erosion”). The flows followed troughs on the seafloor and formed flow tubes similar to submarine basalts. Komatiites were typically charged with suspended olivine crystals. During cooling, cumulates and vesicular textures formed. Because of the extreme temperature difference between ocean water and Mg-rich melts, flow tops are characterized by skeletal growth of olivine and pyroxene (“spinifex textures”; Shore & Fowler 1999).

Elongate massive sulphide bodies, which were clearly formed from liquid sulphide melt, occur at the floor of flow tubes and grade upwards into disseminated (matrix or net-textured) ore (Figure 1.4). Ore textures reflect gravitational settling in the liquid phase. Sulphide melts can only form upon sulphur saturation, implying high sulphur content. The common association of sulphide mineralization with the presence of sulphur-rich interflow sediments and isotopic compositions of sulphur (Bekker *et al.* 2009) are strong arguments that admixture of crustal sulphur is the main difference between fertile and barren komatiites. The availability of nickel (and elements such as platinum) for partitioning into iron sulphide melt is favoured by low redox conditions. In that case, nickel is dissolved in the silicate liquid as uncharged Ni^0 and is not available for incorporation into olivine. Apart from the redox constraints, nickel content of magmatic sulphide liquids is largely controlled by partitioning equilibria and the mass balance between silicate and sulphide melt (the “R-factor”; Campbell & Naldrett 1979), including dynamic factors such as mixing and redissolution. The ore minerals of komatiite nickel deposits comprise pyrrhotite, pentlandite, chalcopyrite and pyrite, with nickel concentrations in ore reaching 20%. Prendergast (2003) describes the nickel-bearing komatiites of Zimbabwe as proximal and basal parts of submarine volcanoes that were quite flat and extended over hundreds of kilometres. The Neoarchaeon komatiites of Western Australia (2.7–2.9 Ga) host the majority of the world’s komatiite-associated Ni-Cu-PGE deposits. Palaeoarchaeon komatiites are depleted in platinum group elements (PGE) because the metal source of the younger, metalliferous komatiites, i.e. cosmic matter bombarding the Earth during the period from 4.5 to 3.8 Ga, was only gradually mixed into the mantle (Maier *et al.* 2009). In contrast to Western Australia, the closely comparable Abitibi Greenstone Belt in Canada is richly endowed with volcanogenic massive sulphide deposits (e.g. Kidd Creek, Noranda). Both regions display abundant orogenic gold deposits. It is assumed that the disparity is due to a different lithospheric structure (Barnes *et al.* 2007).

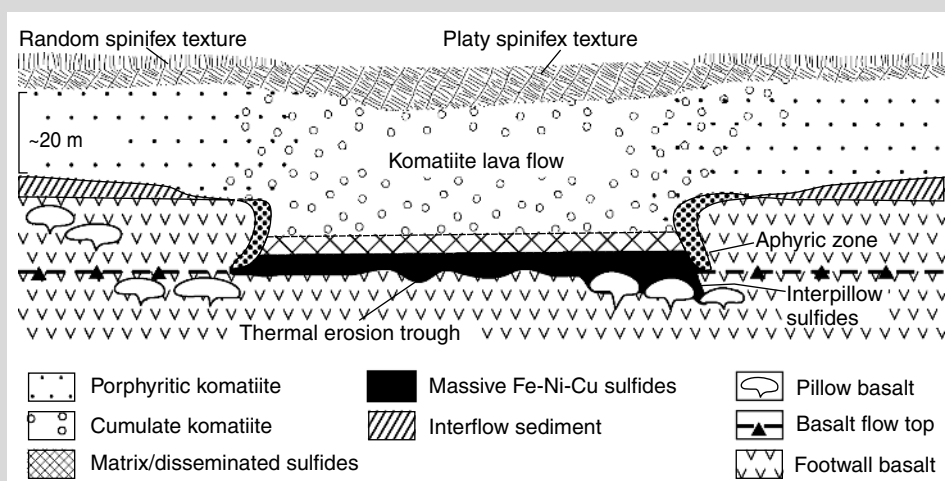


Figure 1.4 Massive and disseminated nickeliferous pyrrhotite orebodies (Lunnon shoot, Kambalda, Western Australia) at the base of an Archaean komatiite lava flow (adapted after Groves *et al.* 1986). By permission from Macmillan Publishers Ltd. *Nature* © 1986.

BOX 1.2 Orthomagmatic ore formation in the Bushveld Complex

The Bushveld Intrusive Complex comprises the Rustenburg Layered Suite and the Lebowa Granites. The first term designates the layered mafic-ultramafic intrusion, which was formed in the Palaeoproterozoic at ~2054 Ma, and which contains enormous metal resources. The granites have nearly the same age and host less important fluorite and tin deposits. The roof of the Bushveld Complex and the overlying granites consists of thick precursor basaltic andesites to rhyolites (the "Rooiberg Group" volcanics). Rooiberg volcanics and the intruding granites are the products of crustal melting caused by the giant mass of hot mafic melt. Country rocks of the Bushveld intrusion are Palaeoproterozoic sediments and volcanics of the Transvaal Supergroup and Archaean basement. The Rustenburg Layered Suite reaches a thickness of 9000 m. It is strongly layered at all scales. The major units from bottom to top comprise (Figure 1.5 and Figure 1.6):

- the Lower Zone with dunite, bronzitite, and harzburgite;
- the conspicuously banded Critical Zone with a lower part of orthopyroxenite, chromitite bands and some harzburgite, and a higher part marked by the first cumulus plagioclase and by cyclic layering of economically significant platiniferous chromitite, harzburgite, bronzitite, norite and anorthosite in this order (cyclic units); its upper boundary is marked by the Merensky Reef (Pt, Ni, Cu);
- the Main Zone with gabbronorite and minor layering;
- the Upper Zone with magnetite (ferro) gabbro and ferrodiorite, which contains numerous magnetite (V-Ti) layers.

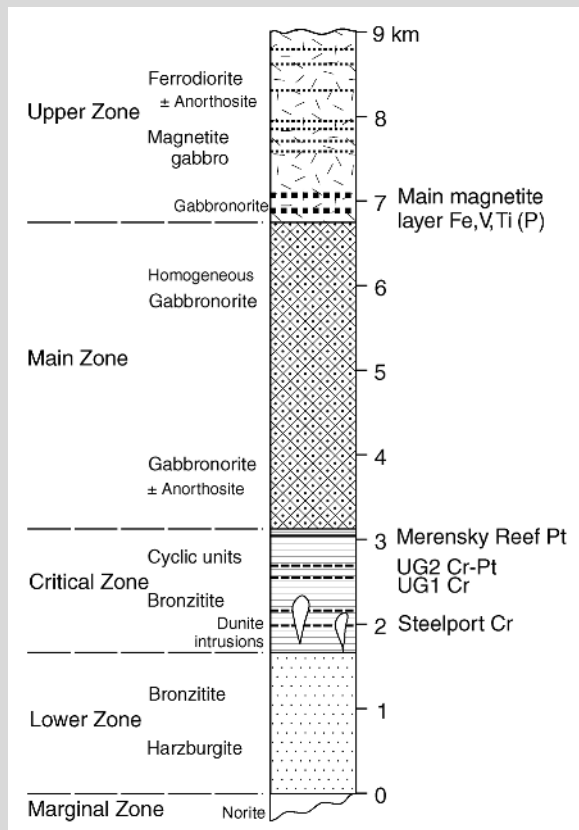


Figure 1.5 Simplified lithostratigraphic column of the mafic Rustenburg Layered Suite in the Eastern Bushveld, South Africa, with major ore horizons.



Figure 1.6 Bushveld Upper Group (UG1) chromite seam in anorthosite at Dwars River, S.A. Thin bands at the bottom display bifurcation, illustrating the complexity of cumulate ore formation in layered mafic intrusions. Courtesy Bernd Lehmann, Clausthal.

An extremely detailed lithostratigraphic scheme has been established for most parts (“lobes”) of the intrusion (Vermaak & Gruenewaldt 1986, Eales & Cawthorn 1996). Strontium isotope stratigraphy reveals that the intrusion formed by numerous influxes of magma of contrasting isotopic composition with concomitant mixing, crystallization and deposition of cumulates. Locally, in all five lobes of the Complex, remarkable differences in thickness and facies of layers have been noted that point to proximity of magma inflow (Maier & Eales 1994). The cyclic units of the Critical Zone were formed by mixing or mingling of two different magmas, a resident magma of Main Zone type (or T-type) precipitating plagioclase, and fresh inflows of Critical Zone type (U-type) contributing orthopyroxene (Naldrett *et al.* 2009). Apart from chemical processes, pressure fluctuations are thought to have controlled rhythmic layering and ore deposition in the Bushveld melt chamber (Cawthorn 2005b). The Bushveld contains the world’s largest exploitable resources of chromium, platinum metals and vanadium. For the future, large amounts of titaniferous magnetite and apatite are available that have at present no economic value.

undergo thermal and chemical diffusion that can concentrate ore metals. Although much less obvious than in many felsic intrusions, mafic melt bodies may also experience unmixing and expulsion of magmatic fluids that can form ore. The largest preserved layered intrusion in the world is the Bushveld Complex of South Africa, hosting an exceptional variety and mass of high-grade metal ores (Box 1.2; Vermaak & Von Gruenewaldt 1986, Eales & Cawthorn 1996).

Layered mafic intrusions occur in several geodynamic settings:

- Archaean greenstone belts;
- intracratonic regions (the Bushveld);
- at passive margins of continents; and
- in active orogenic belts.

Intracratonic regions that experienced tensional tectonics can also exhibit unstratified, very complex mafic-ultramafic intrusions with Cu-Ni-PGM ores. The most important district of this kind is Noril’sk-Talnakh in Siberia, which originated at the Permo-Triassic boundary as a feeder to the giant Siberian trap basalt province (Yakubchuk & Nikishin 2004, Li *et al.* 2009).

Impact magma bodies with orthomagmatic ore deposits

Mineralized impact structures are very rare. A giant example is the Sudbury Igneous Complex (SIC) of Ontario, Canada, the second-largest source of nickel (plus much copper and platinum metals) in the world, after Noril'sk in Russia. The SIC is the remnant of a voluminous melt body that has been produced by the impact of a meteorite into continental crust 1.85 Ga ago (Dietz 1964). The surrounding rocks comprise Archaean granites and gneisses, and metamorphic Palaeoproterozoic volcano-sedimentary suites. The elliptical outline of the intrusion is thought to be due to later orogenic deformation. Hydrothermally altered (Ames *et al.* 1998) suevitic breccias, shales and turbidites (Whitewater Group) cover part of the intrusive complex, forming a central basin. Ore deposits occur mainly in embayments of the footwall contact of the intrusion, in radiating dykes ("offsets", Figure 1.7) and within intensely

brecciated footwall rocks up to 2 km from the contact. There is a lithologic zonation from the footwall upwards and towards the centre of the intrusion: Marginal norite, gabbro and quartz-diorite with dunite inclusions and the Ni-Cu-sulphides form the "Sublayer Norite" and the offsets, followed by norite of the "Lower Zone", quartz-gabbro of the transitional "Middle Zone" and granophyre of the "Upper Zone". The rocks are clearly the product of crustal melting (Therriault *et al.* 2002), but are very different from typical layered intrusions (e.g. there is no rhythmic banding). At Sudbury, lithologic zonation is interpreted to be due to gravity separation of mafic and felsic liquids that formed an emulsion immediately after the impact, and subsequent vigorous thermal convection within the norite and granophyre layers (Zieg & Marsh 2005). The ore-bearing sublayer displays typical features of mafic cumulates and gravity segregation of sulphide liquids. Offset dykes and footwall deposits host an important part

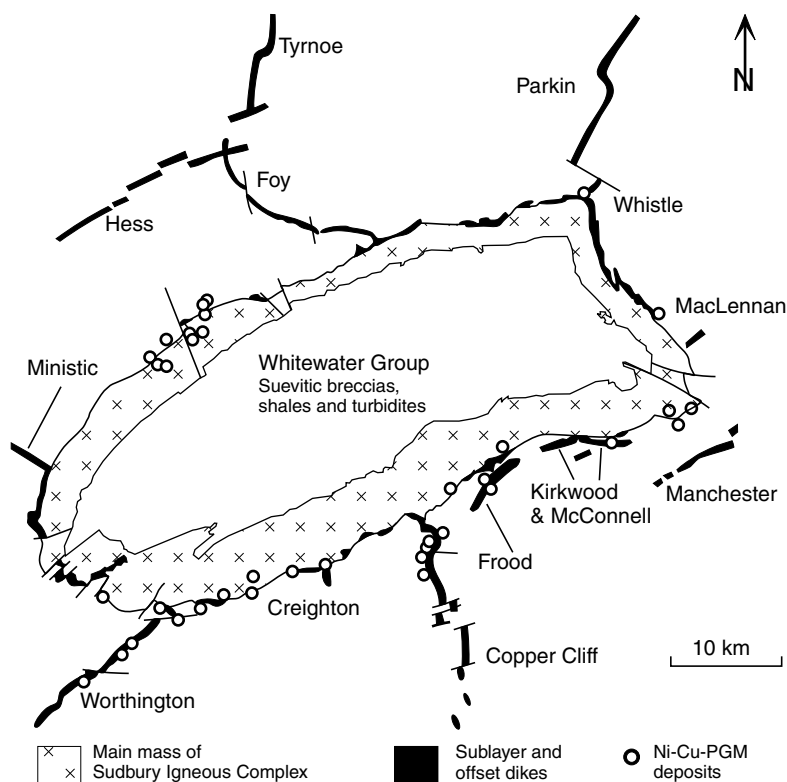


Figure 1.7 Overview map of the Sudbury impact structure, Canada, one of the giant nickel-copper mining districts of the world. Of close to 90 single deposits known (Ames *et al.* 2008), a selection is shown here.

of metal resources. Total past production and current reserves of the Sudbury District are estimated at >1700 Mt of Ni, Cu, Co, Pt, Pd, Au and Ag ore (Ames *et al.* 2008). Among approximately 90 known Ni-Cu-PGE deposits, 14 are currently worked.

Anorthosite-ferrodiorite complexes

Anorthosite-ferrodiorite complexes of Mesoproterozoic age have an outstanding role as sources of titanium (Ashwal 1993). Orebodies consist of ilmenite and/or rutile, magnetite or haematite, and a gangue of apatite and some graphite. Similar rocks of lesser economic importance occur as strata in the upper parts of layered mafic intrusions. The anorthosites are commonly coarsely crystalline, rather massive than layered and consist of >90% andesine to labradorite. Anorthosite plutons may be associated with coeval intrusions of troctolite, charnockite, rapakivi granite, ferrogabbro and ferrodiorite. The latter are often remnant melts after plagioclase crystallized to form anorthosite and are parental to the immiscible Ti-Fe-P melts. Because of their high density, the ore melts accumulate near the base of the magma chamber. Resulting orebodies are stratiform and either massive or disseminated (as at Lac Tio in Quebec, Canada). Some occur as thick dyke-like bodies in deeper parts of the intrusive suite or in country rocks. The origin of anorthosite-ferrodiorite complexes is not fully understood; one hypothesis presumes late to post-orogenic partial melting of tongues of lower crust in the mantle (Duchèsne *et al.* 1999). From these rocks, ~50% of the world's titanium supply is derived; they also contain about half of the total titanium resources. Since the high-grade Ni-Cu sulphides at Voisey's Bay in Canada were found in troctolites belonging to this family, these rare rocks have acquired a new prospective role.

Fe-rich melts segregated from intermediate to felsic magmas

The metallogenic role of these melts is a more contentious case of orthomagmatic ore formation. While there is no doubt that under conditions of

high fO_2 an immiscible FeO_x liquid is in equilibrium with melt of felsic composition (Naslund 1983), there is no general consensus that this is a path to the formation of large ore deposits. One objection is that the high viscosity of SiO_2 -rich liquids should physically inhibit segregation by gravity. Arguments brought forward to support the concept include: i) shearing by slow convection of the melt so that low-viscosity FeO_x liquid may be concentrated; and ii) high content of sodium and phosphorous that act as fluxing agents for iron melt. The process should produce ore of magnetite and apatite in the proportion of about 2:1, as exploited in the Kiruna-Malmberget District (Sweden). High fluorine and chlorine content of the apatites, and the presence of minerals such as amphibole and scapolite, imply an eminent role of magmatic volatiles (H_2O , Cl, F, CO_2 , etc.). Volatiles promote segregation and mobility of ore melt. High fluid and salt content of melt batches segregating from felsic magmas evoke a likeness to pegmatites and, similar to pegmatite systems, the transition to hydrothermal ore formation may be gradual and indistinctive (Borrok *et al.* 1998). The unusual chemical composition of parental magmas and fluids may be due to assimilation of evaporitic country rocks or of migrating saline brines (Barton & Johnson 1996). After the discovery and investigation, at the giant Olympic Dam in southern Australia, numerous iron oxide-rich deposits were subsumed in a new class, the **iron oxide-copper-gold (U-REE) deposits (IOCG)** (Groves *et al.* 2010, Cox & Singer 2007, Pollard 2006, Hitzman *et al.* 1992). Although a hydrothermal origin of IOCG mineralization is generally accepted, the broader group displays a considerable variety of geological setting, the ratio of orthomagmatic and magmatic-hydrothermal mineralization, the nature of hydrothermal alteration systems and mineralizing fluid compositions. In some cases, metamorphic fluids may have formed Cu-Au deposits resembling IOCG (Baker *et al.* 2008):

Kiruna in northern Sweden (Figure 1.8), the largest iron ore district in Europe, is traditionally considered as the type-deposit of orthomagmatic iron ore formation in felsic intrusions (Harlov *et al.* 2002), because



Figure 1.8 Kirunavaara iron ore mountain, northern Sweden. The steeply dipping magnetite orebody was originally mined in an open pit on the left side of the hill. Today, extraction is underground. Courtesy LKAB 2010.

the ore is cogenetic with Palaeoproterozoic magmatic host rocks (trachyandesite, rhyodacite). Lower Ti and V concentrations distinguish this type from massive iron oxides (e.g. nelsonite) segregated from mafic magmatic melts. Repeatedly, arguments have been put forward for a magmatic-extrusive ore formation (Nyström & Henriquez 1994). Still other authors invoke a magmatic-hydrothermal metasomatic origin related to IOCG deposits (Hitzman *et al.* 1992), but Kiruna is not part of this class because it lacks Cu and Au (Groves *et al.* 2010). An extrusive origin is also considered for Pliocene magnetite orebodies at El Lago, Chile (Nyström & Henriquez 1994; but note

the contradiction by Sillitoe & Burrows 2003) and for 30 Ma old Cerro de Mercado (Durango, Mexico). Magnetite or haematite-apatite ores at both sites have been described as massive and vesicular lavas, veins, crystal tuffs and pyroclastic agglomerates deposited by volcanoes built of rhyolite and latite (Lyons 1988, Figure 1.9).

In conclusion, orthomagmatic deposits of iron oxides and apatite in intermediate to felsic igneous rocks (intrusive and extrusive types) share a number of features with IOCG deposits, but are different (Groves *et al.* 2010). However, both may

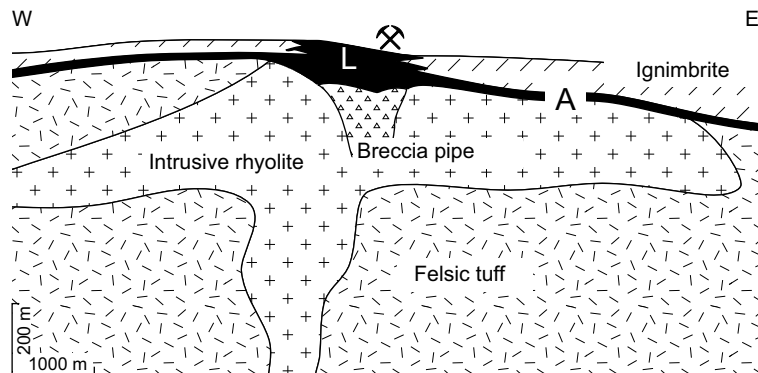


Figure 1.9 Schematic profile of the volcanogenic iron ore deposit at Cerro de Mercado, Mexico (modified from Swanson *et al.* 1978). Magnetite lavas (L) above an eruptive centre pass laterally into haematite tuff (A, both black).

originate by mixing and mingling of (ultra)mafic and silicic melt (Clark & Kontak 2004).

Lower sections of ophiolites also contain orthomagmatic ore deposits. This includes diapiric dunite bodies with streaky or lenticular disseminated and massive chromitite. The dunites occur mainly within deformed refractory harzburgite of tectonized mantle. Tabular chromitite seams may occur in the lowermost ultramafic cumulates of the mid-ocean gabbroic magma chamber. Both cases are considered to be a consequence of chromite segregation from the melts that rise from the mantle beneath mid-ocean spreading ridges. The metallogeny of ophiolites is considered in more detail below.

Ultramafic complexes of the Urals-Alaska type are concentrically zoned intrusions in orogenic and platform settings (Taylor 1967). In the central dunite of the ring complexes, important chromium and platinum ores can be concentrated (Urals: Garuti *et al.* 2003). Orthomagmatic concentrations of minerals and metals are also part of the economic significance of carbonatites.

1.1.2 Ore deposits at mid-ocean ridges and in ophiolites

Exploration of ocean floors resulted not only in the recognition of plate tectonics but also in the discovery of conspicuous signs of active ore forming systems – the “black smokers”. Black smokers are points of discharge of hot metalliferous solutions from the ocean floor. Black smoker fields build accumulations of metal sulphides on the ocean floor, some of which may soon be economically exploitable. Comparative investigations revealed that ophiolites, an association of mafic and ultramafic rocks common in orogenic belts, are remnants of oceanic spreading processes that took place at mid-ocean ridges, in marginal basins in front of or behind island arcs (Dilek *et al.* 2001), or within intra-ocean primitive island arcs. Ophiolites host ore deposits that display features reminiscent of black smoker fields and sulphide mounds. However, fluid venting on the seafloor may also occur in other tectonic settings, including magmatic arcs above subduction zones

(Stoffers *et al.* 2006), hotspot ocean island volcanoes and dewatering sediments of active and passive continental margins.

Ophiolites

Ophiolites are fragments of oceanic crust and mantle that have been transported (obducted) as thrust sheets (nappes) or schuppen towards continental masses. The tectonic emplacement was normally associated with dismemberment of the original succession. Yet there exist some exceptionally well preserved ophiolites (e.g. Cyprus, Oman, Dongwanzi, China). A complete ophiolite sequence comprises (Anon 1972):

- Extrusive basalts of typical chemical (MORB) characteristics at the top, often in the shape of pillow lavas; ocean floor metamorphism of basalt increases from the zeolite facies at the top to greenschist facies at the bottom; however, many ophiolites display volcanic rocks with supra-subduction zone signatures.
- The sheeted dyke complex, consisting of vertical basalt dykes that strike parallel to the former oceanic graben; greenschist facies metamorphism is dominant but may grade into amphibolite facies near the footwall; contact metamorphism resulting from underlying melt bodies may occur; many ophiolites, however, lack sheeted dykes.
- The plutonic complex, comprising higher intrusive homogeneous gabbro, diorite, tonalite and trondjemite (“plagiogranite”), and deeper layered gabbro and peridotites, that display properties of cumulate rocks (the “cumulate sequence”); the magmatic rocks are normally not metamorphosed.
- The tectonized and depleted mantle, dominated by large masses of serpentinite (after harzburgite) and characteristic pods of dunite.

Various marine sediments may cover the igneous rocks, but most frequent are biogenic cherts and pelagic limestones. It is interesting to note that abiogenic exhalite cherts and jasper have only formed before the Middle Cretaceous; since that time, seawater is highly undersaturated with respect to silica because of the emergence of silica-consuming diatoms (Grenne & Slack 2005).

Formation of the ophiolite sequence can be modelled by partial melting of primitive mantle under mid-ocean ridges, due to mantle heat flow and the decompression caused by extension. The liquid rises in numerous melt batches and accumulates to fill large shallow magma chambers. These evolve by fractional crystallization and episodic volcanic processes. Mid-ocean ridges with low spreading rates are composed of sections with high magmatic activity that alternate with sections of tectonic rifting only. The first produces the typically layered ophiolite sequence ("Penrose Crust"); the second may lead to exposure of mantle rocks (serpentinites and peridotites: "Hess Crust"). The latter is quite inconspicuous because black smokers are very rare, and has received little attention. Superfast spreading rates produce thin crust and shallow melt bodies.

Economic interest focuses on deep ultramafic rock suites of the Penrose sequence (for chromite and platinum) and the near-surface volcanic hydrothermal system (for base metals). Tectonized (foliated) harzburgite and the lower cumulates host dunite bodies that may contain massive and disseminated chromite ore. Dunite in harzburgite can be understood as lag segregation from rising basaltic melt diapirs. Chromitites originate from dunite by liquid-liquid immiscibility. Because of ductile shearing in the oceanic mantle, both dunites and chromite orebodies are strongly deformed, resulting in lenticular pod-like shapes.

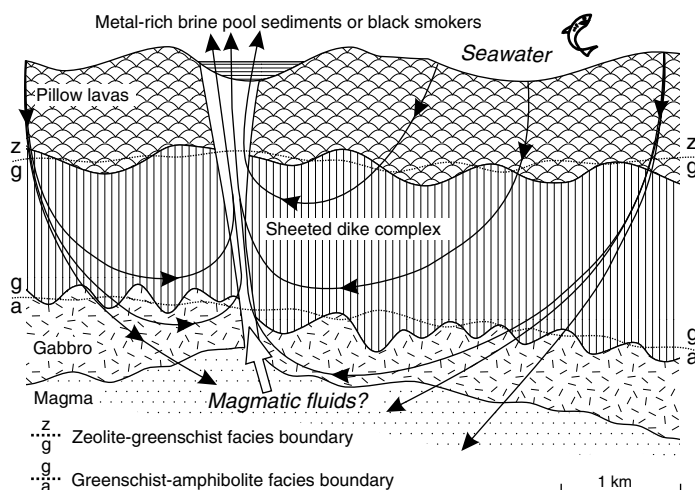
Chromites in cumulates occur in seams that lack early deformation.

From the beginning of geological history, newly-formed ocean crust was cooled by convecting seawater. This is at the origin of ocean floor metamorphism and possibly, of earliest life on Earth (Russell *et al.* 2005). Processes taking place along the mid-ocean ridges are interconnected with the whole Earth System (Halbach *et al.* 2003). Rising branches of convection cells transport metals and reduced sulphur leached from mafic and ultramafic rocks towards the ocean floor (Figure 1.10). Some of the volatiles and metals may be derived from magmatic fluids. More than 100 active submarine venting sites have been discovered over the last 30 years along the 60,000 km-long worldwide network of mid-ocean ridges. Most vents are basalt-hosted and of the black smoker type (Herzig & Hannington 1995).

Black smokers

Submarine black smoker vents are hydrothermal cones or chimneys that may reach a height of about 20 m, built on outcrops of bare basalt (Figure 1.11). From an opening at the top, a high-speed jet of hot clear fluid is ejected. The vents are tubes with zoned walls, from pyrite and chalcopyrite inside through sphalerite, marcasite, barite, anhydrite and amorphous SiO_2 to the exterior (Figure 1.12 and Figure 1.13). Oxidation of

Figure 1.10 Seawater convection, ocean floor metamorphism and focusing of rising hot fluids by apical parts of a mid-ocean magma chamber and by faulting (modified from Gass 1980). By kind permission of Geological Survey Department Cyprus.



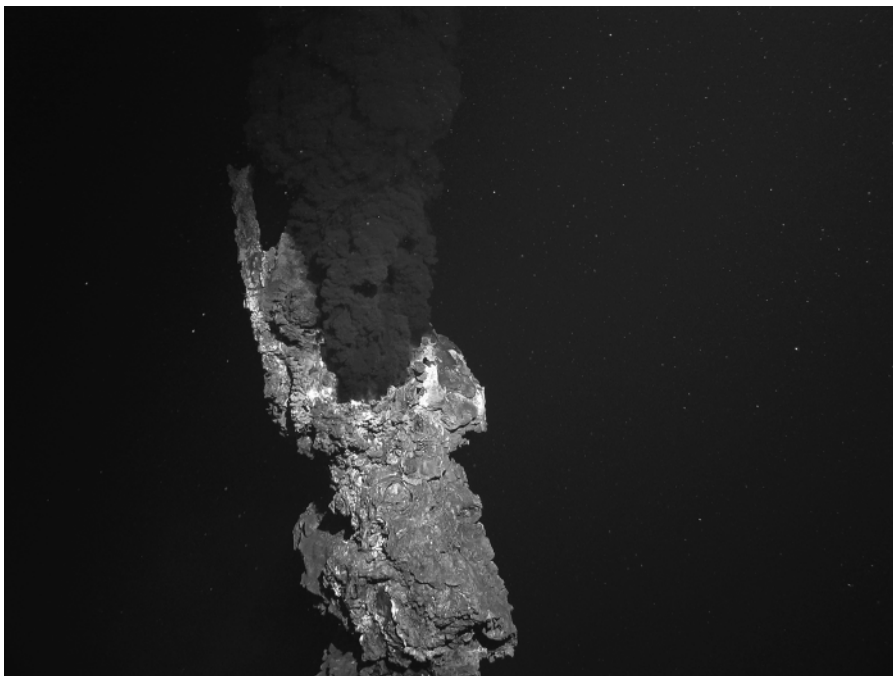


Figure 1.11 (Plate 1.11) Black smoker in the Mid-Atlantic Ridge graben, 4°48 S, 12°37 W, at a water depth of ca. 3000 m. Courtesy P.M. Herzig, IFM-GEOMAR (ROV Kiel 6000, 2009).

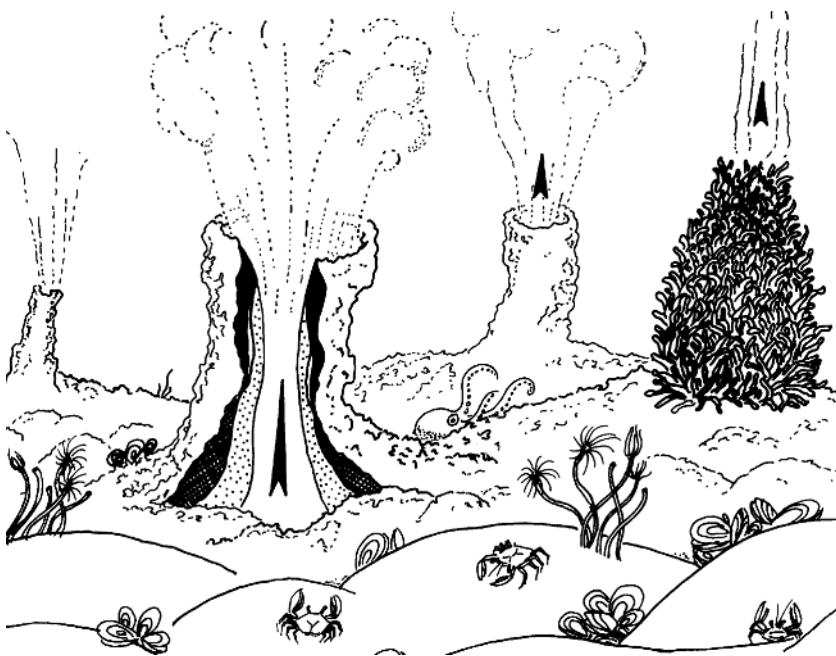


Figure 1.12 Hydrothermal vents on pillow basalt lava in a mid-ocean rift. Adapted from Haymon (1983). With permission from Macmillan Publishers Ltd. *Nature* © 1983. In the foreground “black smoker” vents, white smoker on the right. Section from interior to exterior: Dotted = Cu-Fe-sulphides; hatched = weathered sulphides; white = talc and sulphides; black = anhydrite and sulphides.

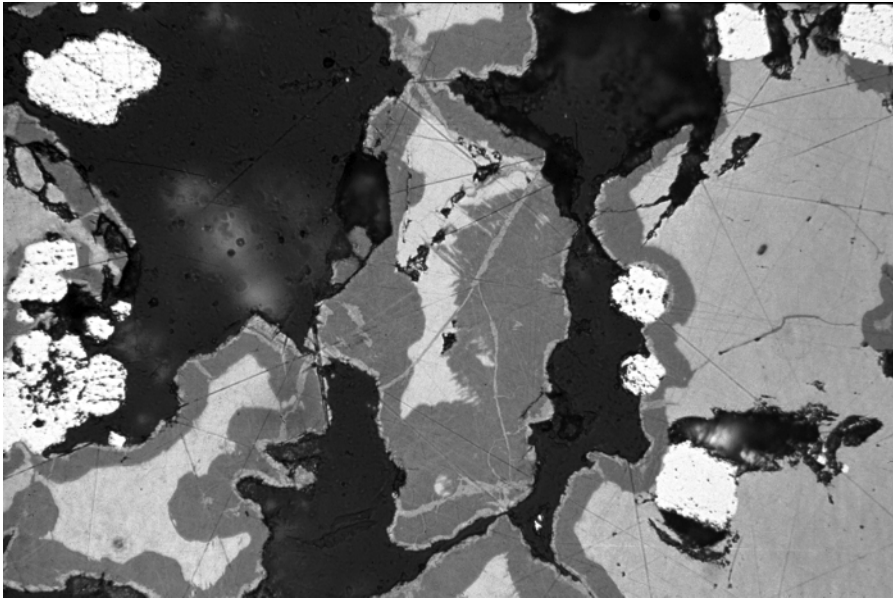


Figure 1.13 (Plate 1.13) Mid-oceanic copper mineralization in chimney fragments from inactive Sonne Field in the Central Indian Ocean. Courtesy P. Halbach (©FU Berlin). The polished section shows pyrite (white) as the earliest sulphide phase, followed by chalcopyrite (yellow), and increasing hydrothermal depletion of iron in bornite (Cu_5FeS_4 , blue-brown) and a thin rim of digenite (Cu_9S_5 , pale blue). The long side of the image corresponds to 0.6 mm. Pore space filled by casting resin is variably dark.

sulphides by seawater (“seafloor weathering”) produces varicoloured ochreous alteration fragments, which mainly consist of iron oxy-hydroxides that assemble on the floor around the vents and build gossan-like mounds. Because the leaky vent tubes draw in cold seawater, an amazing macro-fauna of large mussels, bright-red tube-worms, crabs and shrimp finds perfect ecological conditions (Van Dover 2000, Fisher & Girguis 2007). The base of the higher life forms are thermoacidophilic and hyperthermophilic chemotrophic microbes (bacteria and archaea, e.g. *Pyrolobus fumarii*) that inhabit the vent walls at temperatures up to 121°C (read more about archaea, the third domain of life, in Friend 2007). Macrofossils similar to some of the fauna living on active vents today were described from the Cretaceous sulphide ore deposits of the Troodos ophiolites on the Mediterranean island of Cyprus (Little *et al.* 1999). The expulsion temperature of the metalliferous solutions is most often at ~350°C. With 407°C (fluid) and 464°C (vapour), the highest

temperatures were measured in the equatorial Atlantic (Koschinsky *et al.* 2008). Alkaline “white smokers” and diffuse discharges of warm water with little dissolved matter have lower temperatures.

The hot Na-Ca-Cl fluids of the black smokers are reducing and have pH from 2 to 5.5 (mostly 4–5), salinities from 0.1 to 3 times seawater, elevated iron, copper, zinc, barium and SiO_2 , and traces of As, Cd, Li, Be, Cs, Mn, B, Cl, HCl, H_2S , and CH_4 . Different solutes are derived from various protoliths, possibly from magma, and reflect also different conditions of water-rock reactions. For example, copper is enriched relative to iron under moderately oxidizing conditions, whereas a low $f\text{O}_2$ results in a high Fe/Cu ratio (Seyfried & Ding 1993). Deep unboiled fluids display higher metal concentrations than vent fluids (e.g. Cu 14–17 ppm, Zn 5–27 ppm: Hardardóttir *et al.* 2009). Fluid properties change by phase separation, boiling, alteration and mineral precipitation during rise to the seafloor. Manganese, iron

and ^3He of the venting fluids disperse in ocean water and form a wide geochemical halo that is a guide to the search for submarine hydrothermal zones. Indications for supercritical unmixing of fluids before discharge into a depleted gas phase and a metal-rich brine were found at several spreading ridges. Supercritical unmixing and normal boiling followed by condensation of vapour and mixing of products are thought to explain the spread of salinities and unusual compositions of vent fluids (Cathles 1993). Only one site is known where fluids discharge at supercritical conditions (the critical point of seawater is at 298 bar and 407°C: Koschinsky *et al.* 2008).

Upon discharge at the ocean floor, hot acidic fluids mix with cold alkalic seawater, which results in immediate precipitation of solutes. If iron prevails, black or grey smoke-like plumes of amorphous iron sulphide and iron-manganese oxy-hydroxides rise several hundred metres upwards and disperse over a distance of many kilometres. Zinc forms bluish, SiO_2 , barite and anhydrite white clouds (white smokers). So-called “snow-blower vents” emit dense clouds of white filaments of native sulphur that is produced from H_2S by sulphur-oxidizing bacteria (Taylor & Wirsén 1997). Particle chemistry and ^3He , CH_4 and H_2S content of seawater near vents allow predictions of temperature and composition of vent fluids (Feely *et al.* 1994).

White smokers

White smoker vents discharge fluids between ~100 and 300°C (Halbach *et al.* 2003). They form mainly: i) in the early stage of a newly established hydrothermal system; and ii) by subseafloor mixing of hot black smoker fluid with cooler waters. The second probably leads to precipitation of sulphides at depth. Therefore, white smokers may indicate the presence of hidden stockwork and vein deposits of copper and zinc. In Figure 1.12, the third vent from the left in the background is a “white smoker”, consisting of barite, anhydrite and amorphous silica.

The activity of vents seems to be constant for a long time. Sudden large hydrothermal plumes are related to seismic seafloor spreading events, rapid

injection of dykes and seafloor extrusion of basalt lavas (event plume, or megaplume; Palmer & Ernst 1998). In common vents, seismic strain causes changing temperature and discharge rate.

The origin of mid-ocean submarine hydrothermal systems is mainly seawater convection in hot young oceanic crust, on top or above the flanks (Cathles 1993) of shallow magma bodies 1 to 3 km below the seafloor (Figure 1.10). This setting explains the steep geothermal gradient (up to 500°C/km), that is deduced from several observations. The required high permeabilities are provided by intensive tensional fracturing in mid-ocean rifts and around calderas. In the periphery, seawater flows downwards to more than 3 km depth. Because of the retrograde solubility of calcium sulphate, anhydrite is precipitated at moderate temperature during down-flow. At higher temperature and deeper levels, seawater reacts with basalts causing ocean floor greenschist facies metamorphism. Oxygen is rapidly consumed by reaction with Fe(II). Newly formed hydrated minerals (e.g. chlorite, amphibole) incorporate OH^- , which increases H^+ concentration in the fluid. The reduced state and high acidity favour dissolution of metals and of sulphur.

Alteration of basalt at low water/rock mass ratios leads to a paragenesis of albite, epidote, chlorite and actinolite. The product is greenstone (note the absence of penetrative deformation such as schistosity). Extreme alteration produces epidiosites (equigranular epidote-quartz-titanite rocks) and chlorite-quartz rocks (e.g. beneath the Bent Hill deposit: Teagle & Alt 2004). Similar alteration products are known from ophiolite-hosted sulphide deposits. Magmatic fluids may mix with altered seawater and do have a role in mineralization (Yang & Scott 1996, 2005), as indicated by high ^3He and CO_2 content, although stable isotopes imply mainly seawater. Part of the fluids could have a multi-stage history, for example dehydration of hydrated basalts by prograde thermal metamorphism induced by a new magma intrusion. Near transform faults, rocks of the deeper ophiolite sequence may be hydrothermally altered (e.g. formation of chlorine serpentinite from peridotite). Ultramafic-hosted hydrothermal systems produce highly reducing and high-pH

vent fluids, such as the Lost City hydrothermal field at 30°N on the mid-Atlantic ridge (Seyfried *et al.* 2007). In these systems, the coexistence of dissolved CO₂ and H₂ favours the formation of methane (toukos & Seyfried 2004). High-energy, fast-spreading mid-ocean ridges are dotted by submarine volcanoes and intrusions extending to an off-axis distance of 25 km from the graben margin. Hydrothermal fields and large ocean floor orebodies display a similar range (Fouquet *et al.* 1996).

Although most of the emitted metals are diluted in ocean water and sediments, approximately 250 metalliferous bodies of economic mass and grade have meanwhile been discovered. One example is a low sulphide mound on the mid-Atlantic rise at 26°N with a diameter of 250 m and a height of 50 m, that contains about 10 Mt of metalliferous sediments, sulphide debris and anhydrite, covered by oxidized sulphides and active as well as inactive chimneys. It is underlain by a sub-seafloor stockwork (Petersen *et al.* 2000). This is comparable to ancient volcanic-hosted massive sulphide (VMS) deposits of obducted ophiolites (the Cyprus type). The Bent Hill deposit on the San Juan de Fuca ridge is remarkably copper-rich, very much like the ores on Cyprus (Ziehrenberg *et al.* 1998). In the shallow crust beneath vent fields, large Cu, Zn and Au accumulations are probably formed by precipitation because of boiling and vapour loss during depressurization (Hardardóttir *et al.* 2009). Metalliferous mud in several depressions of the Red Sea represents the largest known submarine base metal mineralization. Sulphides in the Atlantis II basin, for example, cover 60 km² and reach a thickness of 30 m. The deposit comprises nearly 100 Mt (dry) of sulphides (Halbach *et al.* 2003). In these locations, the causative hydrothermal activity is not spectacular because metal-bearing solutions do not vent but discharge into stratified brines (Blanc & Anschutz 1995).

Ore deposits in ophiolites include two major groups: i) Chromite of the “Alpine” type (so-called because of the numerous former mines in the Alpine chains of southeastern Europe), in rare cases with co-precipitated exploitable platinum (Lord & Prichard 1997); and ii) exhalative volcanic massive sulphide (VMS) deposits of iron, copper and zinc sulphides ($\pm$ Ag and Au, but note the

virtual absence of Pb), including possible underlying stockwork ore. Because the ophiolite-hosted VMS deposits have been historically of great significance on the Mediterranean island of Cyprus, they are also termed “Cyprus type sulphide deposits”. However, most ophiolitic VMS sulphides are pyrite-rich and have low base metal grades. In the future, recently formed concentrations of this type that occur on the floors of the world’s oceans may become viable sources of metals. Ophiolites host other important mineralizations that they have “acquired” during obduction, nappe transport, deformation, metamorphism and finally weathering. These include asbestos, magnesite, gold (in listvaenite), talc, and lateritic Ni-(Cr-Co-Fe) ore in deeply weathered soil profiles.

1.1.3 Ore formation related to alkaline magmatic rocks, carbonatites and kimberlites

Rocks of these families generally have low SiO₂ and high alkali element content, especially of sodium and potassium. They occur commonly in cratonic, consolidated portions of continents, rarely within oceanic plates. An anorogenic setting is affirmed by their clustering near continental rifts, in lithospheric distension zones and over heat anomalies of the mantle (hot spots, plumes, superplumes). Occurrences of the typically “continental” rocks, nephelinite and carbonatite in association with oceanic intraplate volcanism, are very rare. Most magmas of this group originate by a low degree of partial melting of enriched mantle material, but for some melts the reverse is true. The enrichment may stem from subducted oceanic crust, or more probably, from metasomatized lithospheric mantle (Pilet *et al.* 2008). Nephelinite magma is the most common mafic alkaline liquid that crystallizes to give a range of igneous rocks (termed the ijolite suite). They are typically associated with the much rarer carbonatites that have a more prominent metallogenic role. However, complex intrusions displaying felsic rocks (e.g. A-type granite) in addition to the mafic ones are not rare. This is due to secondary melting and assimilation of deep continental crust.

Alkaline melts form in the subcontinental mantle lithosphere by rising temperature, falling

pressure, or under the influence of volatile and incompatible substances (mantle metasomatism), the ultimate origin of which may be mantle plumes or subducted crust. "Shallow" carbonatitic and deep kimberlitic melts with high CO_2 and low H_2O content originate in lithospheric mantle at 120–260 km depth. The high gas content facilitates rapid rise of magma diapirs to the surface where eruption takes place. The present outcrop pattern depends on the depth of erosion. By erosion to subvolcanic levels, ring complexes or diatremes are exposed, whereas recent uneroded examples are simple stratovolcanoes (such as the active alkali-carbonatite volcano Oldoinyo Lengai in the East African rift, Tanzania: Bell & Keller 1995; Figure 1.14). Examples of erosion to deeper levels are (B) Napak, Uganda and (C) Chilwa Island, Malawi. Kimberlite volcanoes build maar-like circular depressions or maar lakes.

Carbonatites

Carbonatites are igneous rocks with more than 50% of carbonate minerals. They are further subdivided depending on the nature of the carbonates (calcite, dolomite, and ankerite) and the silicate phases (biotite, pyroxene, amphibole, etc.). The formation of carbonatite-alkali complexes is probably controlled by i) fractional crystallization and ii) unmixing of carbonate and silicate melts (ijolite, pyroxenite and nepheline syenite) in the crust. Experimental and petrologic investigations of African carbonatites have shown that primary

carbonatite melt can also originate iii) by a very low degree of melting in the mantle at elevated $p\text{CO}_2$, temperatures of 930–1080°C and pressures of 21–30 kbar (Bailey 1993). Anomalous amounts of rare earth elements (REE) are remarkable features of carbonatites, especially of the light REE elements. Half of all known carbonatites occur in Africa, and of those, most are related to the East African Rift System.

Metals exploited from complex intrusions of carbonatite, alkali-pyroxenites and nepheline syenites include copper, rare earth elements, iron-titanium-vanadium, uranium-thorium and zirconium; non-metallic resources are the industrial minerals vermiculite, apatite, fluorite and barite, and limestone (Notholt *et al.* 1990). In southern Siberia, one mine produces nepheline syenite for Russia's aluminium industry. Three characteristic ore associations occur with carbonatites:

- 1 Magnetite-apatite carbonatite and nepheline (e.g. Khibiny, Kola Peninsula) are sources of pyrochlore (a niobium ore), copper (Palabora, South Africa) and zirconium $\pm$ hafnium; at Bayan Obo, Mongolia, iron, rare earth elements and niobium are exploited. worldwide, apatite is the prevalent mineral extracted from carbonatites;
- 2 Rare earths, fluorine and uranium; characteristic ore minerals are bastnaesite (as at Mountain Pass, California), monazite, and strontianite.
- 3 A hydrothermal paragenesis of barite, fluorite, manganese and sulphides.

The first group is orthomagmatic, often concentrated in aplitic and pegmatitic segregations. The

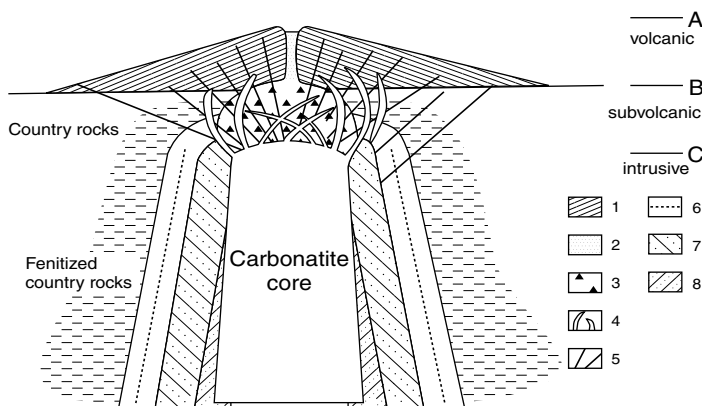


Figure 1.14 Hypothetical section of a carbonatite complex (modified from Kinnaird & Bowden 1991). With kind permission from Springer Science + Business Media. 1: Phonolitic and nephelinitic lava and tuff; 2: Natrocarbonatite; 3: Breccia; 4: Carbonatite ring dykes; 5: Carbonatite cone dykes; 6: Syenitic fenite; 7: Nepheline syenite; 8: Ijolite.

second is transitional, and the third occurs in hydrothermal-metasomatic or hydrothermal vein orebodies. Intruded silicate country rocks are fenitized. The term “fenitization” denotes alteration into a greenish rock consisting of alkali feldspar, aegirine and alkali hornblende. This alteration is a consequence of the high alkali element and volatiles content of carbonatite melt that are released during solidification (Bühn & Rankin 1999).

Kimberlites

Kimberlites are derived from the Earth’s mantle at more than 140 km depth. They are petrographically variable rocks and almost always comprise strongly altered breccias and tuffs. Basically, they are porphyric, SiO₂-undersaturated, K-rich (1–3 wt.% K₂O) peridotites with xenoliths, and xenocrysts of diamond, olivine, Mg-ilmenite and chrome-rich pyrope in a carbonated and serpentinized groundmass with accessory phlogopite, perovskite, Cr-spinel and magnetite (Mitchell 1991, 1986; cf. Chapter 3 “Diamond”). Extremely rare are unaltered kimberlites, which in Siberia have been found to contain at least 8 wt.% of water-soluble alkali chlorides, alkali carbonates and sulphates (Kamenetsky *et al.* 2004). Close relatives of kimberlites are the K-Mg rich, ultramafic lamproites that are characterized by leucite, titanium-phlogopite, clinopyroxene, amphibole, olivine and sanidine. Lamproites received more attention when the great diamond deposit Argyle in Western Australia was found to be hosted in this rock. Kimberlites occur most frequently in subvolcanic pipes and occasionally in sills and dykes, whereas lamproite magmas with lower CO₂ content also form shallow intrusions. Kimberlites in old cratons are more often diamondiferous than others, possibly because of the prolonged and complex evolution of the subcontinental lithosphere. Age dating revealed that kimberlites and their diamonds may have same or widely differing ages. This implies that diamond formation is not directly connected with the phase of melting that produces kimberlite liquid. Diamonds are rather exotic xenocrysts that have been passively extracted from the mantle, in several cases long after their crystallization. It is

important to remember that most kimberlites and lamproites contain no diamonds.

1.1.4 Granitoids and ore formation processes

Granitoids are felsic plutonic rocks with more than 20 mode % of quartz (Streckeisen 1976). The term is sometimes used in a wider sense to include more mafic rocks of an igneous suite.

Granitic rocks are commonly used as construction aggregates, building material and for the production of feldspar concentrates. Weathered granites are exploited for kaolin and quartz sand. Deep granite bodies are a potential source of geothermal energy extracted with the hot dry rock technology. In Sweden and in Finland, granites were chosen for the underground storage of heat-producing radioactive waste. In this chapter, however, the formation of magmatic and magmatic-hydrothermal ore deposits that are spatially and genetically related to granitoids will be discussed. Members of this diverse group include disseminated, stockwork and breccia ores of copper, molybdenum and gold (the porphyry deposits), highly differentiated small intrusions hosting tin and tantalum (“tin granites”), rare element pegmatites with ores of lithium, tin, tantalum and beryllium, skarn deposits of copper, lead and zinc, and hydrothermal vein and stockwork deposits of tin, tungsten and gold that occur in the roof of granite intrusions (Figure 1.15 and Figure 1.16). Apart from metals, many industrial minerals (e.g. fluorite, talc and wollastonite) can be enriched to exploitable grades in the magmatic and hydrothermal aureole of felsic intrusions.

The ore formation potential depends on origin and evolution of the parental granitoid. Important controls are the plate tectonic setting, the nature of source rocks, P/T-parameters of melting, content of water and other volatiles, the depth of intrusion, coeval tectonic deformation, partial pressure of oxygen (redox state) of the melt, assimilation of country rocks and the evolution of the magma by fractionation, cooling and crystallization including fluid segregation. Favourably coinciding factors account for the fertility of a granite intrusion. Understanding these controls and

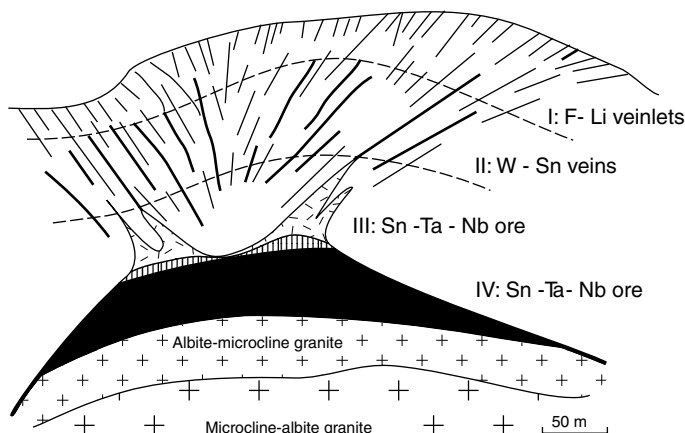


Figure 1.15 Schematic section of the granitic tantalum ore deposit Shuiximiao in southeastern China (modified from Zhu *et al.* 2001). With kind permission from Springer Science + Business Media. I - Fluorite-lepidolite; II - Wolframite-cassiterite-quartz, III - Pegmatite-aplite and stockscheider pegmatite; IV - Albite-topaz-granite. Host rocks are Early Carboniferous limestones and slates.

constructing a holistic model are essential for the search for new deposits (exploration) and for rational exploitation of granite-related orebodies.

Geochemical analysis of trace elements and of isotope systems in granitoids provides valuable information on the source rocks. Fundamentally distinct sources of granitoids are:

- 1 peridotites of the Earth's upper mantle (asthenosphere, lithosphere);
- 2 magmatic and metamorphic rocks of the deep continental crust (infracrustal);
- 3 clastic metasediments and metamorphic equivalents (supracrustal);

4 restites of sediments and of magmatic rocks that have experienced earlier anatexis before a later melting event.

Ad 1: M-type granitoids are sourced in the mantle. Together with gabbro, they intrude the crustal rocks of ophiolites in the form of plagiogranite and quartz diorite, and the thick volcanic piles of primitive oceanic island arcs. Typical ore deposits associated with M-type granitoids are copper-gold porphyries and hydrothermal gold.

Ad 2: I-type granitoids are the most common intrusive magmatic rocks. They display an

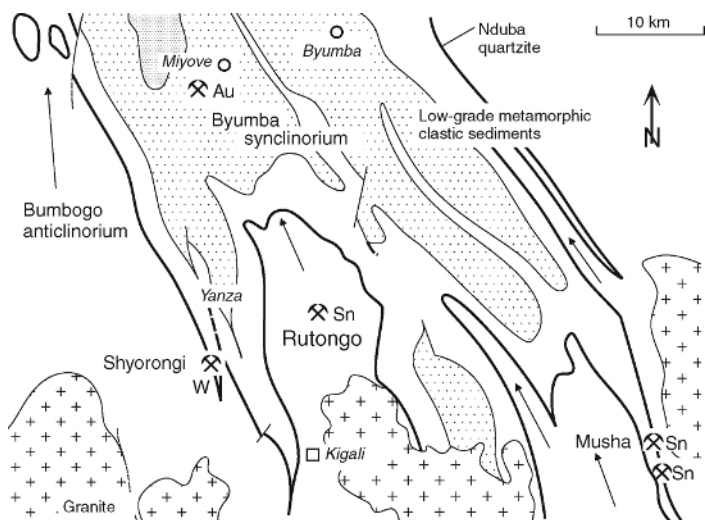


Figure 1.16 Pegmatitic tin (Musha) and magmatic-hydrothermal vein deposits of tin, tungsten and gold in the sedimentary roof of Mesoproterozoic (950 Ma) granites in the Kibara orogen, Rwanda (Pohl 1994). Thick lines denote the distinctive Nduba quartzite marker band. Rutongo produced a total of about 30,000 t cassiterite, Shyorongi ca. 2500 t wolframite. Miyove is a small artisanal mine working a gold vein deposit.

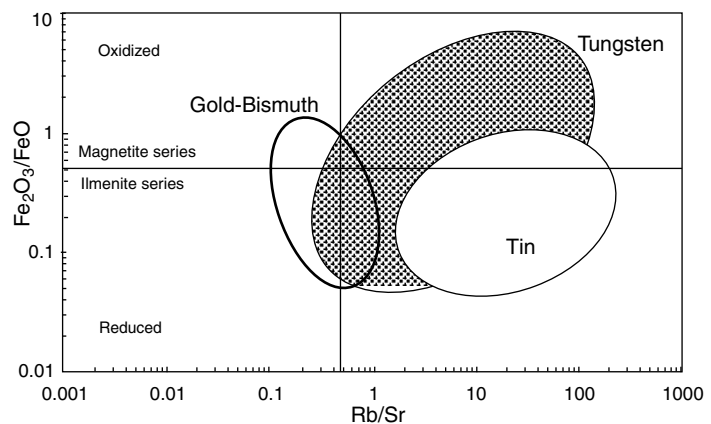
abundance of hornblende and higher concentrations of Ca, Na and Sr compared with granites derived from sediments. Typically, large plutons consist of tonalites and granodiorites, but are often intimately associated with more basic rocks from gabbro to diorite. Some of these melts were undersaturated with water, which enabled them to rise to the surface, forming volcanic rocks (e.g. andesite and dacite). It is commonly accepted that I-type granitoids originated by melting of pre-existing infracrustal igneous rocks (Blevin & Chappell 1995). However, geochemical and isotopic I-type characteristics can also be explained by mixing of rising mantle magmas with anatectic lower as well as upper crustal melts (Kemp *et al.* 2007). Accessory minerals of I-type rocks are often magnetite and titanite, causing their attribution to the class of magnetite-series magmatic rocks (Ishihara 1981, Figure 1.17). This is due to a commonly higher oxidation degree of these magmas, although reduced I-type granitoids are known. Characteristic ore deposits related to oxidized granitoids are the iron oxide-copper-gold (U-REE) deposits (IOCG), copper-molybdenum porphyries, Mo-W-Cu skarn, hydrothermal lead-zinc and certain gold and silver ores.

Ad 3: S-type granitoids originate by continental collision and deep subduction of sediments to great depths and high temperatures, where the transition between metamorphism and significant

melting is attained (Clemens 2003). Products of these partial melts are mainly leucocratic, SiO₂ rich rocks of a monzogranitic nature, often with muscovite besides biotite. Accessory minerals include cordierite, garnet, kyanite and ilmenite as the prevalent opaque mineral. This is why S- (and A-) granites are part of the ilmenite-series magmatic rocks (Ishihara 1981, Figure 1.17). The degree of oxidation of these magmas is low, due to organic carbon in the source sediments. The water of the melts is derived by dehydration of muscovite in the metasediments. The resulting melts are rather “wet” and crystallize at greater depth. Therefore, volcanic rocks are rare in this group. In the Palaeozoic Lachlan Fold Belt (Australia), both I- and S-type granites are common. Highly fractionated intrusions (“tin granites”) of both suites are clearly associated with tin, tungsten and tantalum ore deposits (Blevin & Chappell 1995).

Ad 4: A-type granitoids are the product of repeated melt-extraction from the same source rocks (Eby 1992). Note that with every cycle of melting the source rocks acquire a more pronounced restite composition, marked by enrichment of less mobile substances. The “A” in the term may be translated into “abnormal, anhydrous, alkali rich, aluminous and anorogenic”. Another possible source of A-type magma is lithospheric mantle (Turner *et al.* 1992) and not all A-granites are anorogenic (Whalen *et al.*

Figure 1.17 Typical fields of granites which are genetically associated with tungsten, tin and gold-bismuth deposits, in a plot of redox-state (vertical axis) versus increasing specialization (horizontal axis). Modified from Baker, T., Pollard, P. J., Mustard, R., Mark, G. and Graham, J. L. 2005, Society of Economic Geologists, *SEG Newsletter*, Figure 4, p. 12.



1987). Some granites that have A-type characteristics may be derived by extreme fractionation of I- and S-type magmas (Creaser *et al.* 1991; Taylor & Fallick 1997). Typical A-type granites are the alkali granites of continental rifts, for example the Jurassic tin-mineralized Younger Granites of Nigeria and the Mesoproterozoic Rapakivi granites in Finland, with their large red perthitic alkali feldspars mantled by green plagioclase. Volcanic equivalents include tin-rich topaz rhyolites in fields of crustal distension (Tertiary volcanics in Mexico). Two different ore associations occur with A-type granitoids: i) Sodium-rich granites, striking because of attached albitite bodies, contain concentrations of niobium, uranium, thorium, rare earth elements and some tin, whereas; ii) potassium-rich granites with profuse hydrothermal silicification, tourmalinization and acidity produce deposits of tin, tungsten, lead, zinc and fluor spar. The second association may occur within the granite body (endogranitic greisen, pegmatite, and porphyry stockwork ore) or in vein fields within intruded rocks (exogranitic).

HHP (high heat producing) granites

These granites are U-Th rich granitoids that attract attention because they seem parental to hydrothermal deposits, which formed much later than the granite:

The Early Devonian Weardale granite in Northern England, for example, seems to have produced the hydrothermal Cu-Pb-Zn-fluorite-barite ore deposits of the North Pennines in the Permian. The explanation is its long-lasting heat production due to elevated amounts of K, U and Th (Plant *et al.* 1985), which produce heat by radioactive decay. Latent heat is one element of the HHP ore-forming systems. The second is sufficient permeability that allows deep circulation of down-flowing, usually meteoric water. Crustal permeability is commonly created by tensional tectonic fracturing. Heated water at depth can dissolve substances that are precipitated during ascent. Note that HHP-stocks must be quite large with a minimal diameter of 15 km and a considerable depth extension because the heat of small granites is rapidly dissipated. Typical HHP-granites include the

post-orogenic Variscan tin granites of Cornwall, which are related to important polymetallic mineralization and are now explored for the production of geothermal energy.

Not all granites can be assigned to one of the source categories because of several reasons including complex mixtures of source rocks and extreme fractionation, which leads to increasing convergence of magma chemistry (Taylor & Fallick 1997). This is why the youngest granites in orogenic provinces geochemically approach those that occur in anorogenic settings such as continental rifts, zones of crustal extension and continental "hot spots" (Turner *et al.* 1992). These observations motivate classification of Phanerozoic (and older) granitoids according to tectonic setting: Island arc, active continental margin, post-orogenic uplift, continental collision and continental rifting granitoids (Pitcher 1997).

A time-dependent chemical evolution of intrusions has been noted in many granite-related ore provinces of the world: Early batholithic intrusions (i) are geochemically ordinary, whereas later and smaller precursor granites(ii) are transitional to small, geochemically specialized (iii) and to usually very small, mineralized granites (iv), which are intimately related to ore formation.

Compared with ordinary granites, precursor granites display higher content of K, SiO₂ and granophile trace elements, and less Fe, Ti, Ca, Sr and Mg. Precursor intrusions always predate specialized granites, although they are genetically related. Specialized and mineralized (parental) granites are distinguished by geochemically elevated content of metals, such as Sn, W, Nb, Ta, Mo, U, Th, REE, Rb, Cs, Li, Be, often F (the latter include "topaz granites") and P (Figure 1.17 and Figure 1.18). Petrographically, specialized and mineralized granites are mostly aplitic muscovite-biotite rocks, alaskites and leucogranites that intruded at shallow crustal levels. In specialized granites, rare elements are enriched in silicates and accessory minerals. Mineralized or parental granites, in contrast, stand out by their close relations to ore-grade concentration of rare elements. The geochemical changes from ordinary to mineralized granitoids are mainly caused by a process

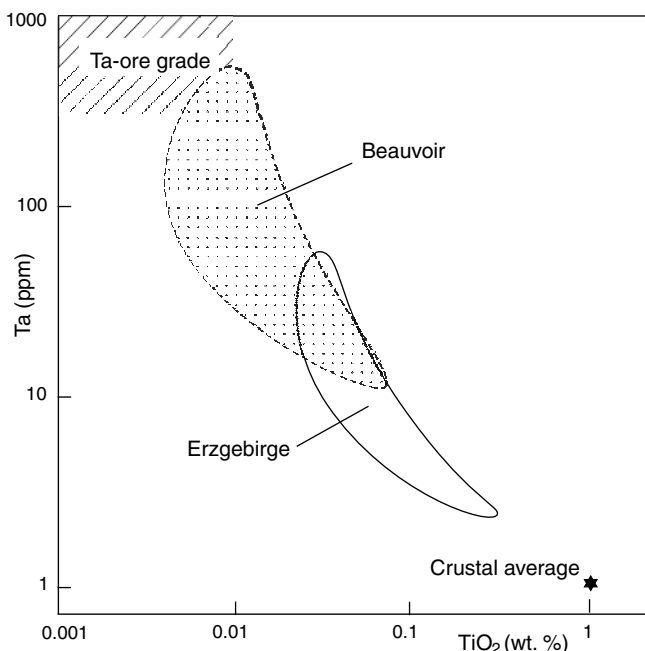


Figure 1.18 Ta/TiO₂ variation of granites from the northern French Massif Central (Beauvoir) and the Saxo-Bohemian Erzgebirge (modified from Lehmann 1990). With kind permission from Springer Science+Business Media.

system, which is generally termed “magmatic fractionation” (see below). The degree of fractionation may be measured by various indices. In metallogenetic research dealing with granitoids, increasing Cs concentration in melt, minerals and fluids is a particularly useful tracer of fractionation (Audétat *et al.* 2008).

Granites and related pegmatites with extreme chemical fractionation are the source (and often the hosts) of deposits of rare elements including Sn, Li and Be. They are enriched in large ion lithophile elements (LILE) such as Rb and Cs, and high field strength elements (HFSE) such as P, Y, Zr, Hf, Nb, Ta, Th and U (Linnen & Samson 2005). If ordinary and precursor granites are present, the enrichment may be traced back to common, geochemically not anomalous crustal rocks (Lehmann *et al.* 2000b, Cerny 1991). Figure 1.18 illustrates this principle and shows how tantalum (an incompatible element) is continuously enriched by increasing differentiation of successively more fractionated (and younger) granite melt batches and finally reaches exploitable grades. Concurrently, concentrations of the compatible element titanium decrease. Derivation of

tantalum from geochemically ordinary crust appears possible.

The increasing differentiation of magmas is caused by fractional crystallization, early crystal settling and/or removal of liquid melt from a solid framework of phenocrysts (Weinberg 2006). Other explanations include a very low degree of partial melting (Robb 2005), or unmixing of melts because of fluid saturation. In some cases, melting of geochemically anomalous source rocks is considered to account for metal enrichment. An example are magmas with a high content of the chalcophile elements Au, Ag, Bi, Sb, Hg and Tl, which are supposedly inherited from a pre-enriched melt region (Tomkins & Mavrogenes 2003). Giant molybdenum porphyry deposits of the southwestern USA are thought to be extracted from an inherent large-scale Mo enrichment of the crust or lithospheric mantle (Klemm *et al.* 2008).

The petrological evolution of mineralized granites can be schematically subdivided into two phases: The first phase comprises the fractionation of elements between melt and early solid phases that crystallize during cooling, and is followed by a second phase of partitioning of trace

elements between the small remaining melt fraction and exsolving fluids, which concentrate volatiles and metals:

Elements that partition preferentially into the solid phase are referred to as compatible because they are included in nascent rock-forming silicate minerals, for example europium in plagioclase. Incompatible elements concentrate in the liquid (melt) phase. Lithophile or oxyphile elements are common in crustal silicates but are incompatible with minerals that have an important role in the formation of mantle magmas (e.g. olivine, pyroxene, spinel, garnet). Lithophile elements include Al, Si, O, alkalis, earth alkalis, rare earth elements and actinides, as well as metals such as Ti, Ta, Nb and W (Goldschmidt 1958). LIL elements (large ion lithophile) such as Rb, Sr, K, Ba, Zr, Th, U and light REE are preferentially enriched in late, highly differentiated melt derived from restites, because these elements are less prone to partition into early water-rich liquids. Cations with a high charge ($+3$ to $+6$) such as Mo, Nb, Zr, Sn, W, Ta, U, Th, Y and REE are normally abstracted from the melt by incorporation in crystallizing biotite, amphibole, apatite, zircon, monazite and magnetite. This process is inhibited by high activity of complexing volatile compounds, which cause these HFS (high field strength) elements to collect in late liquid and fluid phases. Because this is uncommon, elements such as Ti, Zr, Y, Ta, Nb, Hf, Th and REE are generally immobile and useful petrogenetic indicators (Pearce 1982, Pearce *et al.* 1984).

The fertility of granitoids is closely related to differentiation, fractionation and the formation of exsolved magmatic volatile phases. The composition of magmatic volatile phases is investigated by sampling volcanic exhalations, fluid inclusions in minerals (especially from miarolitic cavities) and volatiles included in volcanic glass. Miaroles are crystal-lined cavities in granitoids that are thought to have formed from fluid pockets during the solidification of magma. Fluid and melt inclusions preserved in miarolitic minerals reveal details about segregation, composition and evolution of mineralizing fluids (Audétat *et al.* 2008).

Water is the most common substance in magmatic volatiles. In silicate melts, dissolved water reaches a maximum of 8 wt.% or 25 mole % (Ochs & Lange

1999). Arc magmas are more hydrous (and more oxidized) than those of other tectonic settings. Water is followed in decreasing order by CO_2 , H_2S or SO_2 , HCl and HF, and small amounts of N_2 , H_2 , CO, P, B, Br, CH_4 and O_2 . Trace elements in volcanic emanations include the metals Pb, Bi, Cd, Cu, Zn, Hg, Sb, Te and As, and major rock-forming elements such as Al, Mg, Na and K. The annual exhalative emissions of Etna volcano, Sicily, include ~ 2.5 t lead and 250 t potassium. Metal fluxes in vapour from White Island volcano, New Zealand, are estimated to >106 t Cu and 100 t Au in 10,000 years of volcanic activity (Hedenquist *et al.* 1993). Different volcanoes have ratios of SO_2/HCl and SO_2/HF between 1 and >100 . Ratios from 1 to 10 are typical for volcanoes above convergent plate boundaries, because they discharge more HCl. Gas released in explosive mode by Stromboli volcano (Italy), for example, consists of 64% H_2O , 33% CO_2 , 1.8% SO_2 and 0.33% HCl (Burton *et al.* 2007). Note, however, that molecular HCl is only stable at very low pressure or in the absence of water. Above 200 bar, chlorine occurs as an ion or is dissolved in magmatic water as a complex with Na, K and Fe. In epizonal magmatic water, the average chlorine concentration in solution is 3.5%, or 6 wt.% (range 2–10) NaCl equivalent. The segregation of saturated or hypersaline solutions is only possible at pressures >1.3 kbar. In that case, a hypersaline solution (or should it better be called a hydrous saline melt?) at 700°C contains 84% NaCl.

Fertile granitoid magmas are distinguished by high content of volatiles. Volatiles collect the rare elements that form ore, and also lower density, viscosity and solidus temperature of a melt increasing its mobility (Baker & Vaillancourt 1995). Low magmatic temperatures and high salt concentrations favour the fractionation of metals into the fluid phase (Audétat & Pettke 2003). Oxygen fugacity in the melt is an important control (Figure 1.17). High oxygen in granitic magma causes depletion of tin and tungsten in the liquid and in late fluids, because the metals are abstracted in dispersed accessory minerals already during main-stage crystallization. Behaviour of copper and uranium is quite the reverse. Oxidized magmas (of the magnetite series) dissolve more sulphur (as an “anhydrite component”, compare Streck & Dilles 1998) and derived fluids may produce large Cu-Au deposits. In “reduced”

granitic magmas (ilmenite series), early sulphur saturation causes formation of dispersed sulphide droplets that collect copper and gold. Late fluids will be barren.

Formation of a volatile phase (degassing) during the ascent of silicate magmas through the crust is initiated by decreasing pressure, or in the case of roof fracturing, by sudden decompression ("first boiling"). The solubility of CO₂ in basaltic magmas can decrease rapidly at a depth of 70 km, but most basalts reach this stage at 10 to 15 km below the surface (Lowenstern 2001). Supersaturation leads first to formation of bubbles of liquid CO₂ that expand with further ascent until the density reaches that of gas. Water has a similar behaviour, although changes occur at shallower depths. As a function of the total water content in melt (commonly 3–5%, maximum 6–8 wt.%) and chlorine concentration, felsic magmas start to segregate an aqueous fluid phase at a pressure of ~260 MPa (ca. 9 km, but more often around 4 km below the surface). Commonly at this stage, the melt body will freeze. Kinetic factors may, however, allow further ascent of the magma. In that case, expansion of fluid bubbles will produce a frothy liquid that is able to convect vigorously. Rare elements are effectively scavenged from the melt, and as the fluids move upwards, ore formation can take place either in the apex of the intrusion or in its roof. The remaining melt solidifies rapidly.

After final emplacement, when ascent is stopped and first boiling is finished, the intensive formation of solid phases from melt causes renewed concentration of volatiles. If the amount of volatiles is higher than the mass that can be included in minerals (e.g. OH⁻ in mica), a free volatile phase will form once more ("second boiling"). In the case of relatively shallow intrusions, fluid pressures may cause fracturing of the roof and sudden injection of mineralizing fluids. In this case, fluid-induced stress is larger than the sum of rock mass strength and the minimum natural principle stress (Brady and Brown 2004). Unmixing of a fluid phase from mesozonal intrusions (at pressures >2 kbar) is restricted to a narrow temperature interval. Often in this environment, volatiles form small batches of fluid-rich silicate melt that solidify to coarsely crystalline pegmatites. Shallow epizonal

intrusions degas over a wide temperature interval (Fournier 1999), producing miarolitic and hydrothermally altered granites, but foremost the many variegated magmatic-hydrothermal ore deposits.

In Japan, granites related to magmatic-hydrothermal mineralization display a correlation between the main ore metals and the solidification pressure of the parent pluton. Total Al-content in biotite, the sphalerite and hornblende geobarometers and the petrology of surrounding rocks all suggest that Pb-Zn and Mo deposits formed at pressures of less than 1 kbar, Cu-Fe and Sn at 1 to 2 kbar and W deposits at 2 to 3 kbar (Uchida *et al.* 2007). Deeper intrusions are barren. The principle, although not the precise figures, may be of a wider significance.

In the past, a "pneumatogenic phase" of ore formation was distinguished between pegmatitic and hydrothermal conditions. The assumption was that certain ores were formed by precipitation from a magmatic gas phase of extreme mobility and with high concentrations of rare metals. Greisen orebodies of tin and many skarn ores were thus explained. More recently, the term is rarely used and often explicitly dismissed. Arguments include that water vapour (with a density below the critical density of 0.32 g/cm³) cannot carry more than traces of dissolved matter, and supercritical fluids with densities that reach 2 g/cm³ can hardly be called a gas (Roedder 1984; remember that *pneuma* in classical Greek is "air" or "breath"). Furthermore, the distinction is thought to be difficult, because supercritical fluids may pass into subcritical solutions or gases without any discontinuity (condensation). The limit between pneumatogenic and hydrothermal conditions had been assumed at the critical temperature of water, which occurs at 374°C and 225 bar, but rises as a function of solute concentration:

Even if there is no need for the old term, attention must be drawn to the fact that supercritical fluids do have properties that differ from solutions with the same composition: The density of supercritical fluids varies widely with changing pressure and temperature; they have higher pH (Ding & Seyfried 1996), are able to dissolve many organic substances, and exhibit extreme dissociation of water and diffusion

coefficients. Geologically most important are probably the variable density (from dense fluid to gas), reaction rates and equilibrium constants that control transport and precipitation.

Of course, there is no doubt that magmatic gases and fluids of low density can transport metals (e.g. Etna volcano in Sicily) and precipitate ore. Cassiterite-quartz veins in the Mole granite, New South Wales (Australia), contain two types of inclusions: a saline brine (a solution) with elevated trace content of Mn, Fe, Zn, Pb and Sn, whereas the other is "gas" with ~1% Cu. Observations suggest that both are cogenetic and unmixed from magma. Copper was concentrated into the gas phase (Heinrich *et al.* 1992). A broader investigation of magmatic-hydrothermal ore deposits revealed that boiling of magmatic fluids concentrates Cu, As, Au and B preferentially into the vapour phase, whereas Na, K, Fe, Mn, Zn, Rb, Cs, Ag, W, Sn, Pb and Tl are enriched in the residual saline brine (Heinrich *et al.* 1999, Williams-Jones & Heinrich 2005). The most important controls on this behaviour appear to be fluid density (Pokrovski *et al.* 2005) and sulphur content (Nagaseki & Hayashi 2008).

Exsolution of magmatic fluids and hydrothermal ore formation are an integral part of ascent and crystallization of an intrusion. Cooling down to environmental temperatures drives meteoric, convective hydrothermal systems that are often called "geothermal". In these systems, magmatic fluids and volatiles typically mix with meteoric water. Age determinations, model calculations and observation in nature reveal that an isolated single upper crustal intrusion may sustain a hydrothermal system for ~100,000 years (Cathles *et al.* 1997). Magmatic-hydrothermal processes can be prolonged to millions of years in the case of incremental growth of a pluton by multiple intrusions, regional deep magmatism and autonomous heating, due to radioactive decay that retard cooling.

1.1.5 Ore deposits in pegmatites

Pegmatites crystallize from highly fractionated hydrous residual melt batches of felsic magma

bodies that are enriched in volatiles and incompatible trace elements. Pegmatites are characterized by coarsely crystalline textures, occasionally by giant crystals, miarolitic cavities and by minerals of rare elements. Most pegmatites are related to granites and have a paragenesis of orthoclase (perthite), microcline, albite, mica and quartz. Common minor minerals include tourmaline, topaz, beryl, cassiterite and lithium minerals. Felsic pegmatite melts intruding ultramafic rocks suffer desilication resulting in plumasites that are characterized by corundum, kyanite and anorthite. Gabbro pegmatites are derived from mafic magmas and are composed of anorthite, pyroxene, amphibole, biotite and titanomagnetite, occasionally including carbonates and sulphides (similar to the Merensky Reef "pegmatoid" of the Bushveld Complex). Iron-rich ultramafic pegmatites composed of olivine intrude the cumulates of the upper Critical Zone of the Bushveld Complex (Figure 1.5). Rare syenite pegmatites with microcline, nepheline, apatite, niobium and rare earth element minerals are related to alkaline intrusions. Certain diamonds are thought to have crystallized from kimberlitic pegmatite melt deep in the mantle (Moore 2009). Anatectic pegmatites (metamorphic segregations) that are formed in the upper amphibolite facies are rarely mineralized. Yet, some mineralized pegmatites may have originated by partial anatexis at great depth and not from large magma bodies (e.g. the uranium-molybdenum-rare earth pegmatites of the Grenville orogen: Lentz 1996). Most pegmatites crystallized at intermediate crustal levels, at fluid pressures of ~200 MPa (2 kbar). Therefore, they are commonly found in metamorphic country rocks. Volcanic equivalents of highly differentiated pegmatitic melts are extremely rare.

Classifying granitic pegmatites by their emplacement depth leads to differentiation of the following types:

- Abyssal pegmatites are anatectic stringers in migmatites of amphibolite and granulite facies metamorphic zones.
- Muscovite pegmatites occur in amphibolite facies kyanite-mica schists and are commonly related to granites, but exhibit little fractionation.

- Highly fractionated rare element pegmatites are derived from strongly differentiated fertile granites; host rocks typically contain cordierite and andalusite.
- Mirolitic pegmatites form at low pressure (1.5–2 kbar) and are proximal to granites. They may contain quartz of optical quality, various gemstones and valuable crystals of many rare minerals.

Granitic pegmatites occur in the form of dykes, oval and lenticular bodies. Most pegmatite bodies are relatively small with a thickness that rarely surpasses tens of metres and a length of a few hundred metres. Some pegmatites occur at the roof of granite cupolas and form a thin shell between the intrusion and the roof rock (stock-scheider, i.e. “border pegmatite” in the German Erzgebirge). Giant pegmatites of this type are rare but economically significant (e.g. the tin-tantalum and spodumene pegmatite at Manono, D.R. Congo, which extends over $\sim 12 \text{ km}^2$). Granitic pegmatites may be homogeneous (without a change of mineralogy or texture from wall to wall) and isotropic, or strikingly inhomogeneous and anisotropic (“zoned” or “complex” pegmatites). In contrast to the zonation of the interior of a pegmatite body, an external zonation can also be observed. This term designates the occurrence of different pegmatite types in one district, with a map-scale zonation, ideally around a central parental granite (Figure 1.19 provides pegmatite

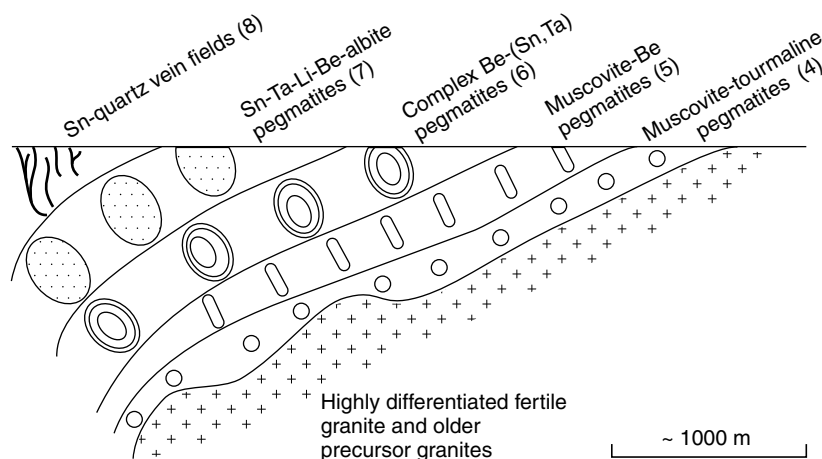
compositions of the field classification by Varlamoff 1972).

The internal zonation of complex pegmatites (Figure 1.20) reflects crystallization from the walls to the centre of a pegmatite body where the last melt solidified. The following zones are distinguished:

- *Border zone*: often fine-grained, aplitic, and very thin;
- *Wall zone*: coarsely crystalline, in some deposits with exploitable muscovite and beryl;
- *Intermediate zones*: which contain most of the valuable minerals (cassiterite, columbite, spodumene, beryl, etc.); the outer intermediate zones are often sugary albitites, followed by coarse albitite (cleavelandite) or microcline towards the core;
- *Core*: which is commonly a solid mass of barren grey or white quartz, but may also contain feldspar, tourmaline and spodumene.

Subhorizontal pegmatite sheets often have asymmetric zones, in contrast to the concentric zones that characterize most steeply-dipping bodies. Flat-lying pegmatites typically display bottom-to-top differentiation (e.g. Kenticha in Ethiopia: Küster 2009). Some cases of internal zonation are so complicated as to appear chaotic. Post-solidus cross-cutting fracture fillings, irregular metasomatic masses and hydrothermal quartz veins can further disarrange the internal structure. Because of crystallization from the wall to the centre, exsolving aqueous fluids will act from

Figure 1.19 External zonation of rare element pegmatites and cassiterite-quartz veins near fertile granites in Central Africa (adapted from Varlamoff 1972; cf. Figure 1.16). With kind permission from Springer Science+Business Media.



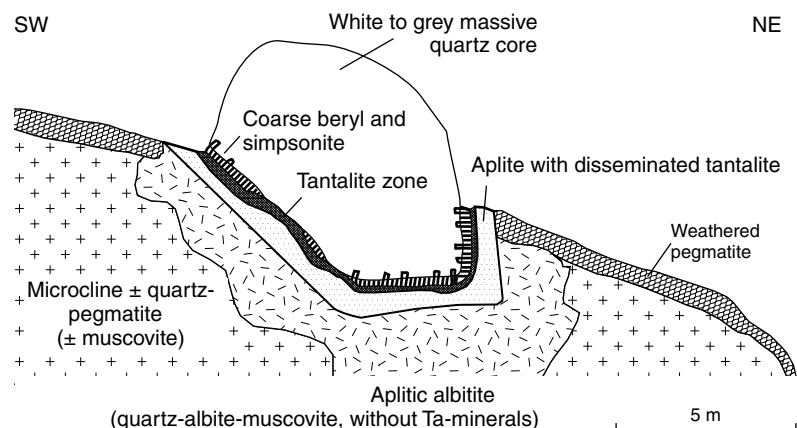


Figure 1.20 Section of the Mesoarchaean tantalum-tin-beryllium pegmatite at Tappa Tabba near Port Hedland, northwestern Australia, with a well-developed internal zonation. After Sweetapple, M.T. & Collins, P.L.F. 2002, Society of Economic Geologists, *Economic Geology* 97, Figure 5, p. 882. Simpsonite is $\text{Al}_4(\text{Ta}, \text{Nb})_3(\text{O}, \text{OH}, \text{F})_{14}$ and indicates extreme fractionation.

the centre outwards. Therefore, post-solidification hydrothermal alteration of magmatic minerals is not rare (e.g. sericitization, kaolinization).

In contrast to granites, pegmatites frequently exhibit striking anisotropic textures. Most obvious examples are the giant crystals of amblygonite-montebrazite, beryl, topaz, tourmaline and other minerals that grow inwards from the cooling surface ("unidirectional solidification textures": Shannon *et al.* 1982). Related features are bands in sugary albitites, and graphic, skeletal or radial crystal growth.

Alteration of host rocks at the contact with pegmatite is often observed. However, the nature of this alteration is not of high-temperature contact-metamorphic type but hydrothermal, for example tourmalinization, silicification and propylitization (cf. "Hydrothermal Host Rock Alteration"). The alteration is due to expulsion of water and other volatiles from the pegmatite. A chemical exchange directed from enclosing rocks to the pegmatite is also possible, as shown by garnet appearing in the wall zone, the plumasite formation mentioned above, or the occurrence of a tourmaline border zone that is due to reaction of iron and magnesium mobilized from the host rocks with boron from the volatile phase of the pegmatite.

Cooling and crystallization of pegmatite melt bodies induces the segregation of immiscible liquid phases, which may include a peraluminous melt containing less water, and a water-rich peralkaline melt, as at Ehrenfriedersdorf in Germany,

co-existing from 720–490°C (Rickers *et al.* 2006). Other phases, such as hydrosaline melt (a highly concentrated aqueous fluid), saline fluids and a vapour phase may appear at certain evolution stages. Inclusions of co-existing melts and hydrothermal fluids in quartz confirm this model (Rickers *et al.* 2006, Thomas & Webster 2000, Thomas *et al.* 2000). Ordinary unmineralized pegmatites crystallize at temperatures between 690 and 540°C, whereas fractionated melts with elevated content of boron, fluorine, phosphorous, chlorine, etc. finally solidify at ~450°C. Below the solidus, aqueous fluids dominate the system. Undercooling of the melt bodies injected into cooler host rocks may play an important role in the formation of zoned pegmatites (London 2008). The development of giant crystals seems to contradict the concept of undercooling, but a low density of nucleation sites, water-like viscosity of the peralkaline and hydrosaline melts, and high diffusion rates explain its feasibility.

The internal zonation in complex pegmatites might have two causes: i) fractional crystallization in a closed system; or ii) repeated injection of new melt batches in an open system. The worldwide similarity of zoned pegmatites (and many other data) argues for a closed system. Undercooling and back-reaction between remaining melt and earlier solids are the main factors supporting the "disequilibrium fractional crystallization through liquidus undercooling hypothesis" (London 2008). The unusual occurrence of nearly monomineralic

rocks such as albitites and part of the enrichment of metals can probably be explained by zone refining. This concept assumes that pore liquids in outer zones, consisting of semi-solid crystal mush, take up solutes and move inwards.

The external zonation of different pegmatites around parent intrusions is explained by the increasing mobility of more fractionated melts, because increasing fractionation lowers solidus temperature, density and viscosity of melts (Cerny 1991). This explains why ordinary pegmatites occur near the parent intrusion, whereas specialized, complex pegmatites and hydrothermal ore deposits are found at a greater distance (Figure 1.16 and Figure 1.19). The degree of fractionation of pegmatites can be determined by trace element analyses of whole rock samples (Li, Rb, Cs, Ta), mica (Cs, Ta, Nb, Zn, Li, U, Be, Ba) and potassium feldspar (Cs, Rb, Na, Ba) (Wise 1995, Morteani *et al.* 2000). Some pegmatites display fractionation to less than 0.05% of the parental melt volume (Evensen & London 2002).

Little is known about details of the physical derivation of pegmatite melts from parent intrusions. The common implication is that pulses of increasingly specialized melt are ejected while the main magma body crystallizes. Rickers *et al.* (2006) report that melt inclusions in parent granites show a gradual transition to embryonic pegmatite melts, along with enrichment of water, B, F, P, Sn, Rb and other incompatible elements. Yet it is not impossible that small pegmatitic melt batches rise directly from the source region of the “parent” granite (Shearer *et al.* 1992).

Pegmatites may host many useful raw materials (Sweetapple & Collins 2002, Morteani *et al.* 2000, Martin & Cerny 1992). These include ores of Be, Li, Rb, Cs, Ta > Nb, U, Th, REE, Mo, Bi, Sn and W, the industrial minerals muscovite, feldspar, kaolin, quartz, spodumene, petalite and fluorite, and gemstones as well as rare mineral specimens (emerald, topaz, tourmaline, ruby, etc.). The derivation of pegmatites from I-, S- and A-type granites is probably the main control of the availability of specific elements for enrichment. The feasibility of pegmatite mining is often limited by a small tonnage and a heterogeneous distribution of economic minerals. The determination of mining

reserves is notoriously difficult. Therefore, pegmatite mining is more common in countries with low labour costs.

1.1.6 Hydrothermal ore formation

Nearly each of the preceding sections contained a reference to the important role of aqueous fluids, although relations between igneous rocks and ore deposits were the main subject. In the following, important aspects of ore formation by hot aqueous fluids are presented.

The term “hydrothermal water” applies to subsurface water with a temperature that makes it an agent of geological processes, including hydrothermal ore formation. “Geothermal waters” are a subgroup of hydrothermal solutions that occur near the Earth’s surface and are mainly used as an energy source, but also for balneology. Thermal springs (Figure 1.21) are common indicators of geothermal reservoirs at depth. Many hot springs and geysers currently display precipitation of minerals and ore. However, most hydrothermal ore deposits were formed at depth, at temperatures of ~700–50°C and pressures of a few hundred to >3000 bar. In the past, the term hydrothermal was mainly understood to imply condensed magmatic vapours below ca. 400°C, based on observations in volcanic geothermal districts. Meanwhile, isotopic investigations revealed that many geothermal and hydrothermal waters are not of magmatic but of meteoric derivation (i.e. from local precipitation). Similarly, hot water in mud volcanoes of oilfields is not magmatic but formation or connate water (diagenetically altered seawater enclosed in sediments). Many other observations confirm that “hydrothermal water” has no unique but many possible sources.

Much has been learnt by studying natural thermal springs and geothermal water tapped by drilling. Most hot waters are dilute solutions of chloride, carbonate and sulphate, but dissolved silica, boron and sulphide are also common (Gallup 1998). Examples of thoroughly investigated hydrothermal systems include the mid-oceanic black smokers, gold-rich hot waters of deep geothermal boreholes in New Zealand (Simmons



Figure 1.21 (Plate 1.21) Geothermal hot springs and siliceous sinter mound at Sempaya in northwestern Uganda. The convective system is related to the large border fault of the Ruwenzori Mountains, with a vertical displacement of more than 10 km between the petroliferous Tertiary Albert Rift in the west and the Palaeoproterozoic crystalline horst in the east.

& Brown 2000, 2007) and base metal-bearing brines of the geothermal field at Salton Sea in Southern California:

Salton Sea is a playa lake in the Colorado River delta of the Imperial Valley graben. It occurs in a transtensional pull-apart basin formed atop the Pacific-North America plate boundary near the transition of the spreading Gulf of California to the San Andreas transform fault zone. The basin fill comprises Tertiary and Quaternary sediments and basaltic sills. Seeps of hot water and gas (CO_2 , methane) are widespread (Svensen *et al.* 2007). Very high heat flow caused by shallow intrusions supports geothermal electricity production. Brine is produced from ~ 1.4 km depth with a temperature exceeding 350°C and content of 506 ppm Zn, 95 ppm Pb and 6 ppm Cu, as well as Na, K, Ca, Cl, S and many other elements. Total salinity reaches 27 wt.%. Zinc is precipitated from the brine after its

passage through the turbines; production attains $\sim 30,000$ t/year. Isotope data reveal that the geothermal water is of meteoric origin and closely resembles Colorado River water. Apparently, river water infiltrates along faults down into the basin sediments, where it is heated and acquires solutes from the rocks. Metal-rich scales in the drill pipes substantiate the hypothesis that focused upflow of such waters is a way of ore deposit formation.

Fluids in the Rotokawa and Mokai geothermal fields of the Taupo Volcanic Zone in New Zealand have an exceptionally high content of precious metals (gold and silver) and of arsenic, antimony and mercury (Simmons & Brown 2006, 2007). Ore deposits, however, have not been found until recently and the systems are only used for the production of electric energy. More than 50 drillholes have been sunk to explore and develop the fields, some of

them to >2600 m depth. Very few surface signs of the vast geothermal zone had existed before. One famous site is the Ohaaki pool with siliceous sinter and ochreous muds that contain 85 ppm gold, 500 ppm silver and 10% antimony as well as high trace content of As, Hg and Tl. This material would be gold ore if the total mass were not so tiny. The geothermal zone is an excellent natural laboratory for investigating hydrothermal ore formation of the epithermal low sulphidation type (Simmons & Brown 2000). Note that high content of solutes is rather a nuisance for geothermal energy production. The precious metals, for example, precipitate from the ascending fluids because of boiling and gas loss, so that tubes are clogged.

Hydrothermal convection

Hydrothermal convection cells, such as the ones at Salton Sea, are established where heat sources below the surface coincide with permeable flow paths, often provided by extensional tectonic deformation (Figure 1.10). Cold infiltrating surface and groundwater is drawn to the “heat exchanger” at depth. The lower density of hot compared to cold water causes ascent of hydrothermal solutions and establishes hydrothermal convection.

Chemical composition

The chemical composition of hydrothermal solutions is extremely variable. Generally, chlorine and sulphur are the most important anions. Salinity ranges from very low to more than 50% and the source of salinity (e.g. halite dissolution, evaporation of seawater, etc.) is detectable by determination of halogens and electrolytes (Botrell *et al.* 1988). Metals are to some extent dissolved as simple ions or ion pairs, but more commonly in the form of complex ions, which combine chlorine, dissociated OH^- groups and bisulphides, as well as NH_3 , H_2S and CO_3^{2-} . The fraction of dissolved matter in hydrothermal solutions varies from less than 1 to over 50 wt.%. Metal concentrations range from less than 1 to several 1000 ppm (parts per million, equal to gram/tonne). Even higher concentrations in solution are possible when metals are part of complex ions. This reduces the mass of water needed to produce an

ore deposit compared to transport in the form of simple ions. Hydrothermal solutions carry metals not only in dissolved form but also as colloidal particles. Colloids are tiny particles (1–1000 nm), which are quite common in many natural waters, usually at low concentrations (Ranville & Schmiermund 1999). High concentrations of dispersed colloids in water are called hydrosols. In many cases, hydrosols are the precursors of gels. Hydrosols and gels may form by local supersaturation of a substance, for example because of a sudden change of pH, T, P or Eh.

Essentially, the chemistry of hydrothermal solutions is the result of interaction between rocks and hot water, in space and time (Barnes 1998). Most important variables controlling these interactions are the initial state of rock and water, the water/rock mass ratio, temperature, chloride concentration, pressure and redox state (Yardley 2005). Geochemical thermodynamic modelling of hydrothermal systems is a tool that provides both a deeper scientific understanding (Moore *et al.* 2000) and solutions to very practical problems, especially in geothermal reservoir and production management.

Possible phase states of hydrothermal waters are liquid, gaseous (vapour) and fluid (supercritical “gas” or “liquid”). In fact, many hydrothermal deposits were formed by supercritical fluids. Water reaches its supercritical state at $T > 374^\circ\text{C}$ and $P > 225$ bar (the critical point of pure water). Increasing salinity moves the critical point to higher T and P (Haas 1971), for example 298 bar and 407°C for seawater. Similar to gas, supercritical fluids are more compressible than subcritical aqueous solutions and have a smaller kinematic viscosity; they are highly mobile (Eckert *et al.* 1996). A fluid comprising CO_2 or CH_4 in addition to water has a high carrying capacity that depends on pressure and density variations. Very small variations cause either dissolution or precipitation of solids. Highly concentrated supercritical fluids have a texture similar to molten salt with polynuclear ion clusters such as $\text{CuNa}_2\text{Cl}_2^+$ or $\text{FeNa}_2\text{Cl}_3^+$. These clusters reach the size of megacomplexes with over six constituent ions that can transport metals efficiently at very low concentrations (Oelkers & Helgeson 1993). In contrast to

subcritical solutions, which form a gas-rich vapour with low content of dissolved matter when pressure is released (true boiling), supercritical fluids segregate into a brine and a dense vapour, which is capable of effective metal transport (Pokrovski *et al.* 2005).

Hydrogen ion activity (pH) of hydrothermal solutions varies from moderately acidic to moderately alkalic. Exceptions occur, of course, and can be recognized by formation of indicative alteration minerals. Acidic conditions, for example, cause formation of kaolinite, alunite or topaz from feldspar. Deep hydrothermal water is normally reduced; oxygen content may increase near the surface by mixing with fresh meteoric water. Bituminous substances are a common accessory in hydrothermal deposits, for example pyrobitumen in the silver veins at Kongsberg, Norway, and oil in the Pb-Zn deposit at Pine Point, Canada. This can be a sign that the hydrothermal solutions were sourced in basinal sediments (e.g. diagenetic formation water mixed with hydrocarbon fluids). Present-day examples are submarine seeps of hot solutions in the Guaymas Basin (Gulf of California) that contain large drops of petroleum (1–2 cm diameter); the vents are mainly built of barite. Organic-chemical investigations (of biomarkers, etc.) allow a very detailed reconstruction of causative processes, covering both hydrotherms and hydrocarbon genesis (Jochum 2000, Svenson *et al.* 2007).

Biological processes

Biological processes at depth influence many hydrothermal solutions. Hyperthermophilic bacteria and archaea are known from hot springs at the Earth's surface to black smoker vents on the ocean floor. With descending branches of convection systems, microbes can be swept deep into crustal rocks. At $\sim 100^\circ\text{C}$ and in the presence of sulphate (from seawater) and organic matter (oil or gas, kerogen), the anaerobes reduce the SO_4 ion to H_2S . This has been observed in oil reservoirs where flooding with seawater was employed in order to boost production. High H_2S content favours dissolution and transport of a number of metals. At falling temperature, however, H_2S contributes to precipitation of metals.

Precipitation of ore and gangue minerals

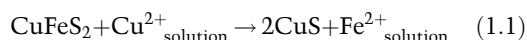
Many causes may induce the precipitation of ore and gangue minerals from solutions. Their understanding is an important element of the search for ore. In the first place, decreasing temperature and pressure reduce solubility. Precipitation is a function of the relative stability of metal complexes and decreasing temperature often results in the common sulphide precipitation sequence from early Cu to Zn, Pb, Ag and finally Hg. Pressure drops may cause fluid immiscibility, such as the formation of two fluids (e.g. aqueous and carbonic) from an originally homogeneous fluid (aqueous-carbonic). This can drastically change pH, f_{O_2} and temperature, thus inducing mineral deposition. Note that rapid pressure fluctuations are typically caused by tectonic events ("seismic pumping" Sibson 1990). Falling pressure is especially effective if common boiling takes place in the two-phase field of liquid plus vapour. Boiling suddenly changes several chemical properties of a hydrothermal solution (concentration, pH, Eh, stability of complex ions), which reduce the solubility of dissolved matter. The term "effervescence" is preferably used in place of "boiling", when gas bubbles form that are not vapour of the host liquid (e.g. carbon dioxide gas bubbles in water). Yet like boiling, effervescence may also induce rapid precipitation of minerals.

Relatively simple systems of this type can be investigated in geothermal power plants where production wells are often affected by mineral precipitation on pipe walls. With time, this process diminishes the open diameter of the tubes ("scaling"). Corrosion, and the effects of re-injecting cooled and depressurized solutions into the reservoir, are also instructive (Czernichowski-Lauriol & Fouillac 1991).

Often, mixing of chemically different waters induces deposition of ores and minerals. A common example is the formation of barite. Barite (BaSO_4) is precipitated when ascending chloride solutions with dissolved barium ions encounter sulphate-ion bearing water (e.g. seawater). Furthermore, the reaction of hydrothermal solutions with host rocks or with previously deposited ore minerals is a very efficient means of immobilizing

dissolved elements. When metal-bearing solutions encounter sulphide minerals, more noble metals are precipitated, whereas less noble elements pass into solution (eq. 1.1). This is a function of properties such as electronegativity, ionization potential, electron affinity, redox potential and the energy of chemical bond formation.

Selective precipitation of more noble metals from solution by exchange with less valuable elements:



Gold (electronegativity 2.4 Pauling's) is more noble than silver (1.9), which is followed by Cu (1.9) and Fe (1.8), explaining common replacement relations. Note that in physical terms, only copper, silver and gold are noble metals. In chemistry, the electric ionization potential of elements is used to define relative nobility. Host rocks exert a strong control on noble metal enrichment. Silver ore veins at Kongsberg (Norway) were fabulously rich in native silver and argentite (Figure 1.22), where they crossed pyrite-rich layers ("fahlband") in host rock gneisses. Gold ore veins of the Mother

Lode system, USA are of higher grade where they intersect pyrite-bearing amphibolite. At the giant Golden Mile deposit, Kalgoorlie, Western Australia, deposition of gold is explained by reaction of sulphide solutions with reduced iron of doleritic host rocks, forming pyrite ("sulphidation"). This triggered a radical decrease of reduced sulphur in the hydrothermal solutions causing gold precipitation.

Organic substances (coal, kerogen, oil, gas) also provoke immobilization of many metals by adsorption or reduction. Gold ore veins at Ballarat, Australia and the metasomatic gold orebodies of Carlin, USA are enriched where host rocks contain kerogen-rich layers. Sulphide precipitation in Mississippi Valley deposits is often caused by reaction between solutions and the organic substance of host rock carbonates (Spirakis & Heyl 1995). Incompletely oxidized sulphur (e.g. thiosulphate, $\text{S}_2\text{O}_3^{2-}$, polysulphides, S_nS^{2-} , or colloidal sulphur, S^0) supports high metal content in solution. These compounds, however, are easily reduced by contact with organic matter so that metals are instantly immobilized as sulphides. An indirect consequence is the precipitation of gangue, such as barite and fluorite.



Figure 1.22 Hydrothermal native silver crystals (isometric, malformed) from Kongsberg in Norway. Gangue includes calcite, barite, zeolite, fluorite and quartz. Courtesy Wolfhart Pohl, Washington.

Although reduction is a frequent means of ore mineral deposition, oxidation can have a similar role, most often concerning iron and manganese. Hydrothermal solutions transport these metals in reduced form (Fe^{2+} , Mn^{2+}) and precipitation of haematite, magnetite or pyrolusite requires oxidation to Fe^{3+} or Mn^{4+} .

Contact of metal-bearing solutions with carbonate rocks is a frequent factor of precipitation. Individual agents include the “pH-shock” upon contact with alkaline rocks and formation fluids, a larger permeability compared with pelitic country rocks, a higher solubility of carbonates in acidic or CO_2 -rich solutions (which may result in the formation of “hydrothermal karst”), and mixing with formation water in carbonate rocks. Orebodies in carbonates take the form of veins, breccia and karst pipes. They can also occur as stratiform orebodies with irregular outlines (“mantos”) and as cross-cutting cloudy masses. When the replacing masses consist of sulphides, it is obvious that dissolution of the original carbonate rock and replacement (“metasomatism”) by ore must have taken place. The same process term is used for cases where only cations are exchanged (e.g. siderite in limestone). Systems of delicately balanced dissolution of one component and precipitation of another are best investigated by geochemical modelling based on thermodynamic principles (Anderson 1996; Bethke 1996).

Source and origin of hydrothermal fluids and solutions

Source and origin of hydrothermal fluids and solutions may be related to quite different geological process systems:

- magmatism (exsolution of an aqueous fluid phase from silicate magma);
- heating of meteoric, oceanic or formation water by convection within or near cooling intrusions, in HHP granites and other heat anomalies, including large faults or uplifted hot metamorphic complexes;
- diagenesis (mainly physical dehydration of sediments by increasing pressure and temperature because of increasing overburden, thrust sheet

superposition, or accretion on active continental margins);

- metamorphism (mainly chemical dehydration of minerals that include OH-groups in their crystal lattice, caused by prograde metamorphic reactions);
- mixing of two or more of the mentioned source systems.

“Juvenile water” is more a concept than reality. The term refers to water that originates from degassing of the mantle, and that has never before been at the Earth’s surface. The second stipulation cannot be proved with present scientific methods. Casual usage of the word wrongly implies any magmatic water. Note that “geothermal water” does not refer to a specific origin but to any hot water that occurs near the surface. Usually the term is employed in the context with production of geothermal energy.

Differentiation of the various genetic possibilities is often difficult, as is shown by the persistent discussion concerning the precise origin of many mineral deposits. Geological and geochemical arguments are most decisive, especially based on isotope systems including noble gases that characterize major earth domains (e.g. ^{40}Ar the crust, ^3He the mantle: Kendrick *et al.* 2001, 2002). Halogens, such as Br and Cl, conserve source ratios and isotope compositions through subduction and magmatism (Nahnybida *et al.* 2009).

In the Earth’s crust, aqueous solutions and fluids are ubiquitous (Yardley 2005, Fyfe *et al.* 1978) and therefore, hydrothermal ore deposits occur in a fascinating diversity. This includes veins (e.g. “orogenic gold”), metasomatic bodies in carbonates, breccia ores in magmatic rocks (“porphyry deposits”), ore stockworks and pipes, volcanogenic terrestrial and submarine exhalations, stratiform base metal ore beds in marine sediments (sedimentary-exhalative ore) and stratiform diagenetic Pb-Zn-Ba-F deposits in marine carbonates. More detailed information on these deposit types and their formation is provided in later sections. Here, it is essential to introduce first the most important methods, which provide data that constitute essential building blocks of genetic models.

*Methods of genetic investigations (1)**Isotope Geochemistry – The Origin of Water and Minerals, and the Age Determination of Hydrothermal Mineral Deposits*

The application of isotope geochemical methods provides a new dimension of metallogenetic research (Hoefs 2009, Allègre 2008, Faure & Mensing 2004, Valley & Cole 2001, Dickin 1995). Isotope systems indicate the source of water, gas, metals and other compounds in hydrothermal solutions, illuminate reactions between solutions and host rocks, reveal formation temperatures and expose mixing processes between solutions of different origin. In addition, isotopes are invaluable means of age determination of hydrothermal, magmatic and supergene ore deposits. Isotope geochemistry is an essential element in the quest for a full understanding of genetic processes. Too often, however, complex relations still limit reconstruction of past processes (Hoefs 2009).

Unstable (radioactive) isotopes are distinguished from stable (non-radioactive) isotopes. Radiogenic isotopes or daughter elements (nuclides) originate by radioactive decay of unstable parent elements. Isotopes of an element have an identical electron configuration but different mass. In physical, chemical and biological processes, this causes thermodynamic and kinetic effects. Isotopes of light elements that have a high mass difference display isotope fractionation. A simple example is evaporation: Lighter isotopes preferentially enter the vapour phase because of their higher vibration energy. Mass difference also affects reaction rate and bond strength, inducing fractionation between syngenetic minerals, and between a mineral and its parent solution. Because the fractionation is a function of temperature, several isotope systems (e.g. sulphur, oxygen, silicon) are very sensitive geothermometers, although only if full equilibrium was attained (Onasch & Vennemann 1995).

Isotopic compositions are measured relative to a standard, using mass spectrometers. Therefore, the fractionation of stable isotopes is commonly expressed as the deviation (δ , in ‰, per mil, of mass) from a standard (eq. 1.2).

Calculation of isotope fractionation as a deviation from a standard:

$$\delta(\text{‰}) = 10^3[(R_{\text{Sample}} - R_{\text{Standard}})/R_{\text{Standard}}] \quad (1.2)$$

R is the ratio of an isotope pair, for example $^{18}\text{O}/^{16}\text{O}$, D/H , etc. Negative δ values indicate an enrichment of the light isotope relative to the standard, whereas the heavy isotope is enriched if the sign is positive.

Isotope age dating of minerals that originated as a consequence of ore formation processes is based on the time dependence of the genesis of a stable daughter nuclide (D) by radioactive decay of an unstable parent element (P). The age expressed in unit “annum” (a, ka, Ma) is calculated with the following equation 1.3.

Determination of geological ages by radioactive decay:

$$t = 1/\lambda \cdot \ln(1 + D/P) \quad (1.3)$$

Time (t) is the date before present, when radioactive decay started, D is the number of atoms of the daughter element, P the number of atoms of the parent element, and λ the decay constant of the parent element ($\lambda = 0.693$ divided by its half-life). Resulting age data or model ages can only be considered as real ages if the analysed system was closed for both parent and daughter element during the whole time span (Dickin 1995).

Commonly, gangue silicates or alteration minerals, including K-feldspar, white mica (muscovite, sericite), biotite, apatite, monazite, rutile, titanite, xenotime and zircon, are used for the age determination of hydrothermal ore deposits. Several isotope systems can be studied, for example U-He, U-Pb, Pb-Pb, Rb-Sr, Sm-Nd, K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$. Also, ore minerals such as cassiterite, columbite, sphalerite, several sulphides and scheelite can be dated with these systems. U-He, U-Pb, Th-Pb and K-Ar systems, however, are subject to complications by α -recoil that will damage the “container” with time, allowing partial loss of parent and daughter. Moreover, very careful investigations revealed that many isotope systems are impaired by later thermal events or the passage of migrating fluids, even at relatively low temperature (Kerrick & Cassidy 1994, Selby *et al.* 2002). Clearly, the geological significance of age data and model ages must always be critically examined.

The age of most ore minerals (e.g. sulphides, oxides) cannot be determined precisely with the above mentioned methods, because they rarely host lithophile elements in their crystal lattice. One alternative is direct dating of sulphides, oxides and even gold using the chalcophile-siderophile element rhenium. The rhenium-osmium method is based on the β -decay of ^{187}Re to ^{187}Os with a half-life of 41.6 Ga. Thus, the age of molybdenite, arsenopyrite, sulphides and oxides can easily be established. This is especially useful for investigating gold deposits (Morelli *et al.* 2007). Similar to lead isotopes, the Re-Os system allows conclusions concerning the source of metals apart from dating (Stein *et al.* 2001).

Improvements of the precision of dating techniques allow increasing resolution of ages and with that, reliable measurement of the duration of ore deposit formation. Results show that many hydrothermal ore deposits have been formed in geologically very short time (several thousands to a few ten thousands of years), which is just about the error margin of present methods. Some data imply that other hydrothermal systems may have been surprisingly long-lived (hundred thousands to millions of years).

Stable isotopes of water

Stable isotopes of water, including ^1H (hydrogen) and ^2H (D, deuterium) as well as ^{16}O and ^{18}O , are exceptionally revealing keys for the comprehension of hydrothermal processes. Average ocean water is employed as a standard (SMOW = Stan-

dard Mean Ocean Water). Evaporation of ocean water is the starting point of precipitation/evaporation cycles that produce isotopically “lighter” water vapour (and derived precipitation), as the distance to the sea and to the equator increases. The isotopic composition of precipitation, surface and shallow groundwater forms a band that is termed the meteoric water line (Figure 1.23). “Meteoric water” is water that has been part of the meteorological cycle evaporation–condensation–precipitation (excluding seawater). The meteoric water line is in reality a band because of local deviations. Note that “formation water” is not a genetic term but simply designates water of unknown origin and age in sediments; formation waters generally show an increase of $\delta^{18}\text{O}$ with increasing burial depth. Brines that form by evaporation in semi-closed marine lagoons are isotopically heavy. Isotope exchange between rocks and ocean or meteoric water produces fluids that retain largely the original hydrogen isotopic composition. Oxygen isotope ratios, however, are considerably altered by partial exchange with oxygen contained in rocks. An equivalent effect is commonly observed in geothermal fields; while the fluids are increasingly enriched in heavy oxygen, the hydrothermally altered rocks are depleted in ^{18}O . The depletion zones allow mapping of fluid passage and can be vectors to ore (Hoefs 2009, Holk *et al.* 2008).

In the $\delta\text{D}/\delta^{18}\text{O}$ diagram, waters of magmatic, metamorphic and sedimentary origin occupy partly overlapping fields (Figure 1.23) so that they cannot always be clearly discerned. Water

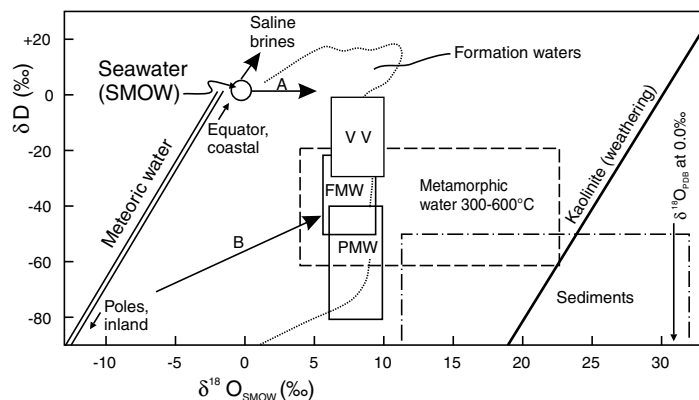


Figure 1.23 Isotopic composition of waters that participate in hydrothermal ore formation (adapted from Hoefs 2009). With kind permission from Springer Science+Business Media. PMW is primary magmatic water; FMW felsic magmatic water; VV is volcanic vapour. Path A shows evolution of ocean water to formation water. Path B suggests mixing of magmatic with meteoric water.

involved in fossil hydrothermal systems can be sampled from fluid inclusions in minerals, but this is fraught with various limitations (Faure 2003). The use of gangue minerals with hydroxyl (OH^-) groups is generally less error-prone. In that case, however, the mineral/fluid fractionation factor must be known. Later isotope exchange with passing fluids (e.g. the common flooding of cooling magmatic bodies and of hydrothermal systems by meteoric and formation waters) needs to be investigated. Ore formation systems involving high pressure fluctuations (e.g. Sibson's "seismic pumping") are characterized by wide variations in D/H fractionation between water and minerals (Horita *et al.* 1999). This is intensified at conditions above the critical temperature of water and generally with fluids of very low "gaseous" density (Driesner 1997).

Carbon isotopes

Carbon consists of the stable isotopes ^{12}C and ^{13}C . Because of its short half-life (5730 years), age dating with cosmogenic ^{14}C is limited to very recent geological processes. The origin of carbonate minerals and rocks is investigated by stable carbon and oxygen isotope fractionation relative to the PDB standard (belemnites found in the Cretaceous Peedee Formation, Carolina, USA). Consequently, marine carbonates have δ_{PDB} values about zero, mantle carbon about -7‰ and kerogen between -20 and -30‰ . Hydrothermal carbonate carbon varies from -6 to -9‰ indicating a deep origin of the CO_2 . However, the source signal may be veiled by inorganic isotope fractionation of carbon, which is a function of oxygen partial pressure, temperature, pH, ionic strength and carbon concentration, complicating genetic interpretations. Comparative investigations of the large travertine deposits near Florence, Italy and warm ($29\text{--}34^\circ\text{C}$) springs in the same area that deposit travertine (Guo *et al.* 1996), provide an instructive example. Recent calcite shows an increase of ^{13}C with higher distance to the spring orifice, due to two factors: i) simple degassing ($^{12}\text{CO}_2$ evaporates preferentially,

whereas $^{13}\text{CO}_2$ is retained in the solution and collects in the travertine); and ii) bacterial fractionation. Bacteria predominantly abstract ^{12}C from the solution, so that $\delta^{13}\text{C}_{\text{Calcite}}$ is increased compared to abiotic processes.

Sulphur isotopes

Sulphur isotopes provide genetic information on sulphides and sulphates of ore deposits. Standard is troilite (FeS) from the Cañon Diablo meteorite that has about the same $^{34}\text{S}/^{32}\text{S}$ ratio as the Earth's mantle. Therefore, basalts and other mantle magmas and sulphide ore deposits derived from them have $\delta^{34}\text{S}$ near zero. Clearly different is sulphide sulphur produced by organic fractionation with $\delta^{34}\text{S}$ from -20 to -30‰ (the so-called "bacteriogenic sulphur"; Canfield & Thamdrup 1994) and marine sulphates with $+10$ to $+30\text{‰}$. This is why the origin of sedimentary sulphur can often be determined with high precision. Magmatic and hydrothermal ore deposits may contain sulphur of mixed origin, veiled by inorganic fractionation. The isotope fractionation between cogenetic sulphide minerals, or sulphides and sulphates can be a useful geothermometer (Zheng 1991).

Strontium isotopes

Strontium isotopes also provide evidence of the derivation of ore solutions. The system comprises radiogenic ^{87}Sr , a decay nuclide from ^{87}Rb , and the stable ^{86}Sr . It is the base of a widely used method of age determination. In hydrothermal ore deposits, the ratio $^{87}\text{Sr}/^{86}\text{Sr}$ is a means of characterizing fluids that formed carbonates (Ca, Mg, Fe), sulphates (Ca, Ba, Sr), fluorite and apatite. Samples used should have extremely small rubidium content. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of large source reservoirs such as the Earth's mantle, continental crust and seawater are quite different. Seawater displays systematic variations in geological time. On that basis, hydrothermal and marine-sedimentary carbonates can be distinguished. Analysis of

time-dependent diagenetic processes is possible (Schreiber & Tabakh 2000).

Lead isotopes

Lead isotopes are an especially powerful tool to trace metal sources in mineral deposits, because their geochemical behaviour in aqueous fluids resembles that of many associated metals (e.g. Zn, Cu, and Ag). Also, traces of lead are ubiquitous in most rocks and in many ore minerals. Terrestrial lead consists of four stable isotopes:

- 1.0–1.6 wt. % ^{204}Pb , primordial (not radiogenic), used as a reference base;
- 20.8–27.4% ^{206}Pb , radiogenic decay product of ^{238}U ;
- 17.6–23.6% ^{207}Pb , radiogenic decay product of ^{235}U ;
- 51.2–56.2% ^{208}Pb , radiogenic decay product of ^{232}Th .

Because of the minimal mass difference between lead isotopes, fractionation by geological processes is very small. Their inherent useful information rests in formation and mixing of the radiogenic isotopes. Both are controlled by properties of the source rocks, including age, lithology (Chiaradia & Fontboté 2003) and geochemistry (uranium and thorium content). Uranium concentrations in the source are described by μ -values (the ratio $^{238}\text{U}/^{204}\text{Pb}$). Because uranium and thorium are markedly lithophile elements, they are enriched in the continental crust (with high μ) relative to the mantle. The evolution of present-day lead started with the primordial or meteoritic composition $\sim 4550\text{ Ma BP}$ (before present), which is derived from troilite in the Cañon Diablo meteorite (like sulphur isotopes). Since then, radiogenic lead increased because of uranium and thorium decay in the major geological reservoirs (mantle, lower and upper crust). Without any disturbance, ordinary lead is the result. When ordinary lead is separated from uranium and thorium, and concentrated in ore deposits (e.g. as galena), its isotopic composition reveals both the age of mineralization and the source reservoir of the

lead (“plumbotectonics”, Zartman & Doe 1981). “Single stage lead” is derived by single-phase extraction from a very large reservoir, probably continental lower crust or uppermost mantle and is present in a number of large ore deposits (e.g. Mt Isa, Broken Hill, Australia). Other ore deposits have lead of an anomalous composition, which originated by multi-stage processes. Typically, anomalous lead provides model ages that are clearly different from the geological age. Two extremes shall serve as an example:

An unusually high radiogenic fraction was found in lead of the Tri-State mining district (USA). Its source is thought to lie in uraniferous Cambrian sandstones and Precambrian basement rocks that had a very low content of ordinary lead. Therefore, the migrating hydrothermal brines took up the easily soluble radiogenic lead from decayed U-Th phases. Lead model ages of the resulting galena plot in the geological future, whereas the mineralization took place in the Late Palaeozoic (Symons *et al.* 2005). In the mining district of Bleiberg, Austria, the lead model age is Mesopalaeozoic, but the ore deposits clearly formed much later, in Triassic time. It is assumed that the lead of Bleiberg is derived by leaching of feldspars in Palaeozoic gneisses that contain up to 50 ppm Pb, but very little uranium ($<1\text{ ppm U + Th}$). Therefore, hardly any radiogenic lead was available for extraction by the hydrothermal solutions.

Accordingly, lead model ages are very often not “dates”, but nevertheless provide important information on ore genesis. Lead isotopes may indicate the source of the metal and this is an essential element of genetic modelling (cf. Everett *et al.* 2003).

Many other isotope systems provide deeper insight into ore forming processes. Examples include chlorine (Nahnybida *et al.* 2009, Banks *et al.* 2000), nitrogen (Jia *et al.* 2003), iron (Johnson *et al.* 2009, 2008, Staubwasser *et al.* 2006, Beard *et al.* 2003) and boron (Perez Xavier *et al.* 2008). Subrecent geological processes (younger than $\sim 20\text{ Ma}$), such as the age of supergene ore deposits, are investigated with cosmogenic nuclides (e.g. ^{10}Be , ^{14}C , ^{26}Al , ^{36}Cl and ^{129}I ; Siame *et al.* 2006, Muzikar *et al.* 2003) and with the uranium-series disequilibrium method (Reich

et al. 2009). Typically, results reveal extraordinarily long durations of supergene processes, although hardly at constant rates.

Methods of genetic investigations (2)

Temperature and pressure of hydrothermal ore formation

Apart from geochemical parameters, temperature and pressure of a hydrothermal system are essential determinants of solubility, transport and precipitation of elements and compounds. In order to understand such systems, formation temperature and pressure have to be measured. Unfortunately, there are relatively few methods that allow the precise determination of pressure, but the reverse can be said concerning temperature. Conventional petrologic geothermometers and geobarometers can rarely be applied to hydrothermal mineralizations.

Frequently employed “geothermometers” of economic geology include:

- microthermometry of fluid inclusions in minerals;
- cation-exchange geothermometers, indicating the temperature of the last equilibration of fluids with host rocks (e.g. silica: Fournier & Potter 1982; magnesium-lithium: Kharaka & Mariner 1990);
- trace element geothermometers (e.g. Ti-in-zircon for very high temperatures: Watson *et al.* 2006);
- different modifications of minerals (e.g. α - vs. β -quartz at 573–600°C);
- exsolution or unmixing of phases during cooling (e.g. cubanite lamellae in chalcopyrite that formed at >205°C);
- oxygen, silicon and sulphur isotope fractionation in cogenetic minerals (stable isotope geothermometry);
- the distribution of certain elements in cogenetic minerals (e.g. Fe-Zn-S or Au-Ag-S systems; As-contents, e.g. in arsenopyrite);
- chlorite and muscovite mineral geothermometers.

All of the above-mentioned geological thermometers are inaccurate due to factors that control the results but cannot be precisely determined. It is best practice in economic geology to combine

several methods, for example microthermometry of fluid inclusions (Roedder 1984, Samson *et al.* 2003), the arsenopyrite geothermometer (Kretschmar & Scott 1976) and the fractionation of stable isotopes.

Fluid inclusions

During formation of minerals from fluids or solutions, irregularities on growth planes often cause inclusion of tiny droplets of the parent liquid (primary inclusions). Quite common are also inclusions that are hosted by microfractures in a mineral (secondary inclusions). Fluid inclusions are usually very small (below 100 μm), so that investigations are carried out on polished thin or thick sections using a microscope. At room temperature, many inclusions contain an aqueous liquid with a gas bubble that occupies ~10–40% of the volume (type 1 of Figure 1.24). Upon heating of the sample, the bubble disappears at a determinate temperature that is described as the homogenization temperature T_h . In the simplest case, T_h is equal to the formation, or trapping temperature T_t , because the bubble results from cooling and shrinking of the hot inclusion within a volume fixed by the surrounding host mineral. However, T_h is only the minimum temperature of trapping since pressure at the time of formation controls size and density of the bubble. An accurate determination of the formation temperature is only possible if the formation pressure is known and the so-called pressure correction can be calculated (actually, this is a correction of temperature as a function of pressure: Roedder 1984). The density of the inclusion, its degree of fill (liquid vs. total volume), the salinity of the liquid (mostly due to dissolved NaCl, but Mg, Ca, K, etc. may be involved), the presence of daughter crystals (common are halite cubes: type 3 in Figure 1.24), of fluid hydrocarbons and contents of non-aqueous gases (frequently CO_2 , followed by CH_4 , N_2 , etc.) are all needed for a full understanding. Investigations must also address the identification of groups of associated inclusions that were trapped from a fluid of the same composition at the same time, temperature and pressure (a “fluid inclusion assemblage” or FIA). Natural minerals

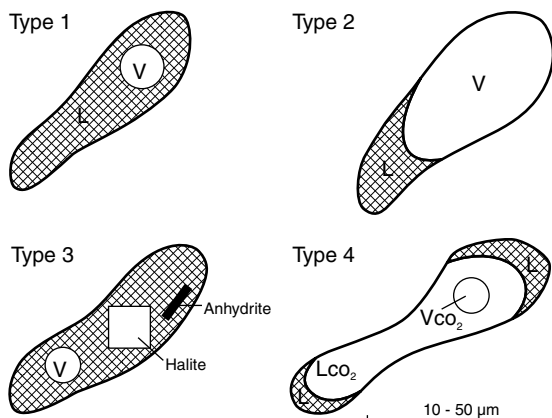


Figure 1.24 The four most common types of fluid inclusions as they appear under the microscope at room temperature.

typically contain many different FIAs, which reveal the evolution of a hydrothermal system.

Most fluid inclusions observed in hydrothermal ore deposits belong to one of four groups (Figure 1.24):

1 Type 1: Liquid (L) aqueous inclusions of low to moderate salinity (<26.5 wt.% NaCl, which marks saturation at room temperature), a water vapour bubble (V) and a density of $\sim 1 \text{ g/cm}^3$;

2 Type 2: Water vapour occupies >60% of the inclusion volume, the salinity is similar to type 1; the density is clearly $< 1 \text{ g/cm}^3$; if types 1 and 2 (or 2 and 3) are cogenetic in the same sample,

true boiling (as opposed to effervescence of a dissolved gas like carbon dioxide or methane in water) of the solution below the critical point or at boiling curve conditions is indicated; this gives rise to the term “boiling assemblage” (Figure 1.25);

3 Type 3: Highly saline (26.4 to >50 wt.% salinity) aqueous inclusions with halite daughter crystals and with a high density; fluids of this nature can result from dissolution of evaporites, seawater evaporation, segregation of brines from melt at magmatic temperatures (Audétat *et al.* 2008), by formation of residual brines because of vigorous

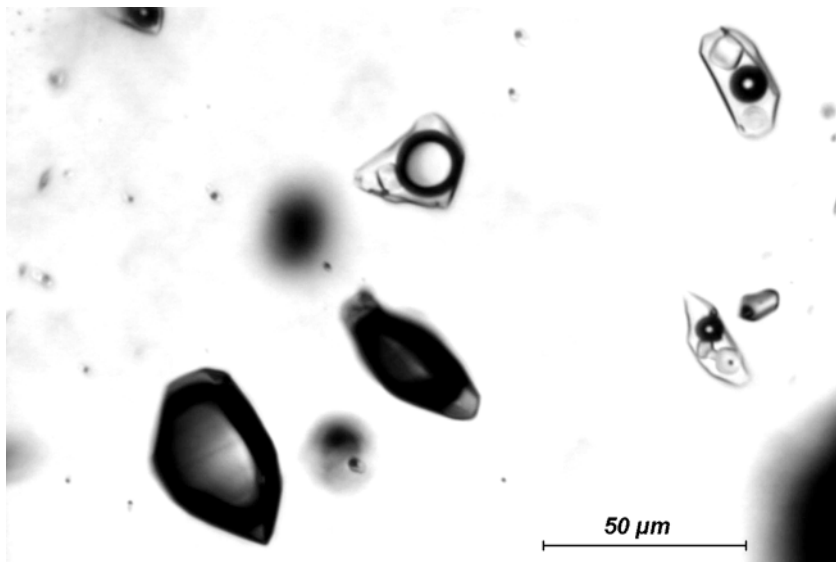
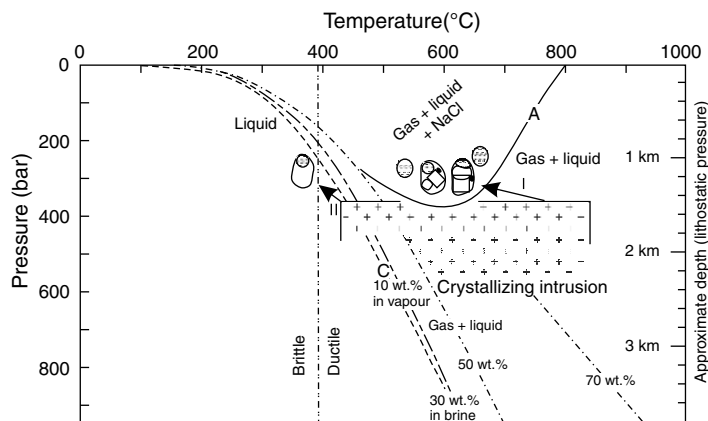


Figure 1.25 Fluid inclusion assemblage (FIA) formed by subcritical boiling in quartz from miarolitic cavities in the barren Torres del Paine granite (Patagonia, Chile). Vapour (dark), concentrated Cu and As, whereas the brine inclusions marked by halite crystals are enriched in metals such as Mn, Fe and Zn (Lüders *et al.* 2005). Courtesy Volker Lüders, GFZ Potsdam.

Figure 1.26 A crystallizing shallow intrusion may exsolve (I) early and very hot brines, or (II) later saline fluids of intermediate temperature, resulting in characteristic fluid inclusions (after Brathwaite *et al.* 2001). With kind permission from Springer Science + Business Media.



subcritical boiling (abstraction of vapour causes concentration of salt in the liquid phase and by supercritical phase separation;

4 Type 4: CO_2 -rich inclusions, with little water; at room temperature carbon dioxide in the inclusions occurs in both liquid (L_{CO_2}) and gaseous phase (V_{CO_2}).

In Figure 1.26, path I is entered by very hot, hypersaline magmatic liquids ($\pm$ vapour). Above the phase boundary A, cogenetic type 2 and type 3 fluid inclusions segregate. Path II illustrates the fate of late, less saline and much cooler fluids. Part of these may be derived from vapour that because of cooling contracts at higher pressure into the liquid phase. Inclusions trapping these fluids are type 1 with low to intermediate salinity (3–20 wt. % NaCl). Phase boundaries between liquid and gas+liquid are shown for different salt contents. Boiling assemblages must have formed at a point along such a phase boundary. C is the critical point for an aqueous solution with 10 wt. % NaCl.

The salinity of 26.4 wt. % separating type 1 and type 3 inclusions is the solubility of NaCl in water at room temperature (20°C). In practice, the presence of other salts, such as CaCl_2 lowers the NaCl saturation to ~ 23 wt. %. The salinity of fluid inclusions is determined by freezing with liquid nitrogen and remelting, i.e. the temperature is allowed to rise back to ambient conditions. Because dissolved salts depress the freezing point (Bodnar 1993, Potter *et al.* 1978), the melting temperature of ice ($T_{\text{m ice}}$) provides a precise

measure of salinity. Results are expressed in the form of equivalent weight percent of NaCl (wt. % NaCl equiv.). The chemical determination of the composition of inclusions is complicated by the tiny mass of individuals. Yet, a number of methods are available; most advanced is the approach with laser ablation (LA) connected to ICP-MS (Sylvester 2008, Audétat *et al.* 1998). Merging the data with results from high-resolution investigations of the hydrothermal paragenesis (e.g. SEM-CL, Scanning Electron Microscope-Cathodoluminescence: Rusk & Reed 2002) allows a detailed unravelling of the chemical and physical evolution of a hydrothermal system.

The investigation of fluid inclusions is somewhat restricted by the need for samples that are transparent to visible light, thus excluding most ore minerals. Of the opaque oxides, sulphides and sulphosalts only few, such as wolframite, iron-rich sphalerite, and antimonite are transparent for infrared light and can be examined with the methods described above (Figure 1.27). The result is that most fluid inclusion investigations are based on gangue and not on ore minerals. This may introduce severe errors (Wilkinson *et al.* 2009), for example if ore and gangue formed from differing fluids (Lüders 1996). Other problems are connected with post-formation changes of the inclusions, for example by renewed equilibration at different P/T-conditions. Metamorphic shearing and recrystallization often destroy fluid inclusions. Even synmetamorphic inclusions in mobilizates are usually decrepitated because of pressure

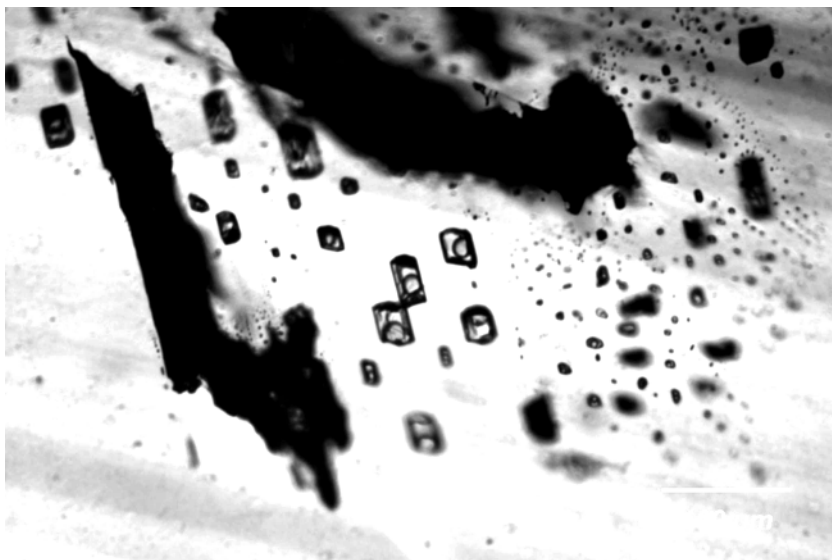


Figure 1.27 Aqueous fluid inclusions in wolframite of Panasqueira mine, Portugal, studied by near-infrared microscopy. The fluids homogenize between 320 and 325°C and have a salinity of ~12% NaCl (Lüders 1996). Note the large vapour bubbles in inclusions which resemble type 2 of Figure 1.24. Courtesy Volker Lüders, GFZ Potsdam.

release during uplift (e.g. Joma Mine, Norway: Giles & Marshall 1994). However, in spite of many obstacles, petrographic and microthermometric work on fluid inclusions brought great advances of understanding hydrothermal ore deposit formation. Even eminently practical questions can be solved, such as the differentiation between mineralized and barren veins.

The broad application of microthermometric methods suppressed the older decrepitation analysis. Its principle was to count acoustic emissions, while a mineral was submitted to stepped heating. Because each micro-acoustic signal is due to a bursting inclusion, maxima were taken to indicate roughly the temperature of formation. Of course, precise genetic data cannot be obtained with this method. But as decrepitation analysis is relatively simple and gives quick results, it may be a valuable tool in exploration. In the Cowra Gold District, New South Wales, Australia, auriferous veins can easily be distinguished from sterile quartz veins, because the first contain much more CO₂ and display a unique decrepitation pattern (Mavrogenes *et al.* 1995).

Traditionally, hydrothermal ore deposits were grouped according to assumed formation temperatures into hypo- or katathermal (500–300°C), mesothermal (300–200°C) and epithermal (below

200°C). This classification was quietly abandoned, while a wealth of data has been acquired on real temperatures of hydrothermal processes and resulting deposits. Temperatures vary widely, even during the lifetime of one single hydrothermal system. Accordingly, temperature is a poor criterion for classification, although, of course, an integral part of the description of the formation of mineral deposits. In many scientific reports, the terms named above are still used in a very wide sense, indicating rather depth than temperature. In this usage, epithermal deposits are those formed in the uppermost part of the crust (<1 km from the surface) and below 200°C (but note that the most important member of this class, the “epithermal gold deposits”, typically originated at ~300°C). “Meso-” and “hypothermal” describe increasing depth and temperature. However, depth and temperature are not always correlated. Fluids in shallow porphyry copper deposits, for example, may originally have had a temperature approaching 800°C (Figure 1.26). Clearly, depth (or pressure) is a much more useful criterion to describe related groups of hydrothermal deposits. Therefore, Gebre-Mariam *et al.* (1995) suggested to adopt the terms “epi-, meso- and hypozonal” (Table 1.2), similar to the notations referring to metamorphism or the intrusion depths of granites. The

Table 1.2 Depth-zone classification of hydrothermal mineral deposits

Epizonal	150–300°C	0.5–1.5 kbar	<6 km depth
Mesozonal	300–475°C	1.5–3.5 kbar	6–12 km
Hypozonal	475–700°C	3–6 kbar	>12 km

Temperature is not a classification criterion. T-values given here apply to epigenetic Archaean gold deposits only (Gebre-Mariam *et al.* 1995).

proposal was aimed at epigenetic Archaean gold deposits, but could be advantageously used for all hydrothermal mineral deposits.

Formation pressures

Rarely, formation pressures of hydrothermal ore deposits can be precisely measured. Usually, geological estimates are derived from the assumed depth of formation and lithostatic or hydrostatic boundary conditions. Other approaches include modern methods of metamorphic petrology in combination with fluid inclusions data. If the minerals are present, methods such as the sphalerite-pyrite-pyrrhotite geobarometer can be applied (Lusk *et al.* 1993): Between 300 and 600°C, the FeS-content in sphalerite in contact with pyrite and pyrrhotite is only a function of pressure. Isochores of fluid inclusions (lines of constant volume and density in P-T space) can be intersected with independent data, such as the solidus temperature of the parental granite (Audétat *et al.* 2008). Some fluid systems allow pressure analysis based on experimental data of thermodynamic properties of synthetic fluids similar to natural inclusions; simple systems, such as H₂O-NaCl provide a good approximation, but high vapour and gas contents cause large error margins. Unambiguous evidence of boiling still provides the most accurate geobarometry data available (Roedder 1984).

Methods of genetic investigations (3) *Mineral succession, textures and structures of hydrothermal mineral deposits*

The precipitation of minerals from hydrothermal solution is controlled by various boundary conditions, some of which have been discussed earlier.

For a reconstruction of the conditions at a point in time and for the whole duration of hydrothermal activity, minerals that formed simultaneously (the paragenesis) must be strictly discerned from the sequential order of mineral assemblages (the paragenetic sequence). Macroscopic observations of mine exposures and hand specimen, ore microscopy and other mineralogical techniques are combined to resolve the evolution of hydrothermal systems.

Because most ore minerals are opaque, microscopic examination is usually based on polished specimen and reflected light. This allows resolution of the intergrowth of different minerals. The position of minerals in one paragenesis or in the whole paragenetic sequence is revealed by observations that include exsolution, replacement along grain boundaries or microfractures and many other textures and structures. Ore microscopy has attained a level of very high perfection (Craig & Vaughan 1994, Ramdohr 1980, Stanton 1972). Methods, such as electron probe microanalysis (EPMA), transmission electron microscopy (TEM), scanning electron microscopy – cathodoluminescence (SEM-CL) and other methods of mineralogical analysis (e.g. QEMSCAN, CSIRO, Australia), confirm and complement optical determination. Even greater resolving power is available with 100-nm-resolution secondary ionizing mass spectrometry (nanoSIMS; Barker *et al.* 2009).

Macroscopic features that assist in establishing the mineral succession include overgrowths and crusts, symmetric vein fillings and cross-cutting relations of veins. This is supplemented by colour, texture type and grain form or crystal habit of minerals, and by examination of fluorescence and luminescence. Because quartz is an important part of most hydrothermal parageneses, recording its structures and textures is most instructive (Dong *et al.* 1995). Combined with results of microthermometry, trace and isotope geochemistry and geological investigations, the evolution of an individual hydrothermal ore deposit can be resolved.

Open space filling is a characteristic feature of many hydrothermal ore deposits. The term implies that precipitation of minerals occurred in open fissures, pipes or caves, which acted as flow channels for hydrothermal solutions. Open space

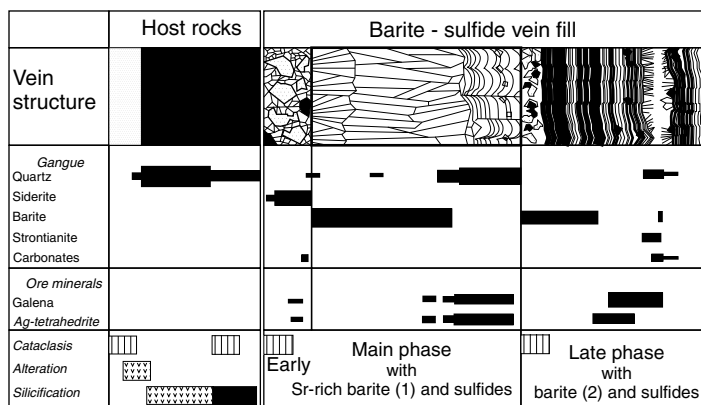


Figure 1.28 Parageneses and paragenetic sequence of Tertiary rift-related lead-silver-barite veins in the Caroline mine, near Freiburg, Germany (modified from Germann *et al.* 1994). With kind permission of R. Lang and LGRB Freiburg.

filling starts with nucleation of minerals on a solid surface of the flow channel walls. This explains the often observed younging of the mineral succession towards the centre. In Figure 1.28, different parageneses of a specific phase of vein formation can be read vertically, whereas the horizontal axis reflects evolution in time (from left to right; crystals in the open space on the right represent the youngest hydrothermal minerals and the vein's symmetry axis). Banding of hydrothermal precipitates results from variations of physical and chemical conditions in time. Tectonic movements during hydrothermal activity cause fracturing of earlier minerals and cementation by younger precipitates. Fibrous texture of minerals, such as quartz aligned vertically or obliquely to vein margins, indicates synchronized opening and mineral growth. In near-surface hydrothermal channels, clastic sediments have been observed that indicate high flow velocity of hydrothermal solutions. Hydrothermal sediments formed in this way include bedded rock flour, clay, sand, solid hydrothermal precipitates and even gravel (pebble dykes). Mainly epizonal features include hydrothermal breccias that may host fabulous orebodies. Many breccias were formed by self-sealing of flow paths and consequent phreatic explosions.

Sedimentary textures of material filling open spaces of hydrothermal veins are not rare (e.g. in the fluorite vein at Rossignol, France). This occurs when solid material is eroded, or when minerals and colloidal particles nucleate in suspension from ascending fluid. Sedimentation of these par-

ticles depends on the ratio of the upflow speed of the fluid to gravitational settling of the particles. Stoke's law can be used to calculate the settling velocity (V) of the particles, allowing an estimate of the fluids' upflow velocity (eq. 1.4). Suspended minerals nucleating and growing in fluids settle to produce "blocky" vein textures (Okamoto & Tsuchiya 2009).

Settling velocity of particles in a fluid:

$$V = \frac{1}{18} \cdot \frac{(\sigma - \rho)g \cdot D^2}{\mu} \quad (1.4)$$

V = free-falling velocity (m/s), σ = density of the particle, ρ = density of the fluid, D = particle diameter (m), g = acceleration due to gravity (m/s^2), μ = viscosity of the fluid (m^2/s).

Hydrothermal open space deposits are usually coarsely crystalline. In certain deposits, minerals may occur in dense, reniform-botryoidal and banded crusts, often with fissures due to shrinkage. Such textures are described as "colloform" and are thought to imply formation from a gel (a hydrosol with a mechanical resistance). Such precipitates are amorphous and may gradually mature into crystalline phases (i.e. opal, wood tin and garnierite) or into proper minerals including chalcodony, reniform sphalerite and malachite. Often, but not necessarily always, the origin of colloform substances may be traced to colloids forming in the hydrothermal fluids. It is also possible that coagulated colloids are transported with the hydrothermal flow and deposited higher up as a gel. Colloidal particles in water typically

have a free negative charge, which leads to electrostatic repulsion and dissipation (Ranville & Schmiermund 1999), similar to heat energy. While the formation of aggregates may be due to van der Waals forces, neutralization of the charge (by mixing with an electrolyte, pH-change, cooling, etc.) frequently effects aggregation and precipitation as a gel. Some hydrosols form "colloidal crystals". Apart from colloids, hydrosols and gels, botryoidal textures may be inherited from microbial mats (Labrenz *et al.* 2000). Obviously, different ways may lead to formation of a colloform mineralization.

The characteristic banding of many colloform precipitates may be due to external factors, but also to self-organization. Heany & Davis (1995) propose that the banding of agate, which is a rhythmic succession of chalcedony and quartz, is the product of a changing degree of polymerization of the solution on the tips of the growing chalcedony fibres. Polymerization decreases when chalcedony is rapidly deposited, so that the system flips to slow quartz precipitation from a monomeric solution. In this phase, diffusion slowly raises the concentration of the solution until the state of a concentrated polymeric solution is again reached. Colloform SiO_2 can also form from "silicothermal fluids" (Wilkinson *et al.* 1996). These are liquids with ~90% SiO_2 that co-exist with an aqueous supercritical fluid in a wide temperature field (~400 to >750°C). Silicothermal fluids might be the explanation of the high frequency of amorphous silica phases in epizonal and especially in epithermal ore deposits.

Replacement of earlier solid phases is very common in hydrothermal ore deposits. As one mineral is dissolved, another forms in the same place, often without a change of volume and with conservation of very fine textures (pseudomorphism). Characteristic examples include cassiterite replacing orthoclase (Cornwall, England) or even crinoids (New South Wales, Australia), scheelite after wolframite, and from low-temperature solutions, the silicification and pyritization of whole tree trunks in coal seams. The term "replacement, or metasomatic ore deposit" is only used if the process produced most of the actual ore. Carbo-

nates are frequently the subject of replacement because of their disposition for chemical reactions. Advection and evacuation of matter is usually enacted by physical flow but diffusion can also play a role.

The waning stages of hydrothermal systems typically display falling temperature, lower mass flow, pervasive fracturing and cataclasis, and often infiltration of oxidizing meteoric water. This leaves fractures and thin fissures of the hydrothermal vein mass covered by films of goethite, haematite or manganese oxides.

Methods of genetic investigations (4)

Hydrothermal host rock alteration

Host rocks influence hydrothermal solutions to the point of controlling the site of ore precipitation, but at the same time they are affected by alterations that emanate from the solutions. The resulting changes ("hydrothermal alteration") may extend from only centimetres off the flow channel (Figure 1.29) to very wide halos in the case of pervasive flow. Alteration zones are important clues for ore deposit exploration and for the prospectivity of an area (Lentz 1994). Some alteration halos can be mapped by remote sensing from space. Hydrothermally altered rocks are often so fine-grained that even the microscope may not suffice in revealing the constituent minerals. Portable SWIR (short-wave infrared) spectrometers are routinely used to determine alteration parageneses.

The changes concern colour, texture, mineralogical and chemical composition including stable isotope ratios in different combinations. The end product is a function of the nature of both the solutions (pH, Eh, T, pressure, dissolved matter) and of the affected rocks (mineralogy, permeability, porosity). Ion exchange is ubiquitous, implicating an open system with import and export of matter (Anthony & Titley 1994). Dissociated water plays an eminent role, because of reactions with silicate minerals that include incorporation of OH^- groups and exchange of cations with H^+ (hydrolysis). Frequently, altered rocks display a zebra-like pattern of rhythmic banding, which is

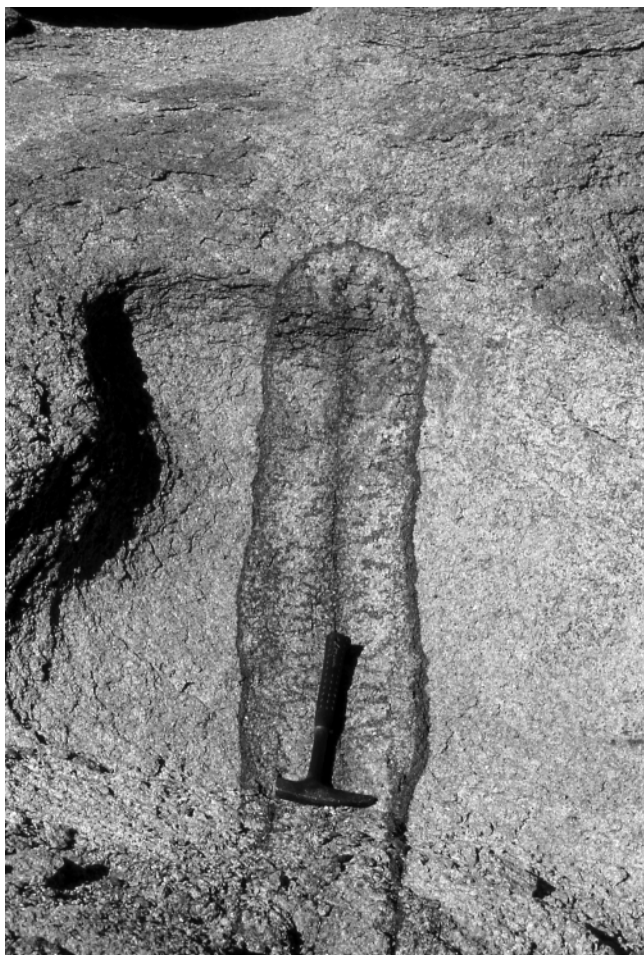


Figure 1.29 (Plate 1.29) The essence of hydrothermal alteration visible at outcrop-scale, depicted by the halo centred on a small fissure branching off from formerly exploited wolframite-quartz veins in Panafrican granite at Gash Emir, Red Sea Hills, Sudan. Note the enhancement by later supergene oxidation.

caused by coupling of diffusion with precipitation reactions (Kapral & Showater 1995). Hydrothermal alterations also affect mass and volume of the altered body, with the possibility of a positive or negative balance. Calculation of the balance relies on assumed immobility of specific elements (e.g. zirconium, titanium). By comparison of concentrations in unaltered rock and in its altered equivalent, enrichment or dilution can be calculated (Herrmann *et al.* 2009).

In many cases, hydrothermal solutions are weakly acidic because of fluorine or CO_2 contents and dissociation of water. In that case, carbonates, zeolites, feldspathoids and calcium-rich plagioclase are especially prone to alteration. Pyroxene,

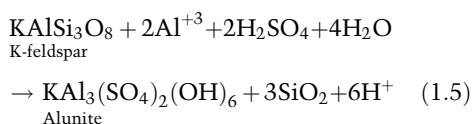
amphibole and biotite are somewhat more stable, whereas albite, K-feldspar and muscovite are relatively resistant. Quartz is rarely affected.

Alteration of pervaded rocks before the solutions reach the site of ore formation may extract trace metals that are then concentrated in the ore. It is quite possible that many ore deposits are a product of this process (e.g. cassiterite ore produced from aqueous solutions that have passed through tin granite bodies: Lehmann 1990). Examples of trace elements that are incorporated in minerals include copper and zinc in biotite, amphibole, pyroxene and magnetite, lead in K-feldspar and accessory uranium minerals, tin in mica and ilmenite, tungsten in biotite, fluorine in

amphibole and mica, and barium in mica and feldspar. Based on appropriate data, genetic ore formation models incorporate such relations.

Not only ascending hypogene hydrothermal solutions may cause host rock alteration. Some alterations are the product of downward-percolating waters. Examples include solutions formed from magmatic-derived HCl, HF, H₂S and SO₂ steam condensating into, and heating shallow groundwater. Resulting strong acids cause acid-sulphate alteration, characterized by alunite (eq. 1.5), typically in near-surface epithermal gold ore-forming systems (Mutlu *et al.* 2005).

Alunite formation under extremely acidic hydrothermal conditions:



Hydrothermal host rock alterations include the less visible change of increased maturation of dispersed organic matter (kerogen) under the influence of heat imported by the solutions (Heroux *et al.* 1996). Along flow paths and around orebodies, the induced thermal anomaly can be mapped by appropriate methods, for example increased reflectance of organic particles (cf. Chapter "The Coalification Process").

Spatial zonation of alteration types

Spatial zonation of alteration types has an outstanding role in ore deposit investigations. Alteration zoning illustrates changing chemistry of the solutions by reactions with wall rocks, and different physico-chemical boundary conditions (temperature, pressure, etc.). Zoning is an extremely useful guide and spatial vector pointing to ore, as this is always connected with a certain type of alteration. Zonation is best illustrated by the classical alteration model of porphyry copper ore deposits.

There are many different hydrothermal alteration types (Thompson & Thompson 1997). Some characterize certain ore deposits, while others are linked to the presence of specific rocks. Propylitization, for example, typically affects andesite and diorite, listwaenitization ultramafic rocks and dolomitization limestone. The names given to alteration types are mainly derived from the most noticeable newly formed mineral, but some have their own traditional rock names (e.g. greisen, propylite). Important examples of hydrothermal wall rock alteration include:

• *Silicification* is the permeation of host rocks with dissolved silica, resulting in increased contents of opal, chalcedony or quartz. The rocks often obtain the aspect of quartzites. Silicification is very frequent around epithermal gold deposits.

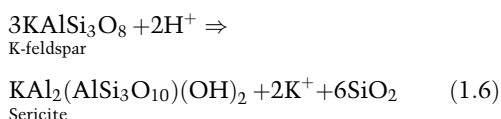
• *Albitization* (or sodic alteration) often affects magmatic rocks by replacing more calcic with sodic plagioclase, but albite ($\pm$ chlorite, epidote, etc.) may be introduced into most rock types. The source of the sodium may be seawater, evaporative brines, or dissolution of salt bodies and transport by basinal or metamorphic brines. Also, sodium is enriched in liquids and fluids segregating at high temperatures from crystallizing magmas.

• *Argillic alteration* is the conversion of rock-forming silicates into clay minerals. Two variants are distinguished, advanced and intermediate argillization. In the first case, the core of the altered rock body typically consists of alunite and quartz, and is surrounded by argillic zone minerals nacrite, dickite, kaolinite and pyrophyllite with variable contents of sericite, pyrite, tourmaline and topaz. The agents are strong acids, which impose a nearly total loss of alkali elements and aluminium enrichment. Advanced argillization is often found with gold or tin mineralization. Intermediate argillization is marked by conversion of feldspars to kaolinite (proximal to main flow channels) or montmorillonite (in a distal position). Extending into the distance, a propylitization halo is often developed.

• *Propylitization* may affect large rock masses in the wider vicinity of ore deposits, by imparting a greenish tinge. It is a complex alteration with neoformation of chlorite, epidote, albite and carbonates (calcite, dolomite, ankerite), which was first observed in diorite and andesite near gold deposits. If one of those minerals prevails, terms such chloritization can be applied and mapped as subzones.

- *Sericitization* is a common alteration of aluminium-rich felsic rocks (granite, gneiss, schists). The typical paragenesis comprises sericite and quartz ($\pm$ pyrite). The involved solutions were acidic and leached part of alkali element contents (Ca, Na and part of K; eq. 1.6).

Sericitization of K-feldspar:



- *Greisenization*: Acidic, fluorine-rich solutions reacting with felsic rocks convert feldspar to topaz. Medieval tin miners in the German Erzgebirge called the resulting grey rock *greisen*. Greisen is a massive or vuggy rock that consists of quartz, topaz and light mica (muscovite or lepidolite). Accessory tourmaline, fluorite, rutile, cassiterite and wolframite are common. Tin and tungsten enriched greisen bodies can be profitable ore (Halter *et al.* 1996).

- *Dolomitization* is the prevalent alteration of limestone adjacent to lead-zinc ore deposits. It is due to import and exchange of magnesium for part of calcium (e.g. Navan, Ireland: Braithwaite & Rizzi 1997).

- Silicate rocks react with CO_2 -rich solutions by carbonatization. Calcite, dolomite and ankerite (more rarely siderite and magnesite) are common alteration products adjacent to gold quartz veins in Archaean and Palaeoproterozoic greenstones (Eilu *et al.* 2001). In practice, the distinction of different carbonate minerals is easiest with colouring techniques (Hitzman 1999). Listwaenitization describes carbonated and silicified ultramafic rocks that may be associated with hydrothermal epigenetic gold mineralization. The altered rocks consist of magnesium-calcium-iron carbonates, chromian muscovite and quartz, with various accessory minerals (Halls and Zhao 1995).

- *Tourmalinization* is common in tin (Lehmann *et al.* 2000a), tungsten and gold deposits. If it is very intensive, tough black rocks ("tourmalinites") result that resist both surficial alteration and the geologist's hammer. Tourmalinites mark the proximity of orebodies. In more

distal position, pervasive growth of dispersed tiny needles of tourmaline in country rock is only revealed by the microscope.

The study of hydrothermally altered wall rocks is an important subject of economic geology. These rocks reveal the nature of the hydrothermal solutions, they assist in the search for ore because they present a much larger and hence more visible target compared to the actual orebodies, and they allow dating of ore formation because of neogenesis of minerals such as K-feldspar, alunite and mica. Zonation mapping provides a vector pointing to the site of possible ore. In addition, hydrothermal alteration is always accompanied by the dispersion of trace metals around orebodies. The resulting trace metal halos are excellent litho-geochemical prospecting guides. And last not least, several alteration products are valuable industrial minerals (e.g. alunite, kaolin, sericite and vermiculite).

1.1.7 Skarn- and contact-metasomatic ore deposits

Many ore deposits are formed close to intrusive igneous rock bodies. The location of the ore may be at the immediate contact between the intrusion and its host rocks, or at a certain distance. In the first case, the host rocks will be affected by contact metamorphism due to heating (e.g. the formation of andalusite in slates and schists). If carbonate rocks are present, skarn (a Ca-Mg silicate rock) is frequently formed by decarbonation and addition of silica. This process releases large quantities of CO_2 that may pass into the magma inducing profound changes, for example of $f\text{O}_2$. Massive orebodies may occur in proximity to the skarn (proximal contact-metasomatic ore). The ore replaces carbonate rocks (or skarn) by a process called metasomatism. The replacement is the result of the passage of hot aqueous fluids that are given off by the cooling magmatic body or by dehydrating country rocks. If the metasomatic ore formation takes place at a distance from the intrusion, the ore will less likely be associated with skarn rock. Resulting mineralizations are either distal skarn, or distal contact-metasomatic orebodies.

Skarn is an old Swedish mining term for a tough calc-silicate gangue that is associated with certain Palaeoproterozoic iron and sulphide ores. Swedish skarn consists of coarsely crystalline andradite, diopside, various amphiboles, scapolite, quartz and carbonate. Skarn bodies are stratabound and pass laterally into fine-grained banded exhalites and iron formations that are hosted in a suite of felsic and mafic volcanic rocks, carbonates and clastic metasediments. Compaction structures around skarn garnets indicate very early formation of these skarns already during diagenesis of the rocks (Oen & Lustenhouwer 1992). This is overprinted by later metamorphic reactions. Similar diagenetic skarn rocks occur occasionally with submarine sediment-hosted sulphide ore and represent exhalative precipitates of Ca, Fe, Al and SiO_2 in a reducing, carbonate-poor environment. High heat-flow that induced syndiagenetic skarn mineral formation during ongoing sedimentation was probably caused by synsedimentary intrusion of subvolcanic magma (e.g. mafic sills). Calc-silicate skarn rocks are also common in high-grade metasedimentary rocks, for example at the contact between carbonate and silicate strata. This “reaction skarn” expresses local exchange of matter during essentially isochemical metamorphism.

“Skarn” in the context of economic geology

“Skarn” (in North America also called *tactite*) commonly describes iron-rich rock bodies of Ca-Mg silicates formed from limestone or dolostone by abstraction of CO_2 and hydrothermal addition of SiO_2 , Al, Fe and Mg in the contact aureole of intrusions. Most skarn ore deposits are related to intermediate igneous rocks, but association with granites and gabbros is known (Lentz 1998). Often, fertile plutons show evidence of magma mixing that enhances the generation of hydrothermal fluids (Grammatikopoulos & Clark 2006). Emplacement of a hot magma body in cool country rocks causes the build-up of a thermal halo with outward migrating isotherms, driving off water and other volatiles. During this prograde phase, mainly anhydrous minerals are formed that include grossular-andradite, diopside, forsterite

and periclase (MgO , if dolomite was present), and part of the ore. Outward from the intrusion, skarn is followed by a narrow zone of wollastonite and a shell of isochemical recrystallization of the precursor carbonate rock to carbonate marble. The export of matter from the cooling magma into the country rocks is due to hot (maximum $>700^\circ\text{C}$) hypersaline melt, saline fluids and gas (Baker *et al.* 2004). The fluid flow in aureole rocks may be quite complex in $T\text{-XCO}_2^{\text{fluid}}\text{-}t$ space. Commonly, initial heating will produce high XCO_2 followed by subsequent passage of magmatic and even meteoric water (Nabelek 2007). Magmatic waters, i.e. hydrothermal fluids continue to exsolve from the intrusion during further cooling and declining pressure. The aqueous fluids represent a retrograde phase, which is characterized by formation of brucite (Mg(OH)_2) after periclase and water-rich silicates (amphibole, epidote, clinocllore, talc, chlorite) replacing earlier anhydrous ones, concurrently with the main mass of the ore. Finally, a system of convective cooling by external, non-magmatic water may be established that imprints low-T hydrothermal alterations.

Limestone and dolostone skarn ores are common. Features that resemble skarn in some aspects are also found at intrusive contacts with intermediate, mafic and ultramafic host rocks, because of their relatively high Ca-Mg contents. Iron formations are generally prone to conversion into skarn as in the Swedish prototype. Archaean iron formations of the Southern Cross greenstone belt in Western Australia host 20 mines and numerous smaller gold skarn deposits, with a total production of >260 t gold (1887–2001). The parent intrusion is a peraluminous two-mica granite (Müller *et al.* 2004). Most skarn bodies occur in host rocks adjacent to an intrusion (exoskarn) but occasionally marginal parts of the intrusions are transformed into skarn because of inward mass transport (endoskarn).

Skarn ore deposits can be related to specific magmas and geodynamic positions: Diorites of primitive island arcs produce mainly magnetite orebodies that may have recoverable contents of Cu, Co and Au. In North America, intermediate to felsic, differentiated within-plate intrusions of active continental margins generated some of

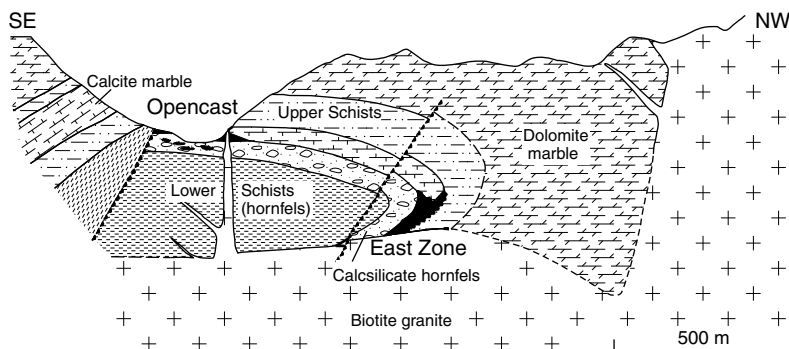


Figure 1.30 Geological section of the scheelite skarn deposit CanTung, North West Territories, Canada (modified from Middelaar & Keith 1990).

the most important tungsten ore deposits (Figure 1.30). At CanTung mine, two tungsten orebodies occur in contact metamorphic Cambrian carbonate sediments above a granite stock: In the open cut, the ore consists of scheelite, garnet, diopside and epidote, whereas ore in the underground East Zone is characterized by pyrrhotite and tremolite. In British Columbia, intrusions of Jurassic island arc terranes are related to polymetallic skarn ore of Cu, Fe, Zn-Pb-Ag, Mo, Bi and Au (Ray *et al.* 1995). Mesozoic, post-orogenic and rift-related ilmenite series granites produced skarn deposits of tin with As, Pb-Zn, W, Mo and some Fe-sulphides (China). These consistent relations are a weighty argument for a predominantly magmatic-hydrothermal derivation of the ore elements, which is confirmed by geochemical data on fluid inclusions (Samson *et al.* 2008).

Skarn orebodies display characteristically irregular outlines that can be explained by the two main factors, lithology and structures of the replaced host rocks, which impose chemical and physical controls on permeability and reactivity. Orebodies are often zoned, for example with copper in a proximal and lead-zinc in a more distal position.

Distal contact-metasomatic ore deposits are closely related to skarn ore formation, although skarn rocks may be absent. Ore formation by replacement of carbonate rocks is solely a hydrothermal process. In the Tertiary Pb-Zn-Ag province in Mexico, for example, the connection between proximal skarn to distal stratiform ore ("mantos") is provided by pipe and chimney-shaped orebodies.

Skarn orebodies are a major source of many metals but also of industrial minerals including

wollastonite, graphite, asbestos, magnesite, talc, boron and fluorite.

1.1.8 Porphyry copper (Mo-Au-Sn-W) deposits

Porphyry ore deposits are a product of magmatic-hydrothermal activity at shallow crustal levels. Primarily copper, but also molybdenum, tin, tungsten and gold occur closely related to epizonal intrusions of porphyric magmatic rocks (Figure 1.26). Porphyries contain phenocrysts of hornblende, biotite, feldspar or quartz in aplitic groundmass, which solidifies by pressure decay, volatile loss and sudden freezing during rapid ascent. This is the only connotation of the term porphyry ore deposits, not the arrangement or distribution of ore minerals. Because of the large diversity of the group, porphyry deposits of Mo, Sn and W are presented in Chapter 2, whereas the following discussion centres on Cu-Au-Mo porphyry ore deposits, which presently supply ~75% of the world's Cu, 50% of Mo, nearly all of Re and 20% of gold. The most significant characteristics of copper porphyries include:

- plug-like multiple porphyric intrusions below comagmatic volcanoes, formed before mineralization;
- an extraordinary tonnage of magmatic-hydrothermal ore;
- the ore occurs mainly in stockwork vein systems within the intrusion;
- metal contents in ore are low to moderate, and supergene enrichment is often the key to exploitability;

BOX 1.3 Porphyry copper deposits

The average porphyry copper deposit comprises ~1000 million tonnes (Mt) of ore. Common hypogene ore grades are 0.5–1.5% Cu, 0.01–0.04% Mo and <1.5 g/t Au (Sillitoe 2010). Giant deposits enclose >2 Mt, supergiants such as Chuquibambilla (Figure 1.31), >24 Mt of copper metal. The largest is El Teniente in central Chile, with >94 Mt of contained copper (Cannell *et al.* 2005). Large copper porphyry open cut mines expose orebodies that extend over several km². Alteration halos surrounding ore can be 10 to 20 times this size. Metal contents are generally low but the large mass allows profitable mining. Apart from copper, by-product metals include significant tonnages of Ag, Au, Mo, Re, Pb, Zn, Mn and minor amounts of As, Bi, Sn, W, U and Pt. Clusters of giant deposits that far exceed average copper porphyry size occur in central and northern Chile, and southwestern Arizona to northern Mexico (Cooke *et al.* 2005).



Figure 1.31 (Plate 1.31) Chuquibambilla open pit in Chile, one of the world's largest porphyry copper mines. Courtesy Bernd Lehmann, Clausthal. The pit measures 2 × 3 km and approaches a depth of 900 m. Total pre-mining resources were nearly 3000 Mt at 1% Cu and by-product Mo. Annual production is ~1.2 Mt copper and 20,000 t molybdenum plus rhenium.

Porphyry copper systems develop above large parental magma chambers at 5 to 15 km palaeodepth, which establish the heat and flux regime of both the porphyry intrusions and the mineralizing fluids. In a non-telescoped system, the potassic hydraulic fracturing-mineralization-alteration is surrounded by propylitization due to moderate-temperature hydration reactions. Above the porphyry level, advanced argillic (quartz-pyrophyllite-kaolinite-alunite) and vuggy quartz lithocaps may be formed by extreme base leaching. The vuggy quartz level is often the site of epithermal high sulphidation gold mineralization (Sillitoe 2010). Intermediate sulphidation mineralization with higher contents of Pb, Ag, Zn and Mn may be formed at a greater distance from the porphyry centre.

Porphyry copper ore deposits display a hydrothermal alteration zoning that is best characterized by the Lowell-Guilbert (1970) model (Figure 1.32a). Note that this sketch is time-integrated and displayed features originate at different times. Typically, sericitization and the main ore precipitation overprint earlier potassic (mafic minerals replaced by secondary biotite) and propylitic alteration. In practice, there is much variance because of complexities such as repeated intrusive activity and previous alteration of affected rocks (Sillitoe 2010). Hydrothermal systems that produce porphyry ores at depth can extend to the surface where shallow veins and hot springs ore deposits may be formed (Heinrich *et al.* 2004, Heinrich 2005). Skarn ore may be generated at contacts of the porphyry intrusion with carbonate rocks.

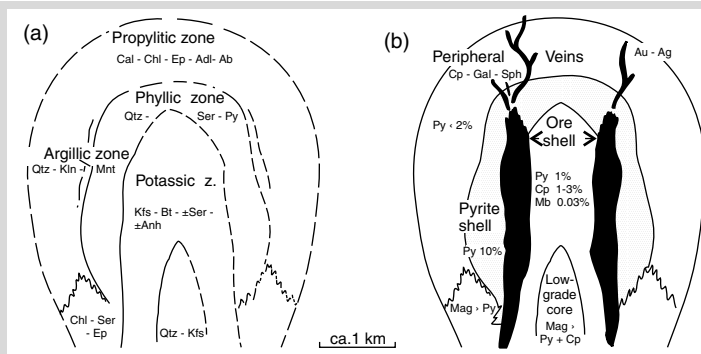


Figure 1.32 Schematic arrangement of hydrothermal alteration zones (a) and mineralization (b) in a porphyry copper-molybdenum deposit, according to the venerable Lowell-Guilbert (1970) model. The sequence from potassic to advanced argillic alteration is due to increasing acidity of the fluids. After Lowell, J.D. & Guilbert, J.M. 1970, Society of Economic Geologists, Inc., *Economic Geology* Vol. 65, Figure 3, p. 379. Abbreviations: Ab - albite, Adl - adularia, Anh - anhydrite, Bt - biotite, Cal - calcite, Chl - chlorite, Cp - chalcopyrite, Ep - epidote, Gal - galena, Kfs - K-feldspar, Kln - kaolinite, Mag - magnetite, Mb - molybdenite, Py - pyrite, Qtz - quartz, Ser - sericite, Sph - sphalerite.

Ore formation and the hydrothermal alteration are caused by magmatic fluids and vapours, at temperatures between ~800 and <300°C. More than 90% of the ore is hosted in a vein stockwork in the outer potassic and/or the sericite zone ("ore shell"; Figure 1.32b and Figure 1.33); some ore replaces silicate minerals ("disseminated ore"). Upwards and outwards from the porphyry ore, a halo of small but high-grade gold, silver and base metal vein deposits may be present. At Butte, some of these veins were mined along a distance of 7 km across the district and to 1.5 km depth (Rusk *et al.* 2008). Sulphur isotopes have a magmatic signature, whereas water and strontium isotopes clearly document the passage from early magmatic to late meteoric fluids. During mineralizing events, different fluids pervade the deposit and are trapped in

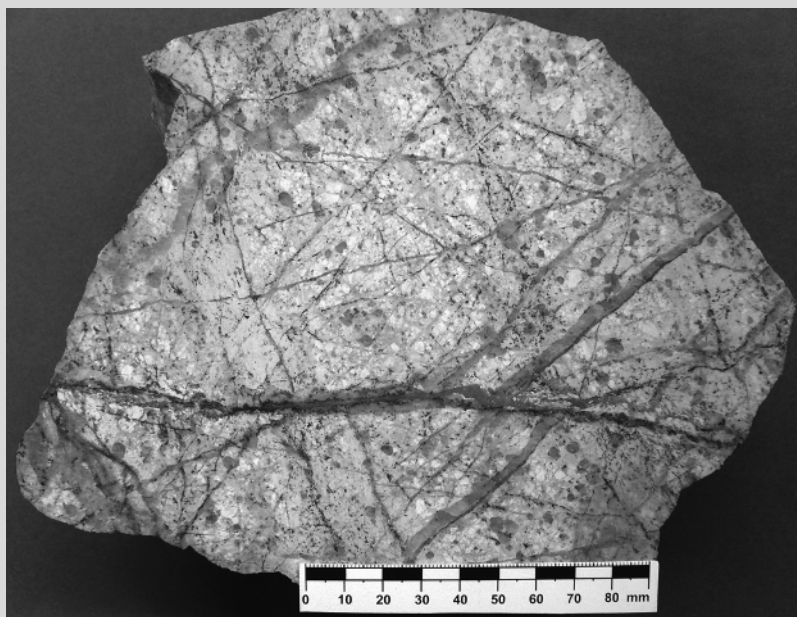


Figure 1.33 (Plate 1.33)

Typical copper porphyry ore from Chuquicamata, displaying brecciation and quartz veining, pervasive sericitic (greenish) and argillic alteration. Courtesy Bernd Lehmann, Clausthal. Grey ore in veinlets is largely chalcocite due to supergene enrichment, which reaches 800 m below surface.

fluid inclusions. In most porphyries, main-stage potassic alteration mineralization is connected with co-existing immiscible brine and vapour. Brine is dense ($>1.3 \text{ g/cm}^3$) and saline (35 to $>70 \text{ wt.}\%$ NaCl equivalent), with variable contents of K, Na, Ca, Fe, Mo and Cu chlorides (Klemm *et al.* 1975, 1974; Rusk *et al.* 2008). The same elements are found in the multitude of daughter minerals in fluid inclusions (halite, sylvite, anhydrite, chalcophyrite, haematite, Fe-chloride, etc.) of minerals precipitated at this stage. Early fluids have metal ratios that correlate with those calculated for the whole deposit, which is a further argument for a magmatic derivation of the metals (Ulrich *et al.* 1999). Another confirmation is the observation that melt and fluid inclusions co-exist in early hydrothermal quartz (Harris *et al.* 2003). Cogenetic supercritical liquid brine and low-density vapour phase inclusions ($D < 0.1 \text{ g/cm}^3$) document boiling and unmixing of the fluids. Vapour collects acidic volatile species (SO_2 , H_2S , CO_2 , HCl, HF) and most Cu and Au, plus much of As, Ag, Sb, Te and B. Vapour flow dominates transport and precipitation. Cooling and contraction of magmatic vapour to a liquid appears to dominate copper mineralization (Klemm *et al.* 2007). Reduction can be induced by magnetite crystallization that triggers sulphate to sulphide conversion. Consequent sulphide precipitation promotes ore formation (Liang *et al.* 2009).

- extensive hydrothermal alteration and metals are vertically and cylindrically zoned in relation to the axis of the intrusion.

Host rocks of copper (Au-Mo) porphyry deposits are shallow ($<4000 \text{ m}$), subvolcanic and mostly cylindric intrusions. The parent rocks are frequently calc-alkaline diorites (or the volcanic equivalent andesite-dacite), monzonites (latite) or granites (rhyolite) of I-type that occur in volcano-plutonic arcs above subduction zones, either on active continental margins or in island arcs. Subduction of topographic and thermal anomalies appears to favour copper porphyry genesis (Cooke 2005). Less frequent are Cu-Au porphyry and related epithermal gold deposits in continental collision zones and post-subduction settings (Richards 2009). The parent intrusives are geochemically not peculiar, apart from high oxidation (Mungall 2002). Their hydrous nature, elevated oxidation and SO_2 contents (including anhydrite as a magmatic phase) are the main differentiating characteristics in comparison to the numerous barren intrusions of convergent plate margins. Porphyries on active continental margins are marked by elevated Sn and Mo concentrations apart from copper, those of island arcs more often contain gold as the second metal. Porphyry deposits older than Early Tertiary are rare (Cooke *et al.* 2005) but the oldest date from the Archaean.

Several porphyry copper ore deposits display a strong epithermal signature (cf. "Volcanogenic Ore Deposits") and overprinting of earlier hydrothermal alteration, for example clays replacing potassic zone minerals, as at the gold deposit

Ladolam on Lihir Island, Papua New Guinea. Such extreme telescoping is best explained by rapid erosion or a sudden collapse of the original volcano (Sillitoe 1994). Moderate telescoping is common, however, because of contraction of the hydrothermal system with progressive cooling.

Sources of the metals concentrated in porphyry copper ore deposits are probably deeper mafic magmas (Hattori & Keith 2001) but ultimately a fertile mantle. Melts and supercritical fluids that originate in the subducting oceanic crust are oxidizing and dissolve chalcophile metals. Absence of reduced sulphur in the source region is a precondition because otherwise sulphide melts would form, which must lag behind rising silicate liquid (Mungall 2002). In epizonal staging chambers, however, an intermediate step of sulphide melt formation may intervene (Halter *et al.* 2002, 2005). Transfer of the metals from mafic melt into the subvolcanic felsic magma may be enacted by highly metal-charged ore brines (Figure 1.34). The shallow felsic magma is the apparent source of ore fluids that cause brecciation, alteration and mineralization in the solid roof, concomitant with the dynamics of a rising stratovolcano. The activity of individual porphyry systems may last for $\sim 100,000$ to several million years; districts are active for 10–20 My (Sillitoe 2010).

1.1.9 Hydrothermal-metasomatic ore deposits

The term "metasomatic ore deposit" implies that the mass of ore was formed by hydrothermal chemical conversion and replacement of a pre-

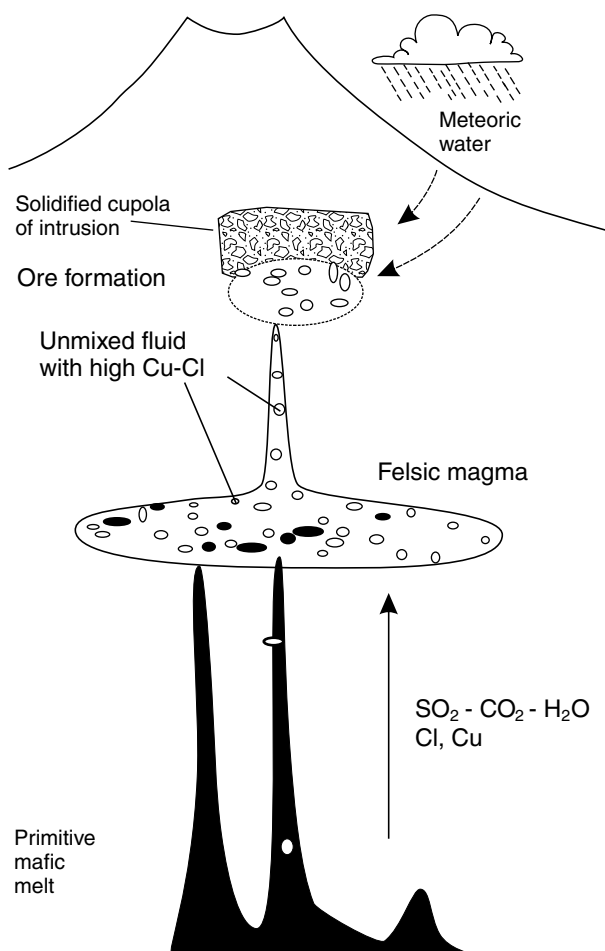


Figure 1.34 Genetic concept of deep magmatic processes preparing the formation of a porphyry copper deposit (modified from Hattori & Keith 2001). With kind permission from Springer Science+Business Media.

existing rock. Local metasomatic processes, for example in ore veins, are ubiquitous co-products of hydrothermal activities, but do not justify attribution to this genetic group. Metasomatic ore formation near igneous intrusions is extremely frequent (cf. Skarn- and Contact-Metasomatic Ore Deposits). In order to avoid repetition, we focus here the discussion on metasomatic ore deposits that have no recognizable genetic relation to magmas. Non-magmatic hydrothermal metasomatic ore formation is usually due to the passage of diagenetic and metamorphic fluids, and especially of evaporative and salt-solution brines (cf. Sections 1.4 and 1.6).

Typically, the metasomatized rocks are marine limestones. This preference can be demonstrated

with numerous examples (e.g. many lead-zinc orebodies, gold as at Carlin, USA, magnesite and siderite: Pohl 1988). Main controls of the replacement process include the reactive surface and permeability of the precursor rock, pH and Eh of the mineralizing solutions, and the relative solubility of the participating minerals. A simplified equation 1.7 describes the metasomatic formation of siderite rock (an iron ore) from limestone.

Metasomatic formation of siderite from limestone:



In this case, cation exchange is the dominant mechanism, replacing each molecule of calcite



Figure 1.35 The metasomatic siderite deposit Erzberg (“ore mountain” in German) in Austria. The active quarry faces away from the camera. The view shows disposal of barren carbonate host rock.

with one of siderite. Because of the smaller molecular volume of siderite, the resulting ore rock should have a reduced volume. This can be observed in the form of drusy ore at a number of siderite deposits (Erzberg, Austria, Figure 1.35; Ouenza, Algeria), but in many other cases metasomatism exchanges equal volumes. Indicators for this process include the conservation of intricate textures and structures of the replaced rocks (e.g. layering, banding, fossils, stylolites, etc.). Generally, however, metasomatism induces a dramatic change in both chemistry and fabric of the precursor. Some metasomatic ores appear to replace newly deposited soft sediment (e.g. in some magnesite deposits: Pohl & Siegl 1986), but well consolidated precursor rocks are more common.

Hydrothermal-metasomatic ore deposits are often stratabound and occur in the same stratigraphic level across large regions. For example, siderite deposits in North Africa and in northern Spain occur in Early Cretaceous micritic limestone, and lead-zinc ores of the Viburnum MVT district of mid-western USA are confined to stromatolite reefs of the Late Cambrian Bonnetterre

Formation. Zinc-rich MVT ores in the Tri-State district occur in Mississippian carbonates. In the past, observations like this were believed to prove syngenetic mineralization. Today, a hydrothermal and epigenetic emplacement is undisputed, but the causes of the preference for certain strata are not always clear. Possibilities include chemical, hydraulic and mechanical parameters.

The emplacement of metasomatic ore is favoured by low-permeability rock horizons (e.g. shales) that form a physical barrier to upward flow (similar to petroleum traps). Focused hydrothermal solutions react more intensively with the carbonate host. Model calculations show that metasomatism is promoted by: i) large temperature differences in flow direction; ii) large focused quantities of fluids; and iii) anomalous phase equilibria (Ferry & Dipple 1991).

The form of many metasomatic deposits is characterized by irregular reaction fronts (“reaction fingering”) between ore and host rocks. Higher permeability tongues may be caused by the commonly smaller volume of the product (“induced permeability”). Orebodies are

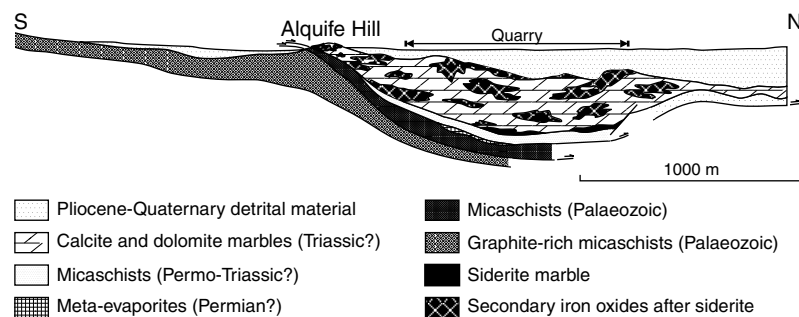


Figure 1.36 Geological cross-section of the Alquife metasomatic iron ore district, Betic Cordillera, southern Spain. Modified from Torres-Ruiz, J. 2006, Society of Economic Geologists, Inc., *Economic Geology* Vol. 101, Figure 3, p. 670. For location refer to Figure/Plate 1.89.

stratabound and cloudy masses with irregular outlines, but some borders mimic structures of the precursor rock (joints, faults, bedding planes). Other ores may take the shape of extensive strati-form bodies (mantos). Both are demonstrated at Alquife in southern Spain (Figure 1.36). In this region, metasomatic siderite was formed during the Triassic by acidic and reducing solutions that leached iron from graphite-rich micaschists in the Palaeozoic basement and ascended along synsedimentary extensional faults into Permo-Triassic cover carbonates. Host rocks and ore were later deformed and metamorphosed by a polyphase Alpine orogeny. In the Tertiary, most of the siderite bodies were affected by supergene alteration and now consist of goethite and haematite.

The flow direction of hydrothermal solutions generates two boundary types of very different nature:

1 In the flow direction, various reactions of mineral neogenesis and isotope exchange migrate with different speed in the form of a chromatographic model (Korzhinskii 1970); assuming kinetically fast reactions, several spatially separate reaction fronts should be the result.

2 Boundaries that laterally limit flow channels (e.g. massive impermeable limestone constricting flow in jointed limestone) can display direct contacts between totally unaltered host rock and high-grade metasomatites (Yardley & Lloyd 1995).

Metasomatism can be accompanied or closely followed in time by mineralization with the character of simple open space filling (veins, fissures, druses, karst cavities). In the North African siderite deposits, this role is played by quartz-barite-

fluorite veins, in Bleiberg, Austria by cave-filling ore. Cave ores may include bedded sediments and are a rare, fascinating aspect of hydrothermal systems (cf. "Karst").

1.1.10 Hydrothermal vein deposits

For a long time in the past, ore veins were the most important deposit type. Practice and theory of mining and geosciences grew with the challenges of vein mining, as shown by fundamental books from Agricola (1556) to Lindgren (1933). More recently, the economic relevance of vein mining decreased compared to large-tonnage low-grade operations such as those based on copper porphyries. However, several high-grade base metal vein deposits successfully compete with the mechanized giants.

Veins are tabular bodies of hydrothermal precipitates that typically occupy fissures. Less often, veins originate by metasomatic replacement of rock (replacement veins), propagating from a joint or shear plane. Vein walls range from clean parting planes to "frozen" contacts. Many veins develop upwards into a fan of thinner veins and veinlets (Figure 1.15), which resemble a branching tree. At district scale, veins tend to occur in groups that form vein systems.

Thickness, vertical extent and horizontal length of veins vary widely. Less than 0.5 m thickness may allow profitable mining of high-grade gold and silver ore veins, whereas tin and tungsten require a width of 1 m, barite and fluorite a minimum of 2 m. The world's longest veins may be those of the Mother Lode system of California, with 120 km strike length. Most veins, however,

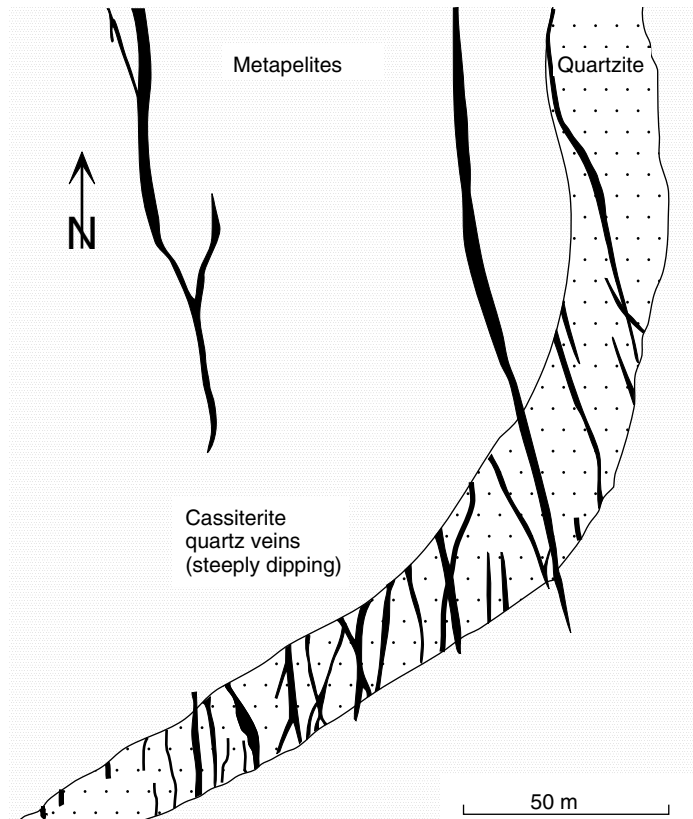


Figure 1.37 Geological map of one level in Rutongo tin mine, Rwanda, showing closely spaced parallel quartz-cassiterite veins (for location, compare Figure 1.16).

have lengths between a few tens to several thousand metres. The disposition of veins in space ranges from horizontal to vertical, but because hydrothermal solutions have a general tendency to flow upwards (more precisely towards lower hydraulic potential) steeply dipping veins are in the majority.

Mechanical properties of host rocks are the most important controls of vein formation, in contrast to metasomatic ore deposits that depend first on chemical properties. Fractures form more readily in competent rocks than in ductile material. Therefore, the cassiterite-quartz (muscovite, arsenopyrite, tourmaline) veins at Rutongo, Rwanda occur preferentially in vitreous quartzites and few cut across low-grade metamorphic schists (Figure 1.37). Very brittle rocks such as dolomite, rhyolite and quartzite are prone to form a network

of short fractures instead of spatially separated longer ones (Figure 1.38). In that case, hydrothermal activity may result in stockwork ore. “Stockwork orebodies” consist of numerous short veins of three-dimensional orientation, which are so closely spaced (e.g. 10–30 veins/m in the tin deposit of Tongkeng-Changpo, South China) that the whole rock mass can be mined.

Many vein deposits are spatially and genetically associated with brecciated rock bodies that may host rich ore (Jebrak 1997). As a rule, fissures and breccias have a much higher permeability than most consolidated rocks, which are commonly aquitards. Therefore, these structures focus fluid flow at all scales, from single veins to large structures such as rift faults and crustal shear zones (Weinberg *et al.* 2004). Many fissures, for example the tin ore veins of Cornwall,

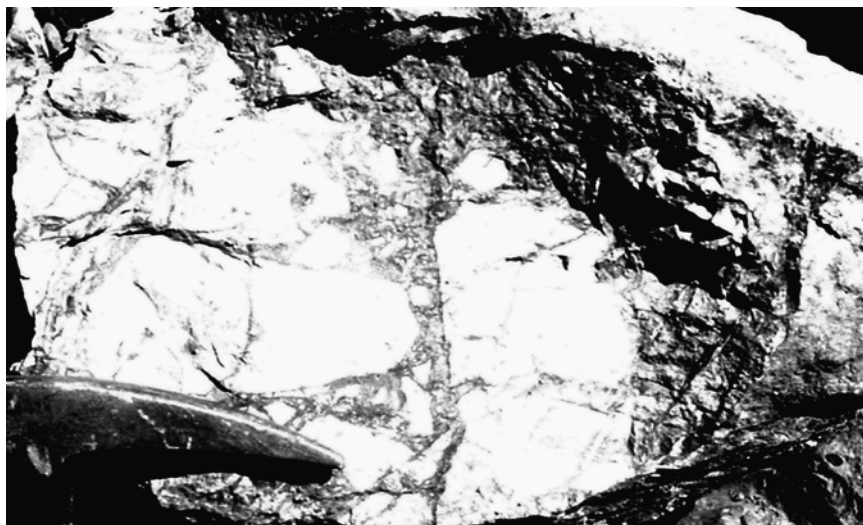


Figure 1.38 Breccia ore at Mammoth copper mine near Mt Isa, Queensland. Supergene secondary chalcocite (grey near hammer) replaces primary chalcopyrite and pyrite in veinlets within quartzite (white).

England, are surrounded by broad zones of intensive micro-fracturing that provide access to fluids from the main flow channel (Dominy *et al.* 1996). It is well-known in the oil industry that in contrast to common permeable faults, clay and shale gouge can transform faults into very effective barriers to fluid flow (Egholm *et al.* 2008). Unconsolidated rocks (clay, sand) are unlikely to fracture but deform ductilely. Typically, this reduces their permeability so that such faults restrict flow.

Veins are channels of former fluid flow. Principally, hydraulic mass flow is a function of hydraulic conductivity and velocity. Flow in a single fissure is controlled by its aperture and secondary properties such as morphology and roughness of the walls. Note that the hydraulic aperture of a vein was hardly ever equal to its present thickness, because most veins were filled while gradually opening. For cases of sheeted vein systems (Figure 1.37), the total cross-sectional permeability can be estimated by incorporating the distance between veins (Lee & Farmer 1993; eq. 1.8). Only in favourable cases, the flow velocity can be measured, for example when upflowing water deposited suspended sediment or hydrothermal

precipitates (cf. eq. 1.4 in section “Mineral Succession”).

Hydraulic permeability (k) of a single vein and of a sheeted vein system:

$$\begin{array}{ll} \text{Single fissure} & k_{\text{vein}} = (\rho \cdot g / \mu) \cdot (a^2 / 12) \\ \text{Sheeted fissures} & k_{\text{sum}} = (\rho \cdot g / \mu) \cdot (a^3 / 12d) \end{array} \quad (1.8)$$

ρ = density of the fluid (g/cm^3), g = gravitational acceleration (m/s^2), μ = dynamic viscosity (m^2/s), a = aperture (m), and d = distance between veins (m).

Methods of fractal analysis (Mandelbrot 1982) were conceived for studying structures built of many elements. Examples of vein-related topics include the statistical distribution of vein thickness and the spacing of veins, and extrapolation of results into adjacent blocks or to different scales (Roberts *et al.* 1998, Marrett *et al.* 1999). In some cases, the fractal distribution of tectonic features and of mineralization, that is their similarity from microscopic to regional scale, can be used for the definition of new exploration targets (Weinberg *et al.* 2004).

Rock mechanic and tectonic interpretation of vein systems play a central role in vein mining, from creating exploration targets to predicting the shifted position of a vein behind a fault. Mining districts display individual controls that must be identified by careful mapping and structural analysis at all scales. Neogenesis and opening of fissures, shear planes and faults reflect spatial orientation and the ratios of principle tectonic stresses during vein formation (Figure 1.39). The opening of fissures is only possible if normal stress is negative (simple tension) or if fluid pressure (u) is high enough to counteract normal stress (effective stress $\sigma_{\text{eff}} = \sigma - u$). This condition is often realized by injection of high-pressured hydrothermal fluids. Many veins display pronounced banding (Figure 1.28) that indicates a correlation between pressure increase of the fluids, movement of the fissure walls and precipitation of hydrothermal fill. This is called “seismic pumping” or “fault valve cycling” (Sibson 1990).

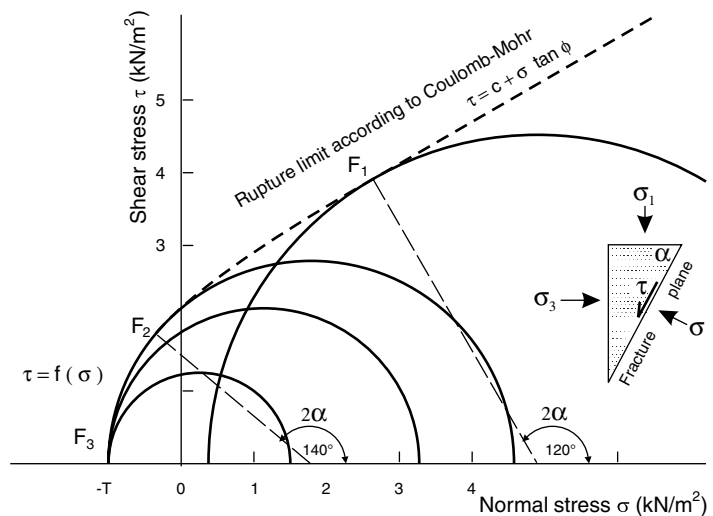
Very large faults and shear zones are rarely the site of hydrothermal mineralization. Orebodies occur rather in clusters of fractured rock near jogs or bends in the large structures. This can be explained by the time-integrated evolution of rock mass permeability after faulting (Sheldon

& Mikleswaithe 2007): Main faults that experience a high displacement seismic event enter a healing regime that rapidly reduces permeability. The rock mass at some distance from the fault, however, undergoes a period of weakening that may result in seismic aftershocks. Because this causes elevated permeability for weeks or months after an earthquake, the time-integrated fluid flow will be larger than in the main fault, favouring the formation of ore.

Tectonic control of ore veins

The tectonic control of ore veins may be neogenesis of new fractures or opening of older structures. Both allow an examination of the tectonic processes that were active during vein formation. Not unexpectedly, many veins are associated with large-scale tensional tectonics including rifting (e.g. silver-lead-barite ore veins near the Tertiary Upper Rhine Rift, Figure 1.28; silver veins at Kongsberg near the Permian Oslo Graben; fluorite in the Tertiary East African Rift near Naivasha, Kenya) and late-orogenic relaxation of orogens (e.g. silver veins near Freiberg, Saxony, lead-zinc veins in the Harz Mountains, Germany). However, veins may also originate during convergent tectonics, synchronous with shearing, folding,

Figure 1.39 The formation of shear fractures (F1), shear fissures (F2) and tensile fissures (F3) with the corresponding angle of fracturing (α), and tectonic stresses $\sigma_1 > \sigma_2 > \sigma_3$ in the Mohr diagram. The inset triangle on the right depicts a section of the upper half of an originally cylindrical sample specimen with the stress geometry of fracture case F1. Fracturing is often assisted by high fluid pressure (u) which reduces strength according to $\sigma_{\text{effective}} = \sigma - u$.



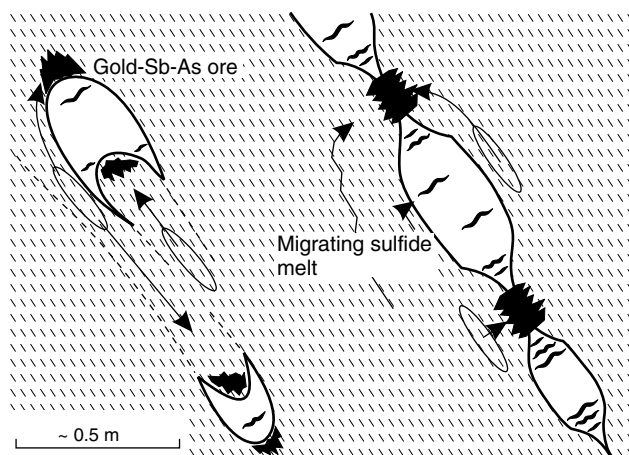


Figure 1.40 Schematic concept of mobilization of disseminated ore melt from high-strain host rock into dilatational sites in folds and boudin necks (Hemlo gold mine, Canada). Modified from Tomkins, A.G., Pattison, D.R.M. & Zaleski, E. 2004, Society of Economic Geologists, Inc., *Economic Geology* Vol. 99, Figure 3 p. 1066.

thrusting and nappe advance (gold quartz veins in Western Australia: Vearncombe 1998; tin and tungsten veins in Central Africa: Figure 1.39; the gold-rich “saddle reefs” in folded shales of Victoria, Australia: Windh 1995). At transitional brittle/ductile conditions, boudinage often controls ore deposition, from the regional to exposure scale (Findlay 1998, Tomkins *et al.* 2004: Figure 1.40). At Hemlo, pre-enriched auriferous sulphides and sulphosalts were partially remelted during deformation and metamorphism. The resulting sulphide liquid migrated to low pressure spaces. Residual ore in the host rocks (baritic metasediments and metavolcanics) includes pyrite and molybdenite ($\pm$ Au), whereas stibnite, realgar, sulphosalts and gold characterize the solidified and recrystallized sulphide melt.

Vein systems may consist of cross-cutting vein sets that reveal changes in time, including both the stress field and the nature of hydrothermal solutions. At Gifurwe in Rwanda, an early vein generation was injected into anticlinal fold hinges and cut across by later subvertical veins, but both systems have the same paragenesis of wolframite, quartz, muscovite, tourmaline and arsenopyrite (Figure 1.41 and Figure 1.42). Vein formation is late orogenic compressional. Initially, high fluid pressure counteracted vertical rock mass stress, followed by near-vertical fracturing and pressure release.

The distribution of ore in veins is inhomogeneous and only a small part of the total vein fill may be exploitable. Related to either surface or volume, the ratio of economic to uneconomic

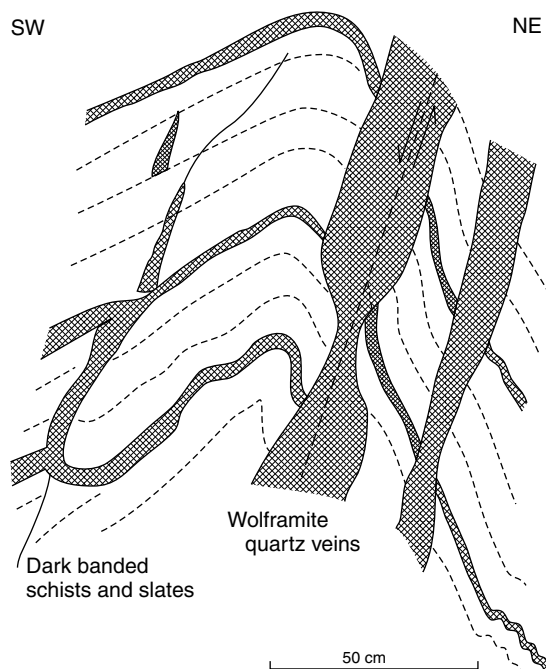


Figure 1.41 Cross-cutting wolframite-quartz veins in folded black shales of the tungsten mine at Gifurwe in Rwanda.

Figure 1.42 Granite-related wolframite veins at Bugarama in Rwanda display a gangue of coarsely crystalline muscovite (white, glittering), dark grey quartz and black shale fragments, which fill steeply dipping bedding-parallel deformation and flow channels between thick competent quartzite beds.



parts of a vein is called the “coefficient of workability” (frequent values are 0.2–0.3). High-grade ore zones (“ore shoots”) display distribution patterns that are important guides to exploration (Figure 1.43). During ore deposit formation, ore shoots were preferential channels of fluid flow and ore precipitation. Intersections of veins are often enriched, as are vein contacts with agents of metal precipitation in host rocks mentioned earlier, such as sulphides, organic matter and carbonates. The morphology of a vein surface is never a perfect plane but includes depressions, furrows and highs that are depicted in so-called “Conolly diagrams” (a map of the vein surface similar to

Figure 1.43). Replete with data on vein thickness, grade of ore, different host rocks and intersecting structures, these diagrams are extremely instructive.

Metal zonation

Most veins display a change of ore and gangue minerals with increasing depth until a barren zone is reached. The vector of these changes points generally downwards, but may have a strong horizontal component. In the Harz Mountains, Germany, lead and silver predominate at upper levels, whereas zinc appears below. In the same area, barite veins end at depth in a barren

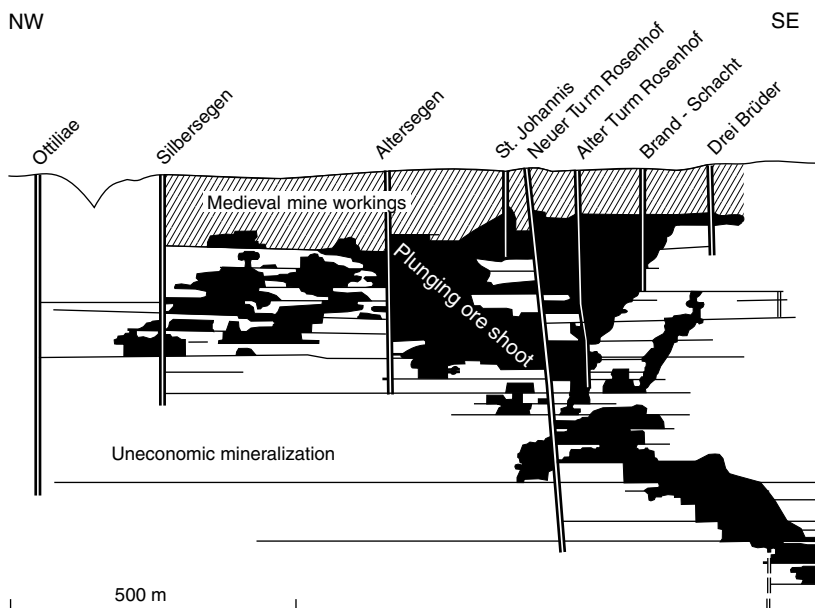


Figure 1.43 Exploited ore shoots (black) of the steeply dipping Rosenhöfer vein, in the lead-silver-zinc mining district west of Clausthal, Harz Mountains, Germany, illustrate the distribution of mineable and subeconomic areas of the vein. With permission from <http://www.schweizerbart.de>.

quartz zone. Such a *primary zonation* is thought to be due to pressure, temperature and chemical gradients. The term *secondary metal zonation*, in contrast, describes the re-arrangement of elements imprinted by supergene weathering. Spatial zoning models can be used to define hydrothermal centres and exploration targets. In the case of complicated and long-lived hydrothermal systems, metal zone reconstruction should be based on specific activity periods or parageneses of the same age. Thermal and geochemical halos of hydrothermal systems may wax and wane in time, which causes overlapping of zones (“telescoping”, Audétat *et al.* 2000).

Vein districts are characterized by recurring parageneses of ore and gangue minerals. In fact, many of these mineral and chemical associations occur worldwide. In the German Erzgebirge, with numerous cross-cutting vein systems, this observation was of high practical relevance to miners and a formal classification of “vein formations” was developed (e.g. “the Pb-Zn-Ag Formation” in the Freiberg District;

cf. Stemprok & Seltmann 1994). For descriptive and practical purposes, notations like this are certainly useful. The word “formation”, however, is ambiguous.

1.1.11 Volcanogenic ore deposits

The formation of a large number of important ore deposits is closely related to terrestrial and submarine volcanism. We have met two members of this group in earlier chapters; the subvolcanic porphyry ore deposits and the mineralization related to the volcanic section of ophiolites (Cu-Zn-Au ore of Cyprus type). Mid-oceanic deposits, however, are commonly subducted and rarely preserved. Here, other economically significant classes of volcanogenic ore deposits are introduced: i) the submarine volcanogenic massive sulphide (VMS) deposits; and ii) the terrestrial epithermal gold-silver-base metal deposits. Banded iron formations of the Algoma type are also a member of this group (cf. Section 1.3 “Autochthonous Iron and Manganese Deposits”).

BOX 1.4 Polymetallic vein fields of Cornwall

Already 3200–2900 BCE (before the Common Era), the tin and copper veins of Cornwall were the destination of adventurous maritime expeditions by the Phoenicians, famous traders in the Mediterranean and beyond. The Cornubian batholith is built of several S-type granite pulses that intruded after the peak of Variscan orogeny (Carboniferous/Permian; from ~300–270 Ma: Chesley *et al.* 1993). The youngest phases of single plutons are fractionated and geochemically specialized, with abundant lithium, boron, caesium and uranium (Chappell & Hine 2006). All granites contain enough uranium and thorium (an average of 11, respectively 19 ppm) to be classified as HHP granites. The relative age of mineralization varies between different plutons. Some veins are synchronous with granites, others apparently up to 40 million years younger. Similar age spreads are displayed by felsic porphyry dykes that cut granites and country rocks, and are controlled by tectonic structures that parallel ore veins.

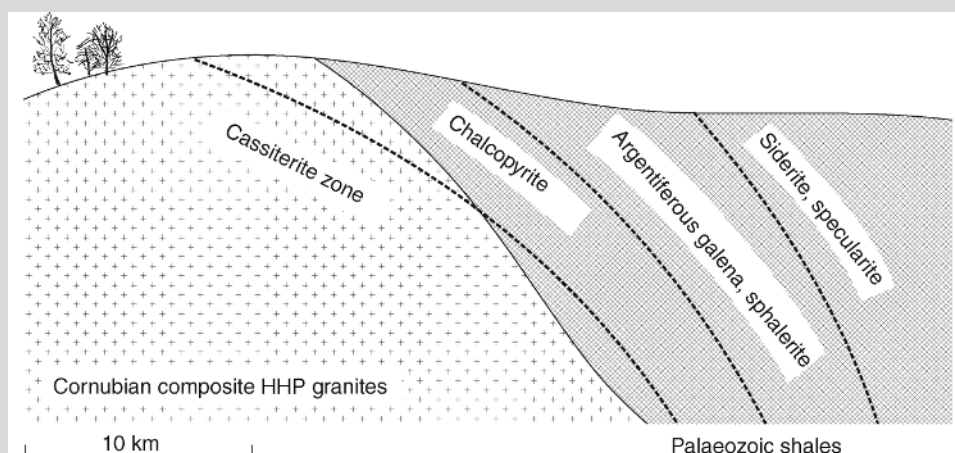


Figure 1.44 Schematic section of primary (hypogene) zonation in polymetallic vein mineralization, Cornwall, England.

Hydrothermal ore veins of Cornwall are zoned about “emanation centres” located in granites, rarely in Palaeozoic country rock schists (Scrivener & Shepherd 1998). Sixty emanation centres are known, with an elliptical shape and a long axis of ~4 km length. The mineralization is not monophase but the product of several activity periods. The oldest episode comprises mineralized pegmatites, sheeted veins with greisen selvages and breccias, all with tin, tungsten and much tourmaline. Highly saline aqueous fluid inclusions with tin, and cogenetic gaseous inclusions with CO₂ and W ± Sn, suggest an origin by unmixing from high-temperature magmatic fluids. The economically prominent main phase of the Cornubian mineralization produced polymetallic (Sn, Cu, Pb, Zn, Ag, Fe, As) veins with a gangue of quartz, tourmaline, chlorite and fluorite, which are very distinctly zoned (Figure 1.44). T_H of inclusions is between 200 and 380°C. The similarity in age of the main polymetallic mineralization indicates formation independent from host granites of varying ages. Relations to younger unexposed pulses of magma are one suggested explanation (Chesley *et al.* 1993). The youngest and last episode of mineralization is represented by low-temperature quartz-fluorite-barite veins with Pb, Zn, Ag and U (the “cross-courses”). Cross-course forming fluids were saline (Na-Ca-Cl), similar to deep formation waters and homogenize at 105–180°C. Until closure of the South Crofty Mine in 1998, the mine production of Cornwall reached a total of 1.75 Mt tin, 1 Mt copper and 0.13 Mt zinc.

Apart from metal ores, Cornubian granites host giant kaolin deposits that occur in the form of pipes, alteration envelopes of veins and horizontal blankets. Many observations suggest kaolin formation by hot, acidic hydrothermal solutions (Dominy & Camm 1998), but water isotopes indicate formation from meteoric water. In fact, many vein mineralizations in Cornwall were precipitated from deeply-circulating meteoric water, with the exception of the early stages of the Permian main phase of Cornubian mineralization, which originated from regional extension, deep heat-flow and crustal melting, followed by fractionation and intrusion of the Cornubian batholith (Chappell & Hine 2006, Shail *et al.* 2003). Later

episodes of mineralization were made possible by radiogenic heat production of the granites. Plate tectonic events, such as the opening of the Atlantic, may have favoured deep convection of meteoric and basinal fluids, which leached metals at depth and precipitated ores in the present vein deposits.

Clearly, hydrothermal metal zoning in veins centred on granites is not sufficient evidence for a magmatic source. The example of Cornwall demonstrates coincidence of both the magmatic-hydrothermal and the post-solidus (retrograde-metamorphogenic) mineralization potential of high heat production (HHP) granites.

Important terms

Generally, ores that were formed by hydrothermal solutions venting on the ocean floor are called “submarine exhalative” or “submarine hydrothermal”. The second term is preferred by some authors, because the word “exhale” *sensu stricto* implies a gas, not an aqueous liquid. “Submarine volcanic-exhalative deposits” are discerned from “sedimentary-exhalative type” (commonly shortened to “sedex”). Whereas the first are clearly localized in volcanic centres, the second occur in sedimentation-dominated basins. In both cases, the rocks consisting of ore and non-ore minerals (gangue) that result from these processes are called “exhalites” or “hydrothermal sediments”. The term “massive ore” designates a body that consists mainly of ore minerals such as base metal sulphides or iron oxides.

Submarine volcanogenic massive sulphide (VMS) deposits

The concept of ore formation caused by submarine volcanic activity, or more precisely, by associated sub-seafloor hydrothermal activity resulting in massive ore mounds on the seafloor, is confirmed by many observations. Their origin by exhalation (outpouring) of metalliferous hydrothermal fluids on the seafloor was recognized by Oftedahl (1958). The concept was further developed by Stanton (1994 and earlier papers), Ohmoto (1996) and Allen *et al.* (2001). Recent exploration of the world’s oceans added a wealth of observations from divergent and convergent tectono-magmatic environments, including submarine arc volcanoes (Stoffers *et al.* 2006, Halbach *et al.* 2003). The VMS class encompasses a wide variety of geodynamic and more local genetic settings. Relations to volca-

noes range from proximity to quite tenuous connections with volcanism, as in parts of the Southern Iberian Pyrite Belt (cf. Chapter 2.2 “Copper”). VMS-deposits with copper and zinc are hosted by sequences dominated by mafic volcanic rocks, and are particularly abundant in Archaean and Palaeoproterozoic greenstone belts. VMS-deposits with zinc-lead-copper occur in sequences dominated by felsic volcanic rocks sourced from continental crust and are best exemplified by the Kuroko deposits of the Miocene Green Tuff Belt of Japan.

Submarine, volcanic-hosted massive sulphide deposits (VHMS, a non-genetic term) may be characterized in more detail, as follows (Stanton 1994, and cited sources):

The volcanic rocks are commonly andesites, dacites and rhyolites, basalts are less frequently hosts to significant mineralization (e.g. in Cyprus-type deposits). Throughout ore districts, the deposits occur characteristically in certain volcanostratigraphic horizons and are related to short and singular geological events such as caldera formation (Stix *et al.* 2003), subvolcanic intrusions and generally, enhanced heat flow. Fertile volcanic rocks are petrochemically distinct (Hart *et al.* 2004). The most important metals in these deposits are Fe-Cu-Pb-Zn, with elevated trace contents of Cd-As-Sb-Bi, more rarely including gold and silver. Polymetallic ore deposits are commonly zoned with Fe-Cu at the base, followed upwards by Zn and Pb, and capped by barite, anhydrite or dense SiO₂ exhalites (chert, jasper: Grenne & Slack 2005). This chemical stratification can in some cases be explained by changes in the composition of the hydrothermal solutions. In other cases, a secondary mobilization of more easily soluble components (e.g. zinc) of early precipitates results in this pattern, caused by continuous flow of hydrothermal solutions upward through the earlier metalliferous hydrothermal sediments (“zone refining”). It is thought that in

the precipitates, colloidal textures and framboidal (microcrystalline) pyrite prevailed initially, before zone refining, diagenesis and metamorphism caused coarsening and recrystallization. In the very low-grade metamorphic Archaean ore deposit Sulphur Banks in the Pilbara craton, Australia, pyritic filaments were found in colloidal-textured sulphides, which may represent fossil bacterial colonies. Banding, synsedimentary soft-sediment deformation and graded bedding of sulphides are often observed in VHMS deposits. Ooids and pisoids form where outpouring solutions caused both ore precipitation and agitation of hydrothermal seafloor sediment (Heikoop *et al.* 1996). Breccias are produced by hydrothermal eruptions. Most probably, breccias were first cemented with anhydrite, which is often later removed by low-temperature solutions because of its retrograde solubility. A wide halo of anomalous manganese contents surrounds sites of submarine hydrothermal activity and these horizons survive into high-grade metamorphism, for example as spessartine bands (Stumpfl 1979). Other deposits occur at distinct exhalative centres in regional metalliferous horizons as in the Ordovician Algoma-Type iron formation of northern New Brunswick, Canada (McClenaghan *et al.* 2009). Exhalative systems with low contents of sulphur and dissolved carbonate ions form stratiform skarn, because silica-iron-calcium precipitates develop into metamorphic assemblages of hedenbergite, grossular, Ca-amphibole, wollastonite and diopside.

Iron-rich sulphides occur predominantly with basalts, whereas Fe-Cu-Zn appear in volcanic terranes of andesite-dacites and Fe-Pb-Zn with rhyolites. Water isotope data suggest that the hydrothermal solutions are mainly altered seawater. Therefore, VHMS ore deposits are thought to result from seawater convection and hydrothermal dissolution of metals from pervaded volcanic rocks (Figure 1.10). This hypothesis, however, does not fully explain the ties between specific metals and certain volcanic rocks. Stanton (1994) proposed that a link with the magmatic evolution and degassing of the volcanic rocks may complement the convection hypothesis. The scarcity of Ti, V, Cr, Co and Ni in VHMS deposits, for example, may be due to early precipitation of magnetite from mafic melt

which extracts these metals. Also, magnetite crystallization triggers sulphate to sulphide conversion (Sun *et al.* 2004), which tends to abstract chalcophile metals. Stanton's hypothesis is supported by recent research. In the Manus back-arc basin near Papua New Guinea, metal-rich glass inclusions in submarine andesites were found close to a presently active submarine hydrothermal system (Yang & Scott 1996, 2005). Sulphur isotope data from the Lau basin indicate magmatic input (Herzig *et al.* 1998). Mass balance calculations by Beaudoin & Scott (2009) confirmed that a very small fraction (~1%) of metalliferous magmatic fluid mixed with convecting seawater accounts best for Pb-enriched sulphides and volcanic rocks in the Pacmanus vent field.

Boiling P/T of submarine hydrothermal systems depends on the salinity of the fluids, and depth of boiling relative to the seafloor controls both form and location of ore precipitation (Finlow-Bates & Large 1978, Figure 1.45):

- 1 If boiling takes place below the seafloor, metals preferentially precipitate within the upflow channels, giving rise to stockwork, veins and disseminated ore.
- 2 Where phase separation and venting coincide at the seafloor, massive orebodies may accumulate.
- 3 Ore with a sedimentary (e.g. bedded) character results from single-phase fluids that vent below the boiling curve and collect in brine pools.

Accordingly, orebodies of VMS deposits show a great variety of forms, including lenses and blankets (the most common), but also mounds, pipes and stringer deposits (Large 1992).

Volcanogenic massive sulphide deposits occur throughout the geological past from as early as the Archaean. They cluster in periods of supercontinent assembly (Huston *et al.* 2010). Many of the older deposits resemble the Kuroko type (e.g. the Cambro-Ordovician deposits in the Charters Towers District, Queensland, Australia: Monecke *et al.* 2006). Generally, they occur in convergent plate boundary settings. However, the prevailing bimodal nature of the volcanic rocks and geochemical indices imply that most VMS were generated during phases of

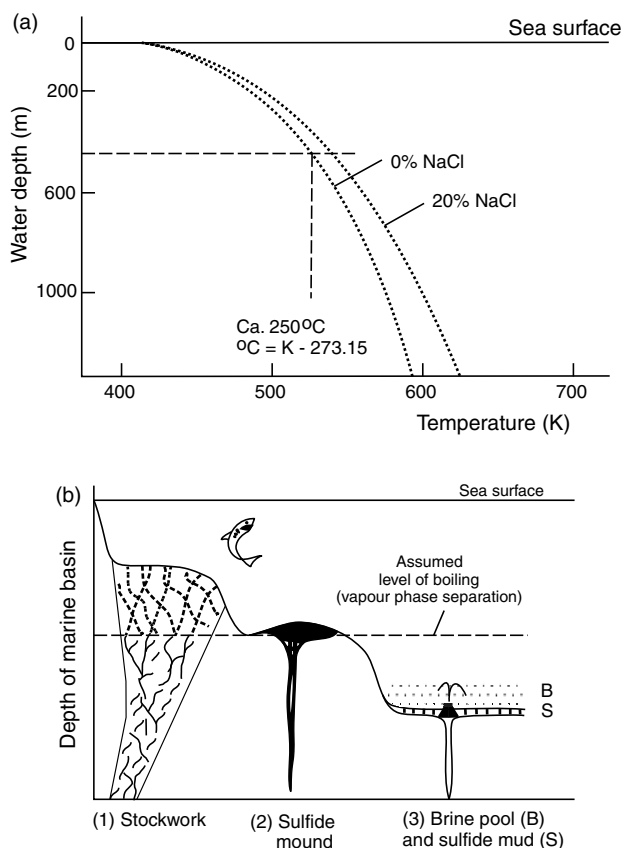


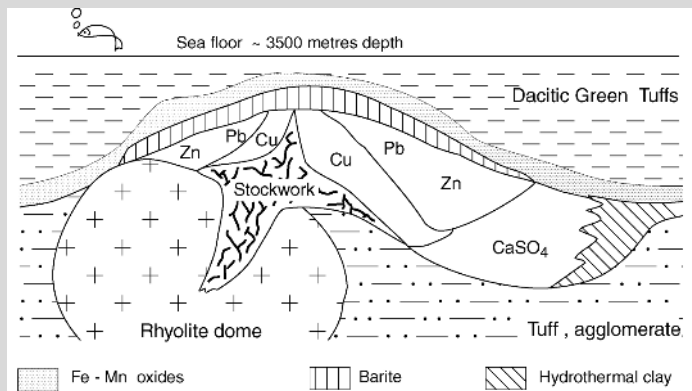
Figure 1.45 Boiling (formation of aqueous vapour) of submarine hydrothermal solutions at subcritical conditions (a) and resulting form and location of submarine ore deposits (b) (adapted from Finlow-Bates & Large 1978). With permission from <http://www.schweizerbart.de>.

BOX 1.5 Submarine volcanogenic Kuroko type sulphide deposits

Among the submarine exhalative VMS deposits, Kuroko ore deposits are an economically significant subtype (Ohmoto 1996, Morozumi *et al.* 2007). The term “kuroko” is derived from the black lead-zinc ore that was exploited in Japan for centuries. Many mines had also stockwork orebodies of yellow ore (“oko”) consisting of pyrite and chalcopyrite ($\pm$ gold). The deposits occur in a belt $\sim$ 800 km long, built of Tertiary submarine volcanic rocks. The horizon hosting the deposits is easily recognized because it separates monotonous Miocene “Green Tuffs” (dacitic pumice) in the hanging wall from a bimodal volcanic series below, which is characterized by calderas, rhyolitic and dacitic pyroclastic breccias, and resurgent domes of white rhyolite-dacite. The breccias are the product of submarine neptunian (Allen & McPhie 2009) volcanic eruptions. Explosive pyroclastics occur down to at least 1700 m below sea level at several mid-ocean ridges (Fouquet *et al.* 1999). Geodynamically, the Kuroko province was undergoing strong extension and rifting within a back arc basin of the Tertiary suprasubduction volcanic arcs of Japan.

Early, fine-grained ores of ZnS, PbS, pyrite and barite were formed during extrusion of rhyolite domes by hydrothermal exhalation through submarine vents and mound-building on the seafloor (Figure 1.46). In this figure, white spaces are zones of hydrothermal-sedimentary sulphide ore of copper, lead and zinc, some of which was syngenetically altered (e.g. by zone refining) and recrystallized. The pyrite-rich stockwork of copper ($\pm$ gold) veinlets is centred below the former. The early ore muds were altered by reaction with upward percolating hot fluids (zone refining) that produced stockwork

Figure 1.46 Generalized section of a VMS Kuroko type ore deposit (adapted from Finlow-Bates 1980). With permission from <http://www.schweizerbart.de>.



veinlets with coarse pyrite, chalcopyrite and quartz. Some elements such as Au, Sb, As, Ag and Sn were “distilled” towards the hanging wall of the orebody. Both the stockwork and the ubiquitous ore breccias imply repetitive hydrothermal explosions. Stockworks below exhalative ore beds mark the ascent of the hydrothermal fluids; they are often independent economic orebodies. Distal sedimentary orebodies originate by slumping or mass flow from proximal sulphide mounds. Because of rhyolite dome extrusion, the temperature of the hydrothermal fluids rose during ore formation from 150 to 350°C. Updoming and steepening of ore beds caused complex syngenetic deformation. Due to the considerable hydrostatic pressure, boiling of fluids was rare. Stable water isotopes indicate a seawater origin of the solutions with a low salinity of <5% NaCl (equivalent). Seawater contributed sulphur, but part of sulphide sulphur was leached from the magmatic rocks. Lead isotope characteristics are those of underlying volcanics and sediments. The hydrothermal alteration in the footwall of the massive sulphide ores is concentrically zoned around the stockwork, from innermost K-feldspar and illite to distal montmorillonite and zeolites. Concurrently with alteration, large masses of calcium and barium were leached from the percolated rocks and reprecipitated on the seafloor forming barite, anhydrite and gypsum (Ogawa *et al.* 2005). The hydrothermal fluids were mostly neutral, reduced and had low sulphur contents, probably because in the downward branch of convection SO_4^{2-} is generally removed from solution. Occasionally, clues have been found for the presence of acidic, oxidized and sulphur-rich magmatic fluids of the “high sulphidation type” (Sillitoe *et al.* 1996b; see “Epithermal Ore Deposits” below).

major crustal extension, which may be caused by slab rollback (e.g. in back arcs), resulting in rifting, subsidence and deep marine conditions (Lentz 1998, Allen *et al.* 2001). Present equivalents of VMS-forming processes, such as metaliferous submarine hydrothermal vents in extensional provinces of island arcs, have been discovered in the Okinawa trough and the Manus basin near Papua New Guinea (Yang & Scott 1996). Iizasa *et al.* (1999) describe a submarine gold-base metal deposit off the eastern coast of Japan, with ~9 Mt of ore. The deposit occurs in a large rhyolitic caldera with numerous black smokers that coalesce above faults and form walls. Recently, mining of a gold-rich volcanic massive sulphide deposit at 1600 m

water depth is seriously investigated offshore Papua New Guinea. The Solwara orebody contains indicated and inferred resources of ~2 Mt at 6.8% Cu, 4.8 g/t Au and 23 g/t Ag.

Many VMS-deposits have undergone metamorphic overprinting and strong deformation (cf. Section 1.5 “Metamorphosed Ore Deposits”). This may destroy original spatial relations and change rocks to a point where identification of their pre-metamorphic nature is very difficult:

Notable examples are Besshi type sulphide deposits. Besshi is one of numerous comparable mines on the Japanese island of Shikoku. Besshi ore consists mainly of pyrite, chalcopyrite and pyrrhotite, with some sphalerite, gold and magnetite. Deposits occur within the Sangabawa high-P/T

metamorphic belt that represents the deepest exposed part of the Mesozoic accretionary complexes in the Japanese island arc. Host rocks include Carboniferous to Jurassic schistose metapelites, metacherts and metabasalts of epi- to mesozonal metamorphic facies that were deformed in the Cretaceous. In the Besshi region, the schists wrap around a large eclogitic ophiolite nappe (Moure & Enami 2008). The orebodies appear to be bound to a regional horizon and are stratiform lenses, either banded or massive, and deformed into spindle-like shapes. Syngenetic formation with host rocks is highly probable. After long disputes, the geodynamic setting was recently affirmed to have been mid-oceanic (Nozaki *et al.* 2008, Watanabe *et al.* 1998). Besshi sulphides are highly deformed and metamorphosed Cyprus Type deposits.

Worldwide, many pyrite-rich beds in metamorphic volcano-sedimentary sequences are known, for example, the “fahlband” (pyritic) gneiss layers in southern Norway. Of course, this does not imply the same genetic setting as that of Besshi sulphides.

Terrestrial epithermal gold, silver and base metal ore deposits

Many important ore deposits are connected with terrestrial volcanism. In previous sections, iron oxide lavas and tuffs, and the subvolcanic porphyry copper ore deposits were mentioned. Here, we

focus on a deposit class that is commonly called “epithermal”. These deposits formed by near-surface hydrothermal processes (they occur at shallow epizonal depth). Epithermal orebodies take the shape of veins, breccias, metasomatic masses and impregnations within hydrothermally altered host rocks. They are closely related to metalliferous sinter mounds that occur on the land surface (“hot springs deposits”). Epithermal ore formation takes place in the aureole of near-surface subvolcanic magma bodies that induce a high heat flow and a steep geothermal gradient. This is the reason for a commonly restricted vertical downward extension of epithermal orebodies. Primary metal zonation occurs in narrow intervals, or the zones overlap and are “telescoped”. Causes for telescoping may be erosion and collapse of volcanoes (Sillitoe 1994) or repeated subvolcanic intrusions that radically change the p/T-field. Epithermal ore deposits are remarkable as a major source of gold, silver, zinc, lead, bismuth and the minerals alunite, barite and fluorite.

Active epithermal systems of today’s volcanic regions are mainly investigated in view of their role as an energy source. Energy can be exploited from geothermal systems (Figure 1.47) where heat is transported close to the Earth’s surface, usually by a combined action of rising magma, magmatic volatiles and convecting non-magmatic waters.

BOX 1.6 Terrestrial volcanogenic epithermal ore deposits

Epithermal ore deposits are remarkable as a major source of gold, silver, zinc, lead, bismuth and the minerals alunite, barite and fluorite. The descriptor “epithermal” was originally given because ore deposition was thought to have occurred near the surface from low-temperature fluids between 50 and 200°C (Lindgren 1933). Today, the temperatures are better known, but Lindgren’s summary of characteristic features is still a valuable guide (freely adapted):

- depth of formation between 0 and 1500 m below the palaeosurface;
- temperature of formation 150–300°C (modern data);
- host rocks may be volcanic or sedimentary rocks, but always close to volcanic centres; ore controls are often faults;
- orebodies occur as veins, breccia pipes and stockworks; stratiform and replacement ore (e.g. in carbonates) is less common;
- main ore metals are Pb, Ag, Zn, Au, Cu, Hg, Sb, Se, Te and Bi; metals occur in native form and as sulphides, sulphosalts, selenides and tellurides;
- gangue includes chert, chalcedony and quartz (often crystalline, e.g. amethyst), chlorite, epidote, carbonates, fluorite, barite, adularia, alunite, dickite, rhodochrosite and zeolite;
- hydrothermal alteration is characterized by moderate to intense silicification, kaolinization, pyritization, dolomitization and chloritization;

- ore textures typically indicate mineral growth in open spaces, in some cases including open space sedimentation; colloform banding is common;
- most deposits have a restricted depth extent; vertical zonation is very pronounced and includes telescoping.

The fluids responsible for epithermal ore formation include magmatic water and vapour, heated meteoric water and in some cases seawater. Magmatic heat and fluids are essential components of the entire hydrothermal system (Figure 1.47). In the centre-right of the figure, oxidized magmatic volatiles and fluids released from subvolcanic porphyry intrusions produce a high-sulphidation Au-Cu deposit ("volcanic-hydrothermal system"). On the left, hydrothermal convection is dominated by meteoric water ("geothermal system"). The heated water dissolves volcanic gas and vapour that are neutralized by reaction with the host rocks. At or after boiling, the solutions precipitate Au-Ag ore of intermediate to low sulphidation type. Solfataras (sulphurous vents) can be associated with the precipitation of native sulphur (S).

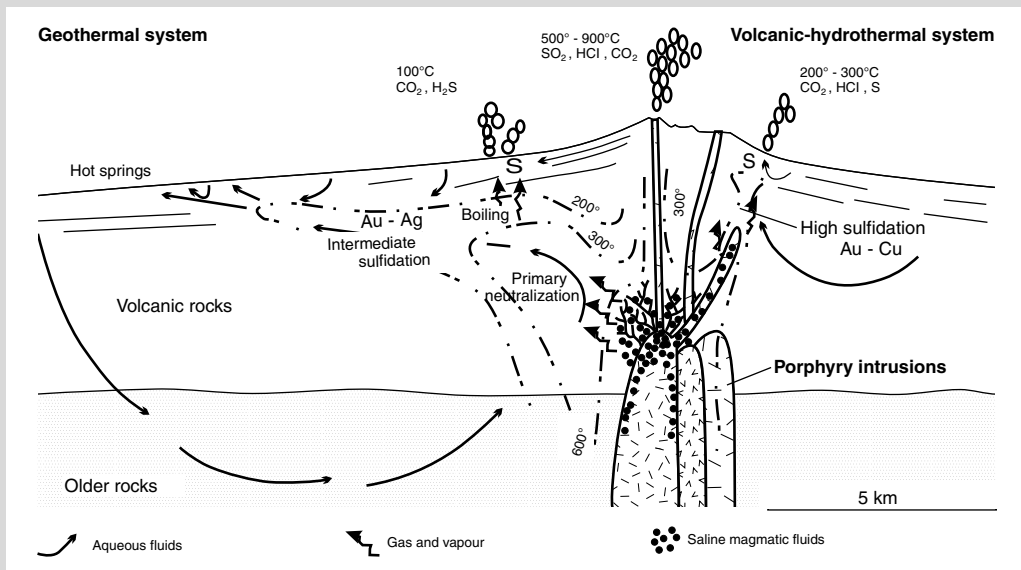


Figure 1.47 Formation of epithermal ore deposits related to an andesite volcano. Modified from John, D.A. 2001, Society of Economic Geologists, Inc., *Economic Geology* 96, Figure 13, p. 1847.

Salinity of fluids is commonly low (<3%) but may be higher in liquids that lost much vapour. Occasionally, the presence of brines has been noted. Ore precipitation is typically by boiling as the hot solutions move upwards and approach the surface (Robb 2005). Self-sealing of flow channels by precipitates (e.g. silica) is common and causes pressure increase until hydrothermal (phreatic) fracturing or phreatomagmatic eruption releases built-up stresses. Large highly permeable breccia bodies and pipes may result that attract the flow of hydrothermal fluids (Davies *et al.* 2008) and may consequently become bonanza ore. Cyclic repetition of sealing and rupture is reflected in banded ore veins. Mixing of rising hot magmatic gas or boiling fluid with cold groundwater is a possible factor of ore deposition. Where epithermal solutions reach the surface, hot springs establish siliceous sinter deposits. Current formation of hot springs precipitates with high contents of Au, Ag, Hg, Sb and As was described from the Californian Coast Ranges (Peters 1991). Hyperthermophilic microbes (e.g. *Sulpholobus acidocaldarius*) are important actors in these environments. Freshly precipitated siliceous sinters are often filamentous and microbe-rich. They age through a range of silica phases from opal-A, opal-A/CT, opal-CT and opal-C to quartz, with surprisingly rapid transformation rates (Lynne *et al.* 2006).

Several scientific studies illuminate the role of geothermal systems in ore formation (e.g. Taupo Volcanic Zone, New Zealand: Giggenbach 1995, Simmons and Brown 2000, 2007; cf. Ladolam, Lihir Island, Papua New Guinea: Simmons & Brown 2006).

Sulphur is an important component of magmatic volatiles. Near the surface, oxidation of sulphur produces strong acids that react with host rocks. The resulting hydrothermal alteration is very conspicuous because of bleaching and extreme argillization (e.g. alunite, equation 1.5). Alunite can also be formed when oxic magmatic exhalations that are enriched in HCl and SO₂ dissolve in groundwater and react with host rocks (Figure 1.47). This is the environment of the formation of epithermal gold deposits of the **alunite, or high sulphidation type** (Hedenquist *et al.* 1993, Simmons *et al.* 2005). High sulphidation (high f_{S_2} in oxic conditions) is indicated by ore minerals such as enargite, tennantite and covellite, and by advanced argillic alteration gangue minerals including alunite, pyrophyllite, dickite and kaolinite. In contrast to the former, epithermal deposits of the **adularia-sericite, or low sulphidation type** are produced by reduced and neutral to mildly alkaline fluids that carry H₂S and other reduced sulphur species (Hedenquist *et al.* 1993, Simmons *et al.* 2005). In these deposits, silver and base metals dominate and typical gangue minerals are calcite, adularia and illite (Figure 1.47, White & Hedenquist 1995). Members of the group with exploitable base and precious metals are called “epithermal polymetallic” (Cu-Zn-Pb-Ag-Au-Bi) or “Cordilleran” base metal deposits (Baumgartner *et al.* 2008). High sulphidation epithermal deposits are often in close spatial association with copper-gold porphyries. In active volcanoes, solfatara fields mark this environment. Earlier speculations that there are physical and chemical links between the two deposit classes are confirmed by modelling studies (Heinrich *et al.* 2004, Heinrich 2005) and field observations (Sillitoe 2010). The described sulphidation types of epithermal deposits are end members of a continuum in nature.

Submarine and terrestrial volcanogenic ore deposits are quite different. However, a number of

transitional, or hybrid ore forming systems, have been found (Hannington 1997, Naden *et al.* 2005), with a setting at volcanoes emerging from the sea (e.g. Milos, Greece). By definition, all volcanogenic deposits were formed near active volcanoes or subvolcanic centres, and occur in a “proximal” position. A number of submarine base metal deposits display several properties that are similar to bedded volcanogenic ore, but are located at a considerable distance from contemporaneous volcanic activity. Volcanism may be indicated only by thin tuff bands in sediments or known as distant volcanic centres (in parts of the Iberian Pyrite Belt, also at Mt Isa, Australia). This corresponds to a “distal” position. In this case, a genetic connection of mineralization and volcanism is tenuous or even unlikely (cf. Section 1.3 “Sedimentary Ore Formation Systems”).

Studies aiming at a full understanding of volcanogenic ore deposits, regardless of scientific or practical objectives, always include investigations of structure, petrogenesis and evolution of the volcanoes, the petrology of synvolcanic intrusions concerning cosanguinity, hydrothermal alteration (Gaboury 2006) and the precise plate tectonic situation (Sawkins 1990a,b). Generally, terrestrial volcanogenic deposits occur in convergent plate boundary and subduction settings, for example in the circum-Pacific “ring of fire”. However, they are not necessarily products of subduction and compressional deformation (orogenesis). Many of these systems were triggered by tensional events. Volcanic graben and horst terranes are especially favourable locations (e.g. the Basin and Range Province, USA), as are subvolcanic domes and resurgent calderas of andesitic to rhyolitic composition.

1.2 SUPERGENE ORE FORMATION SYSTEMS

Weathering of rocks and soil formation are the preconditions of most higher life on Earth. They are also at the origin of many important ore deposits. Raw materials that are predominantly produced from supergene mineral deposits include a diverse range of metals and minerals such as

iron, manganese, aluminium, gallium, niobium and kaolin:

The term weathering integrates a number of processes that are caused by the interaction of Earth materials with the atmosphere and the energy flow from the sun. Physical and chemical process groups can be distinguished, frequently with a strong biological component (Banfield & Nealson 1997, Southam & Saunders 2005). Chemical weathering is dominated by reactions between minerals and rocks with meteoric water containing dissolved oxygen and carbon dioxide. The first causes oxidation, for example $\text{Fe(II)} \rightarrow \text{Fe(III)}$, the second induces moderate acidity (Figure 1.48, eq. 1.14), especially after passage through a humic soil horizon that multiplies CO_2 concentration in seepage water. Generally, chemical weathering removes mobile cations (e.g. Ca^{2+} , Na^+ , K^+) relative to stable residual components (Al^{3+} , Ti^{4+}). Site-specific conditions of pH and Eh are the main controls on reaction products. Weathering rates are a function of climate. Highest rates occurred during periods of high CO_2 in the atmosphere with

consequent warm and humid climate and a profuse growth of land plants as, for example, in the Early Eocene climatic optimum when CO_2 levels reached 1125 ppm (Smith *et al.* 2008).

All forms of life (Figure 1.49) participate in supergene processes. Very direct is the action of land plants, which are the main drivers of rock weathering, not least because they are an important source of oxygen in water and air. Organic acids derived from partial decay of plants intensify rock disintegration. In the Late Archaean and Early Proterozoic, *Cyanobacteria* (blue-green "algae") proliferated to a degree that led to the first oxygenation of oceans and atmosphere ("the Great Oxidation Event"). Archaea were probably always rather specialists for extreme environments, such as very hot, acidic and alkaline settings. In the Mesozoic, diatoms (algae) started to dominate the marine photosynthetic productivity. Remember that for a geologist, the Tree of Life is also a symbol of the time vector of life's evolution on our planet, as first explained by Charles Darwin (1859).

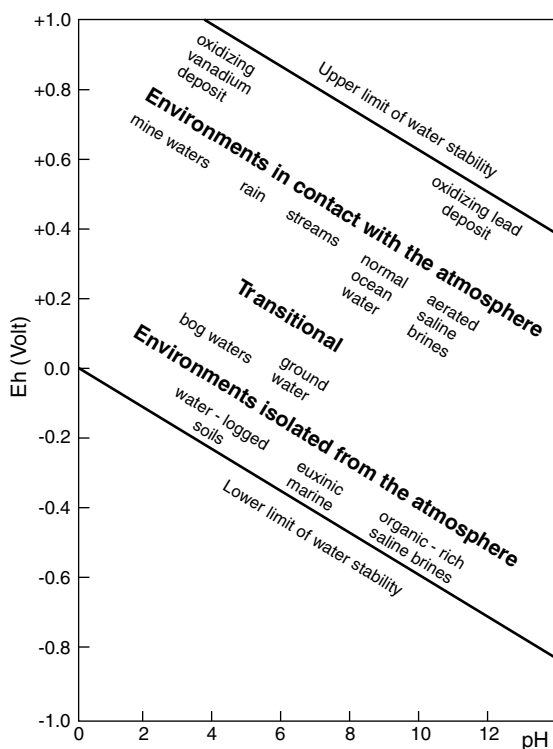


Figure 1.48 Typical Eh/pH range of surface waters (modified from Garrels & Christ 1965). Note that today, the concept of a determinate Eh (pE) is doubted.

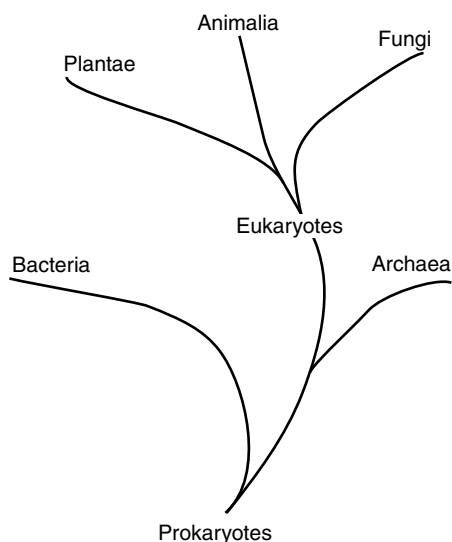


Figure 1.49 The Tree of Life in a very simplified version showing what is poetically called the Kingdoms of Life (consult the complex background in Crandall & Buhay 2004).

The principle of supergene ore deposit formation is the concentration of some dilute but valuable component of the primary rock. 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.
- 2 The valued component is dissolved, transported and concentrated on reprecipitation.

In the latter case, the transport distance is commonly very short (metres to tens of metres). Some ore deposits, however, originate after long-distance transport dissolved in surface and groundwater. Examples include uranium in calcrete and in sandstone, iron in Tertiary river valleys of Western Australia and manganese in limestone karst caves. An important special case of ore formation by weathering with metal transfer by meteoric seepage water is the supergene enrichment of unexploitable low-grade primary mineralizations ("protore"). Many copper, iron, manganese and silver deposits owe an economic ore grade to supergene enrichment processes.

Supergene ore deposits form in regions where weathering is favoured by a humid and hot climate that promotes the profuse growth of vegetation. Vegetation and organic matter affect supergene alteration by two mechanisms. The first is the direct influence of plants on the soil water (e.g. retention). The second is the abundance of organic acids and of microbial activity that promote dissolution of primary minerals. In this environment, iron and aluminium have a very low solubility compared to alkalis and SiO_2 . Therefore, they are enriched in the red, clayey-sandy soils of the tropics and subtropics that are generally called laterites (in soil science variously termed "ferralsol", "oxisol", etc.). Ordinary laterites have little value except for making bricks and building roads (the Latin word *later* translates into air-dried brick).

Lateritic ore

Lateritic ore (of Al, Ni, Co, Fe, Mn, Cr, Au, etc.) is formed when exposure of suitable rocks coincides with favourable morphological, hydrogeological and geochemical conditions that enhance dissolution, transport and precipitation (Valeton 1999). Time also has a role—long-lasting weathering under stable conditions may be expected to result in more mature and higher-grade ores, although peaks of lateritization last less than 100,000 years and occur during global greenhouse events (Retallack 2010). This is why supergene ore deposits are preferentially found in tablelands of stable cratons, for example in wide regions of former Gondwana and less likely in young orogenic belts (one exception are bauxites in the European Alps).

Laterite *sensu stricto* designates the upper leached and oxidized part of certain soil profiles with a well-developed vertical zonation (Figure 1.50). Lateritic regolith reaches more than 100 m in thickness. Principally, the lateritic **regolith profile** comprises an uppermost eluvial horizon (A), underlain by an illuvial zone (B) and the altered but still recognizable precursor rock *in situ* (C) that rests on unweathered fresh rock (R). Depending on the groundwater table, zone (B) is often divided into an upper kaolinitic and haematite mottled layer and a greenish-grey smectitic material below. In (A) or in (B), many laterites have hard



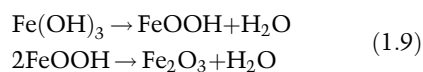
Figure 1.50 (Plate 1.50) Brilliantly white supergene kaolin below red laterite in the rainforest of northern Burundi illustrates lateritic soil profiles which originate by tropical weathering.

crusts (duricrust) that are composed of SiO_2 (silcrete – the geological home of precious opal), iron (ferricrete) or manganese (mangcrete) oxides and oxy-hydroxides. Zone C can be crumbled by hand but often displays an upper clay horizon (feldspars are argillized) and a lower sandy horizon with intact feldspars but vermiculized biotite. The first is called “saprolite”, the second “saprock”. Colours vary from red and brown to white or grey. Of course, bleaching indicates reduced conditions with dissolution and abstraction of iron, which is caused by organic acids derived from decaying vegetation.

Laterite zonation is due to the effect of seasonal changes between dry and wet periods: During dry seasons, soil water moves towards the surface and evaporates, inducing alkaline conditions that promote silica solubility. In wet seasons, acidic rain water seeps downward, dissolves and reprecipitates matter or takes it out of the system. Textures of lateritic soils include banded crusts, shrinking fissures, concretions, pisolites and oolites, small vertical tubular structures, Lie-

segang banding and many more. Newly formed solids are often amorphous and colloform, but diagenetic aging into minerals is omnipresent. An example is the transformation of iron hydroxide gel into goethite and haematite (eq. 1.9).

Aging of Fe(III) hydroxide into goethite and haematite:



The crucial factor for effective leaching is water, modulated by hydraulic properties of soil and bedrock that influence the contact time between water and minerals (Gabet *et al.* 2006). Of course, lateritic ore deposits are a variety of soil and consequently their investigation should always include methods and concepts of soil science:

Relative and absolute dating of supergene ore formation remains difficult. Cosmogenic nuclides such as ^{10}Be are usually employed for dating soil formation (Siame *et al.* 2006). If supergene alteration causes the

precipitation of new minerals, age determination may be possible. One useful mineral is cryptomelane, a K-bearing manganese ore that can be dated with the $^{40}\text{Ar}/^{39}\text{Ar}$ method. Based on this approach, $\pm$ continuous formation of a supergene manganese deposit in South China from 40 to <2 Ma is revealed (Li *et al.* 2007). Supergene alunite in Chile's giant copper deposits was formed between 45 and 5 Ma, followed by atacamite (dated by ^{36}Cl) during the hyperarid Pleistocene (Reich *et al.* 2009). If haematite is present, palaeomagnetic methods may be useful that also provide a measure of palaeolatitude. Oxygen isotopes of hydrous minerals precipitated from weathering solutions (e.g. goethite, clay, gypsum) are effective archives of the past $\delta^{18}\text{O}$ of meteoric water, an important proxy of palaeoclimate (cf. "Isotope Geochemistry").

1.2.1 Residual (eluvial) ore deposits

In residual ore 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 (Ni, Co) and nickel ores, residual enrichment of subeconomic protore iron and manganese, and industrial minerals such as phosphate, magnesite and kaolin.

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. Note that this implies that the oldest parts of the profile are near the top of the regolith, and the youngest at the reaction front. The enrichment is due to retention and accumulation of the component of interest contained in the removed rock and soil volume (Figure 1.51). Theoretically, the mass of metal concentrated in stage (3) equals accumulation from the rock volume ($R1 + R2$). However, the system is not closed, as soil and solutions may move laterally out of it. An illuminating case is eluvial enrichment of phosphate from carbonates by leaching of carbonate whereas apatite remains in place.

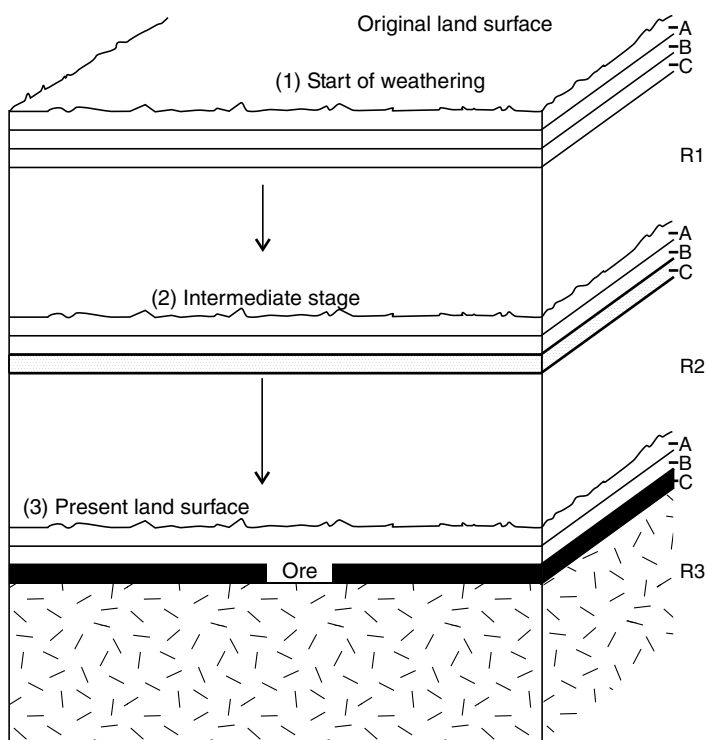


Figure 1.51 Idealized scheme of residual ore deposit formation by enrichment of a valuable component at a reaction front within the regolith [e.g. nickel in C-horizon saprolite].

Residual placers

Residual placers are concentrations of weathering-resistant ore minerals that are due to supergene abstraction of non-ore material. The term *eluvial* (outwash) describes the same result, although with more emphasis on physical removal of barren gangue. Many ore deposits contain heavy minerals that resist dissolution, such as native gold, cassiterite and wolframite. In this case, physical and chemical properties determine enrichment. Residual placers are only stable in flat morphologies, because steeper slopes induce soil creep and with it a down-slope displacement of ore fragments (resulting in colluvial placers). Residual placers often occur at the “stone-line” level of a soil profile, where quartz and durable ore minerals are concentrated.

Bauxite ore deposits

Bauxite ore deposits originate either by *in-situ* weathering of aluminium silicate rocks, or by allochthonous sedimentation after erosion of bauxite soil blankets. Autochthonous upland bauxites (e.g. covering the Dekkan trap basalts in India) are discerned from lowland bauxites that include detrital (sedimentary) deposits. Residual bauxite horizons often extend over large areas and mark regional unconformities that are related to favourable tectonic and climatic conditions (D’Argenio & Mindszenty 1995). Most deposits date from the Mesozoic and the Cenozoic, because the probability of conservation of soil decreases rapidly with increasing geological age. Many aluminium silicate rocks contain an average of 15% Al_2O_3 that must be upgraded by weathering to at least 35% Al_2O_3 to be economically exploitable. Alumina enrichment is caused by leaching of SiO_2 and iron, two substances that are not easily dissolved. The key are the repetitive cycles of favourable pH/Eh conditions in soil water as described above.

Lateritic gold deposits

Lateritic gold deposits as a class are a relatively recent discovery. One of the largest representa-

tives of this group was the Boddington bauxite mine in Western Australia, which until closure in 2001 was the biggest gold mine in Australia with an annual gold production of 2500 kg. Pre-mining resources amounted to 60 Mt of ore at 1.6 ppm Au, apart from bauxite with gold contents of less than 1 ppm. Exploitable gold was located in near-surface, iron-alumina hard crusts that reached a thickness of 5 m and in additional 8 m thick lumpy Fe-Al laterite of the B-horizon. Sources of the gold in soil at Boddington are quartz veins and hydrothermally altered bodies of Archaean greenstone bedrock. Since 2007, resources of 400 Mt of this primary ore with a grade of 0.9 g/t Au and 0.12% Cu are exploited in a new mine. Worldwide, numerous lateritic gold deposits are worked. They are attractive because exploration, extraction and processing of soil is less costly compared with hard rock mining.

Lateritic iron ore deposits

Lateritic iron ore deposits are not an important source of iron, because both deposit size and iron grades are rather low. The ore consists of oolitic, red, yellow or brown haematite and goethite with elevated contents of H_2O , SiO_2 and Al_2O_3 . Most deposits take the form of autochthonous or locally transported hard crusts (ferricrete) that reach a thickness of only a few metres. Nevertheless, lateritic iron ore derived from ultramafic source rocks is exploited in several countries (Albania, Greece, Moa Bay, Cuba and in the Philippines) as a high-iron limonite nickel ore (also termed “oxide nickel ore”) for pig-iron blast furnaces. In oxide nickel ore, nickel is absorbed in amorphous iron-hydroxides or occurs as inclusions in goethite. The new technology of high-pressure acid-leaching (PAL) appears to alleviate the former economic disadvantage of these ores as a source of nickel.

Residual supergene enrichment of iron pre-concentrations is the last upgrading event in the multistage evolution of **high-grade haematite ore deposits** with 60–68 wt.% Fe, which are derived from Precambrian BIF (cf. Section 1.3). Primary BIF are altered, silica-depleted and iron-enriched, in

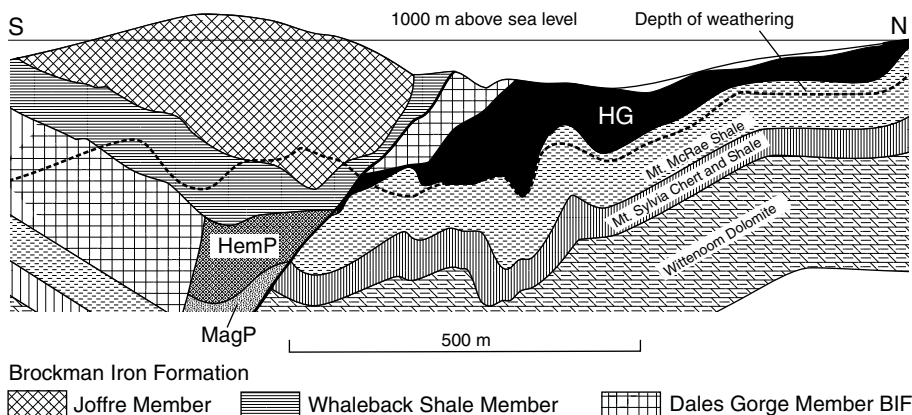


Figure 1.52 Profile of the high-grade haematite orebody at Mt Tom Price, Western Australia. Modified from Taylor, D., Dalstra, H.J., Harding, A.E., Broadbent, G.C. & Barley, M.E. 2001, Society of Economic Geologists, Inc., *Economic Geology* Vol. 96, Figure 5, p. 845.

Western Australia by the passage of diagenetic brines (Thorne *et al.* 2009, Thorne *et al.* 2004). In the vicinity of a normal fault at Mt Tom Price (Figure 1.52), the Brockman Iron Formation of the Palaeoproterozoic Hamersley Group was progressively altered to massive P-rich magnetite bodies (MagP) and microplaty P-rich haematite (HemP). Leaching in the supergene alteration zone is responsible for the final upgrading to economic ore of low-phosphorous high-grade haematite (HG). Note that phosphorous and carbonate abstraction at Mt Tom Price hardly changes iron concentration but makes the ore commercially more favourable.

Residual manganese ore deposits

Residual manganese ore deposits are derived from rocks with above-average manganese contents. Laterites developed from such rocks include hard crusts (mangcrete) or earthy manganese ore that may blanket considerable areas. In contrast to iron that tends to concentrate in the upper soil horizons (ferricrete), the slightly more mobile manganese is typically enriched in lower parts of the laterite profile. Although smaller than sedimentary manganese deposits, lateritic manganese ores are often high-grade and of superior quality. Sources (protore) are manganese quartzites, carbonates and volcano-sedimentary rocks that contain

exhalative-sedimentary pre-enriched horizons. In India, metamorphosed Precambrian protore rocks were called gondite. Gondites consist of quartz, spessartine, rhodonite and rhodochrosite with minor amounts of pyrite, alabandite (MnS) and other minerals. Manganese contents in gondites remain below 30%. Weathering removes carbonate and SiO₂, enriching manganese oxides and hydroxides (at Morro da Mina, Brazil to a depth of >200 m). Carbonates and sulphides in gondite promote weathering and ore formation, whereas purely silicate-based gondites only bear thin ore blankets.

1.2.2 Supergene enrichment by descending (vadose) solutions

Lateritic nickel ore deposits are of major economic importance (Gleeson *et al.* 2003). They form by intensive and long-lived tropical weathering of ordinary ultramafic rocks, which enriches nickel (and cobalt). Two types of nickel laterite are distinguished: i) the oxide type in the upper, oxidized iron-rich part of the laterite; and ii) the silicate type in the lower, reduced saprolitic section of the regolith.

Laterite regolith zonation and the redistribution of nickel (Table 1.3) are the result of meteoric water percolating through the soil. Olivine, pyroxene and serpentine are rapidly decomposed by

BOX 1.7 Lateritic nickel deposits

Nickel laterites were discovered by Jules Garnier in 1863 on the island of New Caledonia in the Southwest Pacific Ocean. Exploitation started in 1876. Meanwhile, numerous similar deposits have been discovered worldwide. New Caledonia remains, however, the largest ore province of this type, with a past cumulate nickel production of 3.5 Mt (metal) and considerable remaining resources. Today, 4 large mines are in operation, based on reserves of ~1 Mt nickel in ore at >2.7 wt.% Ni, and 1 Mt of nickel in ore at 2.5–2.7%.

The ultramafic rocks of New Caledonia are part of a giant ophiolite nappe that was obducted during the Eocene and forms most of the island (Paquette & Cluzel 2007; Figure 1.53). Serpentinized and unaltered harzburgite-dunite displays an average 0.25% Ni (mainly in olivine) and 0.02% Co. Lateritization of the exposed ophiolite probably started in the Miocene, resulting in a mature profile (Figure 1.54):

- *Top*: Massive goethitic iron crusts (ferricrete; French *cuirasse*); low residual nickel concentration;
- *Limonite zone*: with residual manganese, chromium and aluminium; mostly bright red-coloured because of haematite traces; earthy or concretionary texture; nickel, cobalt, magnesium, calcium and silica are leached and strongly depleted; in rare cases, residual nickel is exploitable;
- *Nontronite zone*: Ferrallitic, earthy, red and yellow clays are the norm, but in some profiles massive or network silicification is prominent (opal, chalcedony, jasper, etc.); cobalt may occur in exploitable pockets of asbolane ("earthy

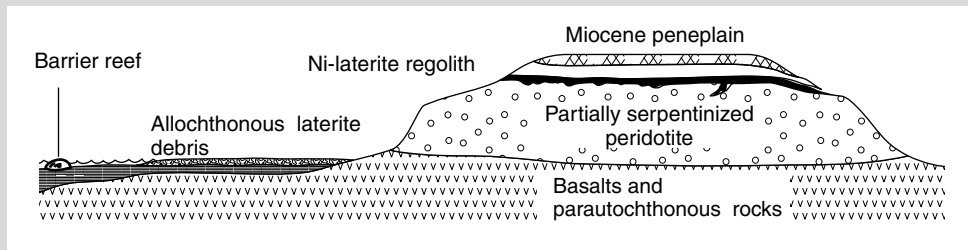


Figure 1.53 Schematic profile of laterite blanket with nickel ore (black, garnierite-saprolite horizon) above peridotitic rocks such as the New Caledonian ophiolite (not to scale).

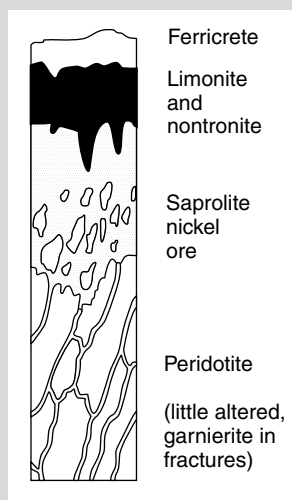


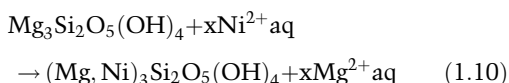
Figure 1.54 Regolith profile of exploitable nickel laterite in New Caledonia. Note the control of garnierite by joints and fractures of peridotite. Modified from Gleeson, S.A., Butt, C.R.M. & Elias, M. 2003, Society of Economic Geologists, *SEG Newsletter*, Figure 3, p. 13.

cobalt", a variety of wad); occasionally, nickel and manganese are enriched to exploitable grades; the depletion of magnesium is minor, SiO₂ contents are equal to those in unaltered parent rock;

- *Saprolite zone*: This is altered parent rock with clearly recognizable structures and textures of the ultramafics; alteration is controlled by joints; in lower parts of the profile, altered rock includes increasingly fresh cores of parent rock until the base of surficial weathering is reached; the saprolite zone is the main nickel ore horizon, with veinlets, pockets and irregular masses of green garnierite ($\pm$ chalcedony and magnesite); in the saprolite, olivine and pyroxene are altered to colloform magnesium silicates that age into the minerals antigorite (serpentine), talc and smectitic clays; nickel is taken up by these minerals in their lattice by cation exchange of Mg²⁺ and may reach several percent in the garnieritic ore; along permeable fractures, garnierite can penetrate far into the unaltered rock below the regular base of the regolith;
- *Bottom*: Unaltered hard rock with rare garnierite in joints and fractures.

acidic rain and soil water. From a surface value of ~ 6 , the pH of deeper soil water turns alkaline (pH 8.5). Nickel is dissolved and flushed downward, where it is immobilized by ion exchange with Mg in newly forming magnesium hydrosilicates. A schematic example of this reaction (neogenesis of the Ni-serpentine *népouite* from serpentine) is given in equation (1.10).

Neogenesis of Ni-silicate in the saprolite zone:



Normally, groundwater removes the dissolved magnesium from the system. Some is precipitated as a carbonate (magnesite) in joints. Whether this process is able to form stockwork ore deposits of magnesite remains doubtful (cf. Chapter 3 "Magnesite").

Supergene enrichment of pre-existing mineralization

Supergene, descendent alteration may be exceptionally beneficial where pre-existing uneconomic mineralization or low-grade orebodies are

Table 1.3 Typical chemical characteristics (wt. %) of the iron oxide and silicate sections of nickel laterite deposits in New Caledonia (Gleeson *et al.* 2003)

	MgO	Fe ₂ O ₃	SiO ₂	NiO
Ferricrete	0.5	84	2	1.2
Limonite and nontronite	1.0	70	2.2	1.8
Saprolite	12.5	11.5	63.2	5.3
Peridotite (little altered)	42.7	9.1	41.3	0.3

affected. Primary ore (protore) in deeper parts of the weathering profile is upgraded by seepage solutions. For sulphide copper and silver ores, iron oxides and certain uranium ore deposits, this process is of economic significance. Non-sulphide zinc ore produced by supergene enrichment is a less common economically attractive target.

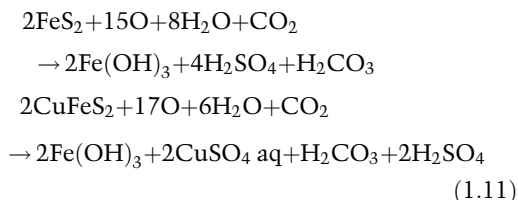
The supergene enrichment of sulphide ore is a consequence of near-surface oxidation of sulphides caused by meteoric water seeping downwards through an unsaturated zone. Other agents include dissolved oxygen and microbes that have a role as "self-replicating catalysts" (Sato 1992). These microbes include chemolithotrophic mesophile bacteria such as (Acidi-) *Thiobacillus* or *Leptospirillum ferrooxidans* and extremophile archaea such as *Ferroplasma acidarmanus* (Newman 2010, Edwards *et al.* 2000). In modern metallurgical processing, sulphide-oxidizing microbes are cultivated in leach pads or large vats in order to decompose sulphide ores of, for example, gold, copper, nickel and cobalt.

Because it is kinetically slow, purely inorganic oxidation of sulphides has a minor share in the supergene enrichment process system (e.g. pyrite: Rimstidt & Vaughan 2003, Balci *et al.* 2007). The role of microbes in the oxidation of sulphides is essentially understood but its biochemistry is very complex (Newman 2010, Nordstrom & Southam 1997). *L. ferrooxidans*, for example, attacks the surface of pyrite at $T > 40^\circ\text{C}$ and pH 0.7–1.0 by catalytic oxidation of Fe(II) to Fe(III). As an electron acceptor, $\text{Fe}^{3+}_{\text{aq}}$ abiotically oxidizes pyrite. *T. ferrooxidans* has a similar function but prefers cooler and less acidic conditions. Contact of $\text{Fe}^{3+}_{\text{aq}}$ with dissolved oxygen causes

precipitation of ferrihydroxide (Schrenk *et al.* 1998). Yet, the source of the oxygen in sulphate resulting from sulphur oxidation is mainly meteoric water, not atmospheric oxygen, as shown by oxygen-isotope investigations (Balci *et al.* 2007). The oxidation of sulphur and iron in one mole of pyrite (or marcasite) produces four moles of acidity. Consequently, weathering of pyrite-bearing rock (and other sulphides) is a natural or anthropogenic source of extremely acidic solutions (**ARD, acid rock drainage, or AMD, acid mine drainage**).

Oxidation of pyrite-rich copper ore is illustrated by equations 1.11.

Schematic reactions describing supergene oxidation of pyrite and chalcopyrite:



The results are acidic solutions, which move dissolved copper, but also silver, zinc and other

metals through unsaturated soil down towards the groundwater. Because of their low solubility in oxic environments, iron hydroxides remain near the surface and form the characteristic botryoidal and cellular limonite-haematite masses of the “gossan” (Figure 1.55). Apart from iron, manganese and gold are enriched in gossans. Traces of minor metals in the primary sulphides may be preserved, such as Ag, Pb, Cu, Zn, Cd, Mo, Ni, As and Sb. Gossans are often collapse breccias, because a large mass of the original ore rock was abstracted. Gossans are conspicuous indicators for the possible presence of hidden sulphide ore and therefore, are prime prospecting guides. Gossans can be orebodies in their own right, mainly of gold. Of course, not all supergene limonite-haematite masses are connected with valuable ore (“false gossans”). The distinction is possible by mineralogical (Blanchard 1968) and geochemical investigations.

Below the gossan, a zone of bleaching and silicate weathering (with kaolin, alunite, etc.) is often developed that reflects the former passage of strong acids. Just above the groundwater table, native copper and copper oxides (cuprite, tenorite), carbonates (malachite, azurite), sulphates (gypsum), chlorides (atacamite) and silicates (chrysocolla) display a strikingly varicoloured

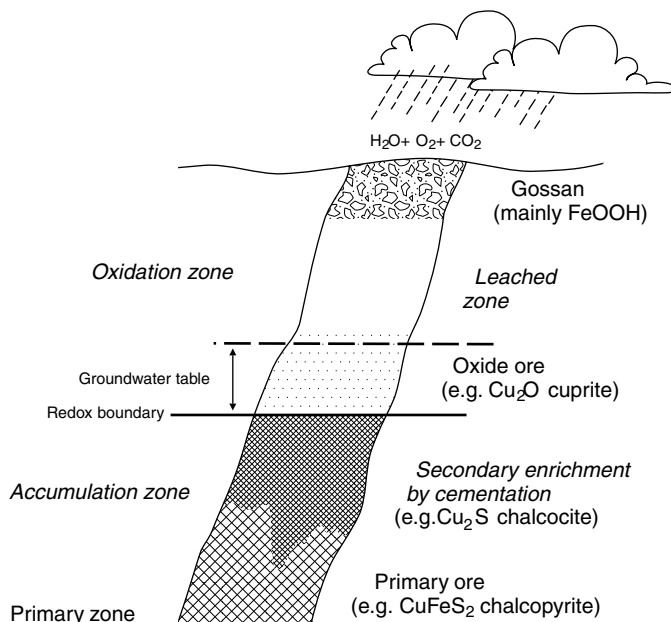


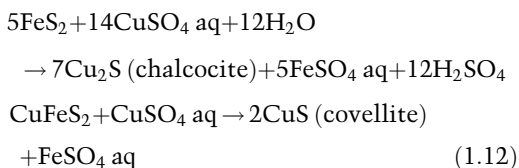
Figure 1.55 Schematic profile of a deeply weathered copper sulphide ore deposit, displaying the supergene “secondary” zonation resulting from redistribution of elements.

paragenesis. In some locations, this zone is enriched to an exploitable volume and grade (Melchiorre & Enders 2003). Prominent examples are several Chilean copper porphyry deposits that have important “exotic oxide” outliers (infiltration deposits, see below). Exotic ores were formed in drainage channels to a distance of about 7 km from the leached portion of the primary deposit (Chuquicamata, El Salvador, El Abra). In the hyperarid Atacama Desert, the copper salt atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$ is an economically important ore mineral of oxide orebodies (Reich *et al.* 2008, 2009).

Where percolating water meets the groundwater table, the active reaction front is reached. Here, exothermic oxidation of primary sulphides takes place, as well as the secondary enrichment (Figure 1.55). Microscopy of replacement textures illustrates these processes. This zone is the preferred habitat of the thermophilic microbes mentioned above. Vestiges of the microbes were demonstrated by electron microscopy of contacts between chalcocite and primary sulphides (Sillitoe *et al.* 1996a). Isotope data indicate heating to nearly 100°C (Melchiorre & Williams 2001). The efficiency of secondary enrichment depends mainly on conservation of the acidic environment, but also on favourable hydraulic conditions (e.g. permeability). Carbonates and other basic host rocks that buffer acidity inhibit both organic and inorganic processes, resulting in very little secondary enrichment.

The chemical reactions produce galvanic mineral interactions (Sikka *et al.* 1991) and an electrochemical field near the orebody, which is a very clear target for geophysical exploration methods. Precipitation of enriched ore can be schematized as a cation-exchange reaction that results in formation of chalcocite, covellite or bornite (equation 1.12).

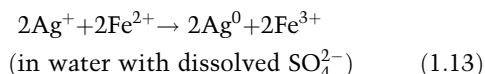
Formation of enriched secondary copper ore:



The primary ore gains more of the valuable metal (here copper), often resulting in spectacularly rich orebodies. Dissolved iron and sulphate are transported away out of the system; part of the sulphate may be reduced by microbes so that additional sulphide is available. It is a frequent observation that many ore deposits are only economically exploitable because of supergene enrichment, based on primary sulphides of poor grade. This is true for a number of porphyry copper deposits, whereas others extract both enriched and primary ore.

Comparative investigation of replacement order showed that more “noble” metals (copper in eq. 1.12) replace more “common” metals (iron in eq. 1.12) that are dispersed. Earlier in this chapter, electrochemical reasons for this behaviour were cited. More noble metals (copper, silver, gold) also exhibit the tendency to occur in the native form, which may be explained by a redox reaction (eq. 1.13):

Formation of native metals by electron exchange:



Overall, weathering of a sulphide orebody comprises a complex system of physical, chemical and biological processes. Often, the observed end products do not match results of thermodynamic calculations. Unexpected parageneses can partly be explained by the argument that at the low temperatures of weathering, the activation energy needed for many reactions cannot be provided. This causes enlargement of thermodynamic stabilities of minerals into what Sato (1992) called “persistence fields” that are in good accordance with geological observations.

Prolonged weathering of a sulphide ore deposit results in a vertical zonation (Figure 1.55 and Figure 1.56) that comprises a leached (oxidation) zone, and a metal-rich cementation zone (supergene blanket), grading into unaltered mineralized rock of the primary zone (protore). In contrast to the primary depth zonation of hydrothermal mineral deposits, the supergene pattern is called “secondary vertical zoning”. In stable cratons, oxidation reaches a depth of over 100 m, mainly as a function of the groundwater table that roughly

Figure 1.56 (Plate 1.56) For over 100 years, the supergene, high-grade chalcocite ore of the black shale-hosted copper deposit at Mt Oxide in the Mt Isa district, Australia, was the symbolic example of fortune and destitution for investors and miners. Gossan (red) covered an accumulation zone of 55 m thickness which graded into subeconomic primary sulphides. A sizeable ore shoot of 15.9% Cu was extracted by underground methods. Later, the pit was excavated and overall, the deposit yielded 23,000 t of copper (J.H. Brooks in Glasson & Rattigan 1990).



limits the penetration of oxygen dissolved in soil water. In special cases, oxidation occurs to much greater depths (Tsumeb Mine, Namibia to 1160 m: Lombaard *et al.* 1986) or far beneath the groundwater table (e.g. Bougainville, where oxidation “fingers” down along permeable faults). Obviously, the full understanding of a cementation or secondary enrichment deposit requires a thorough reconstruction of the morphological and hydrological evolution.

Iron ore deposits as a product of supergene enrichment

Iron ore deposits as a product of supergene enrichment provide an important part of world

iron ore supplies. Protores are usually Palaeoproterozoic BIF (banded iron ore formations), with initial contents of ~25–45 wt.% Fe that are upgraded to 60–63% Fe. Note that there is a sharp divide between: i) medium-grade martite-goethite deposits; and ii) high-grade haematite deposits, which reach a maximum of 68% Fe. Haematite orebodies differ from supergene enrichment systems by reaching a great depth beneath the surface (~1500 m) and huge tonnages (3000 Mt, although most are in the range between 200 and 500 Mt). Based on various observations, current genetic interpretations of high-grade haematite deposits involve mainly epigenetic hydrothermal models (Thorne *et al.* 2009, Clout 2006).

Supergene enrichment is at the origin of common martite-goethite ore (Morris 1985, 1993). However, genetic models are very different from the simple laterite blanket type. It is assumed that near the surface, ferrous iron is leached from BIF by reduced seepage water rich in dissolved carbon and is carried downwards along flow channels such as faults crossing BIF beds. This establishes an electrochemical system that allows flow of electrons. The surface region functions as a cathode, the BIF at depth as an anode. In this system, conversion ("oxidation") of ferrous iron takes place without the presence of free oxygen. Magnetite is replaced by martite (haematite pseudomorphous after magnetite) or by maghemite. The reaction also multiplies the solubility of silica and other gangue minerals that are leached and replaced volume for volume by goethite (FeOOH). By-product acidity causes transformation of BIF shale bands into kaolinite marker horizons in ore. Orebody growth is upward from depth. If exposed by erosion, lateritic hard crusts may form from this ore, underlain by a friable zone of haematite. Let me add that it is quite possible that martite-goethite protore is hydrothermal just like high-grade haematite pre-concentrations; research will soon provide clarification.

1.2.3 Infiltration as an agent of ore formation

Infiltration is a term borrowed from hydrology, where it is used to describe the movement of surface water into soil, porous rock, or karst. Infiltration ore deposits are formed when meteoric waters take up a substance that is dissolved by weathering, and concentrate it after considerable

transport by infiltration in a different geological setting. Uranium is an illuminating example, because during surficial alteration it is easily dissolved from ordinary rocks such as granite, gneiss and felsic tuff, and is transported by creeks and rivers for tens to hundreds of kilometres, until infiltrating into an aquifer where reduced conditions cause precipitation and concentration. Certain deposits of copper, iron, vanadium, silver and Pb-Zn-Ba-F are suggested by some scientists to have a similar origin. In the preceding text, we have mentioned Chile's exotic copper deposits as part of the infiltration class. Generally, the metals may be derived from older preconcentrations or from rocks with common trace element contents. Selective weathering of different minerals may produce a pattern of spatial or temporal separation, for example by first leaching traces of uranium, copper and zinc from plagioclase and Fe-Mn oxyhydroxides, followed by barium, lead and SiO₂ when the more stable K-feldspar is decomposed.

The concentration of solutes in surface and groundwater is generally very low. Enrichment to ore-grade and an exploitable volume is only possible where a large mass flow is focused into a highly efficient filter. For dissolved matter, geochemical barriers are most effective, commonly in the form of a rapid change of pH and Eh. Geological actors include carbonates, H₂S or SO₄ in the pore waters, as well as live, decaying and fossil organic matter (biomats, peat, coal, bitumen), including by-product methane.

Because precipitation takes place in pre-existing rock, infiltration mineralization is clearly epigenetic, not syngenetic. Investigations of infiltration ore genesis always include (palaeo-) hydrogeological methods.

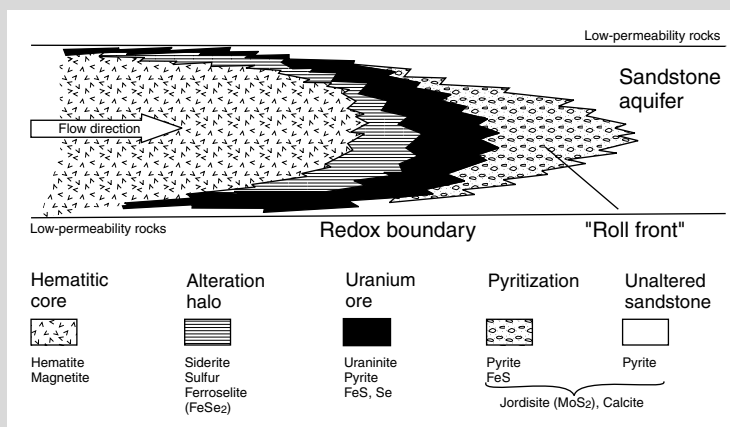
BOX 1.8 Infiltration ore deposits of uranium

Infiltration deposits of uranium are very common and economically important. Oxidative chemical weathering transforms uranium (IV) in rocks to uranium (VI), which forms complex ions with free SO₄²⁻, CO₃²⁻, OH⁻, alkalis and humates. Under oxic conditions in surface and groundwater, these complexes are stable and allow long-distance transport. Geochemical barriers for uranium are phosphates, arsenates, vanadates and carbonates in percolated rocks, strong reduction (e.g. methane) and sorption by colloids of iron hydroxides, silica and organic matter (Min *et al.* 2005). Correspondingly, uranium infiltration mineralization and ore deposits occur in permeable sandstone and conglomerate (Colorado Plateau, or "sandstone type"), in volcanic ash beds, in faults and breccia bodies, in peat, lignite and coal seams,

in asphalt, and in terrestrial calcite crusts of semiarid lands (the “calcrete type”). The genesis of the last includes a pronounced component of evaporation.

The Colorado Plateau is a Precambrian block covered by some 3000–4000 m of little deformed Permian to Eocene sediments. Numerous terrestrial sandstone and conglomerate strata occur in this package. Uranium deposits and occurrences were found in all stratigraphic positions, with the largest endowment in Triassic and Jurassic rocks (Sanford 1990). The time span of mineralization, however, is from 80–50 Ma (Late Cretaceous to Palaeogene), independent of host rock age. The shape of orebodies varies widely, including tabular lenses, sometimes stacked on top of each other, pockets and the characteristic “roll fronts” (Figure 1.57), often in connection with buried river courses. Roll fronts mark the redox boundary in space and time where the infiltrating meteoric water lost its capacity to oxidize the percolated sandstone and to retain uranium in solution. Tabular deposits appear to have been controlled by the interface between two different meteoric waterbodies, a stagnant saline brine and freely flowing fresh groundwater that carried uranium and vanadium. In the tabular type, the main ore mineral is coffinite, in contrast to the uraninite of the roll front type. Oxidation/reduction fronts in the aquifers are clearly visible in the field, by red and grey colours of the rocks. Spotty reduction by coal fragments in sandstone caused formation of high-grade ore pockets, but also the complete replacement of large tree trunks by uraninite. It is thought that sources of uranium were the many tuff bands in the sediments, but other possibilities include former basement islands or detrital uraniferous minerals in sandstone. Ore minerals include coffinite, uraninite, vanadium-rich clays and minor sulphides (of Fe, Mo, Cu, Pb, Zn, Se, etc.). Neogene uplift of the plateau caused a late phase of renewed weathering that affected many deposits and produced highly conspicuous varicoloured secondary uranium minerals.

Figure 1.57 Roll front uranium orebodies develop, where infiltrating uraniferous meteoric water passes through a redox boundary.



The example of the Colorado Plateau demonstrates that infiltration ore deposits are formed by meteoric waters that descend into basins – the reverse from diagenetic-hydrothermal ore deposits, which are also found in marginal areas of basins but are formed from ascending basinal solutions (cf. Section 1.4 “Diagenetic Ore Formation Systems”). Copper, lead and silver ores embedded in haematitic sandstone suites (“red bed deposits”) may have originated in a way similar to infiltration deposits of uranium (e.g. the Transfiguration deposit in Quebec: Cabral *et al.* 2009). There are, however, viable alternative modes of their formation by basin dewatering, so that each case must be carefully investigated. Resemblance and

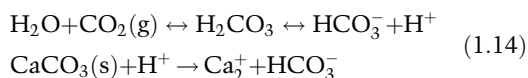
differences are illustrated by the large sandstone-hosted but diagenetic-hydrothermal Zn-Pb deposit at Jinding, Yunnan, China, with ~220 Mt at 7.4 wt.% combined grade (Chi *et al.* 2007, Kyle & Ning 2002). Sandstone ore of base metals and silver is generally low-grade and therefore at present economically not very attractive.

Formation of karst systems in carbonate rock bodies and the contemporaneous deposition of mineralization in the caves may also be related to **infiltration processes**. However, karst infiltration deposits are more a suspected than a proved deposit class. In the Maghreb Region of northern Africa, numerous small deposits of Pb and Zn ($\pm$ barite, fluorite) in solution caves were formerly

exploited. Following earlier authors who studied lead-zinc karst ores in Europe, many scientists proposed that the North African deposits have formed by concentration of dissolved trace metals originally hosted in the karstified carbonates (Bernard 1973, Zuffardi 1976). Meanwhile, the application of modern research technologies suggests an epigenetic hydrothermal origin, probably related to migrating saline basinal brines. However, the karst infiltration model retains its theoretical validity: Examples may be supergene manganese ores in solution caves of Devonian carbonate rocks in South China (Li *et al.* 2007) and in Cenomanian-Turonian dolostone at Imini, Morocco (Gutzmer *et al.* 2006), or vanadium karst ore in Neoproterozoic dolomites of Namibia (Boni *et al.* 2007).

Karst formation is caused by infiltration of meteoric water, which is enriched in CO_2 , for example by percolation through the organic soil horizon. Dissociation of carbonic acid produces acidity (H^+) that is essential in limestone dissolution. Because of a much slower reaction rate, dolomite is less affected by karstification. The reactions of limestone dissolution are described in equation 1.14:

Carbonic acid-induced limestone dissolution:



There are three possible modes of ore deposit formation in karst:

1 Hydrothermal karst originating from hot ascending fluids (e.g. the famous Carlsbad cave in New Mexico, which was formed by hypogene sulphate solutions: Polyak *et al.* 1998); structural relations such as cementation of host rock karst breccia by sulphides reveal simultaneous

calcite dissolution and sulphide precipitation (Figure 1.58); note the possible connection with metasomatic ore formation.

2 Common meteoric karst, formed by downward percolating water with dissolved carbon dioxide, which was later filled by ascending hydrothermal fluids with ore and gangue, independent of karstification.

3 Common meteoric karst, and $\pm$ synchronous supergene infiltration of ore elements.

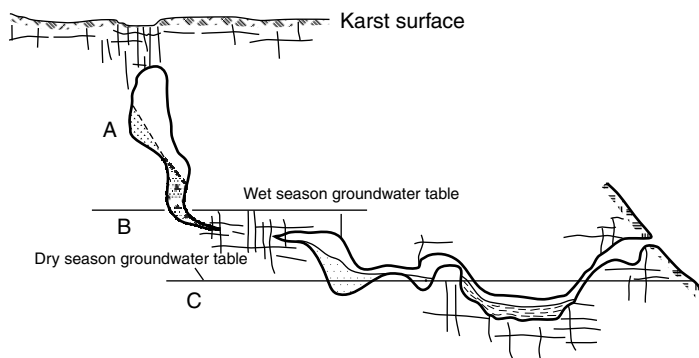
Only the last case answers the definition of a supergene ore deposit. Bernard (1973) discussed the possibility of ore formation in the setting of a common karst system. The hydrogeological zonation is the key (Figure 1.59):

Underneath the karst infiltration surface is the zone of $\pm$ vertical percolation (A). Rain or melt water seeps down rapidly, mechanical erosion and leaching of calcite along flow-tubes are very intensive. Any sediments will be quite coarse-grained. The environment is strongly oxidizing. The following zone of $\pm$ horizontal, highly variable water flow (B) is reached where the vertical seepage is collected by underground rivers. Sediments are mainly of the sand and silt grain size. The environment is still oxic and the only mineralization may be barite. In the lower parts of a mature karst system, a zone that is permanently submerged under water (C) can have sections with a "micro-euxinic" environment. Microbes feeding on imported organic matter reduce sulphate to H_2S . Sediments are either very fine-grained or chemical precipitates. Host rocks are silicified and dolomitized; cave walls are encrusted with limonite and clay. Mineralization grows inward and includes sulphides (mainly Pb, Zn, Sb and Cu), fluorite, barite, calcite, dolomite and occasional vanadium ores. Bernard (1973) thought that the metals were derived from the dissolved limestone (carbonates have contents in the ppm-range), but more often infiltration of weathering solutions from surrounding non-carbonatic rocks is assumed.



Figure 1.58 Lead-zinc ore (black) in a hydrothermal karst tunnel in Zechstein carbonate, Upper Silesia, Poland. Modified from Sass-Gustkiewicz, M. 1996, Society of Economic Geologists, Inc., *Economic Geology Special Publication 4*, Figure 2, p. 174.

Figure 1.59 Hydrogeological cross-section of a mature karst system (modified from Bernard 1973). With kind permission from Springer Science + Business Media.

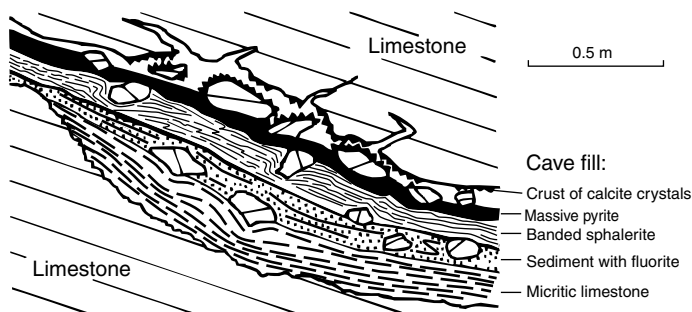


Discrimination of supergene karst-infiltration from hypogene mineralization is only possible with modern analytical methods (e.g. a study of fluid inclusions). Observation alone is unable to decide. This is vividly demonstrated by the scientific controversies concerning the origin of the Mississippi Valley type deposits, which lasted more than half a century. Consider the sedimentary geopetal (gravity-induced) structures of ore, gangue and internal sediments in a cave in an Alpine lead and zinc deposit (Figure 1.60). The bedding planes of host and cave fill are nearly parallel. Both were tilted, as shown here by later tectonic movements. Similar to Figure 1.58, repeated caving of the roof is visible. Obviously, the pattern may be due to both ascending or descending solutions. Complicating the situation even more, in a near-surface setting (in this case an emerged reef) both super- and hypogene processes may interact at the same time.

Karst has several properties that may occur alike in hydrothermal and common meteoric

water systems (Ford & Williams 2007). These have to be fully understood for rationally exploring and mining karst orebodies. Most important is the observation that thick carbonate strata always have horizons that are more prone to the development of solution caves and tunnels. This is, of course, a first-order guide for finding orebodies. Causes for easier karstification may have been higher initial porosity or brittleness and high purity of the carbonate rock. Clay beds often enhance mineralization by channelling or constricting the flow of water or of hydrothermal fluids. Faults and joints are additional elements that, together with stratigraphic ones, control the three-dimensional structure of a karst system. It is also important to elucidate the fourth dimension, that is the evolution of the system in time. Very practical aspects of mining a karst system concern hazards such as sudden inrushes of water, mud and debris, unstable surroundings of mine openings and damage to water rights owned by third parties.

Figure 1.60 Section of a Late Triassic hydrothermal karst cave at Bleiberg, Austria, that shows sedimentary layering involving fluorite, zinc ore and clastic cave sediment.



1.3 SEDIMENTARY ORE FORMATION SYSTEMS

The processes of sedimentation include physical, chemical and biological components. The prevailing regime lends its name to the major subgroups of sediments and sedimentary rocks: mechanical, chemical and biogenic sediments. Sediments are also classified according to the provenance of the material (allochthonous/autochthonous), and the manifold variations of locality and environment of deposition (Nichols 2009). Classifications of ore deposits that originate by sedimentary processes apply analogous criteria.

Allochthonous, terrigenous materials of prime economic importance are gravel, sand and certain clays. The source of the particles composing these rocks is distant from the deposits, the material was transported. Metallic ore deposits of this genetic group are called placers. Placers are mechanical enrichments of heavy and chemically resistant native metals and minerals by flowing or otherwise agitated water.

Autochthonous raw material deposits were formed at the site of the deposit. This group includes chemical precipitates and partially biogenic substances such as carbonates (limestone, dolomite, magnesite), evaporites (rock salt, potassium salt, gypsum), some massive and oolitic ironstones, banded iron formations, marine phosphates, sedimentary sulphide ores and manganese ore beds. Organic formation is the prevailing component for coal, oil shale, diatomite and for part of the limestones (e.g. chalk). All forms of life (Figure 1.49) participate in sedimentary mineralogenesis. In sedimentology, soils are also considered as autochthonous sediments. However, ore deposits related to soil formation processes were presented in the preceding section.

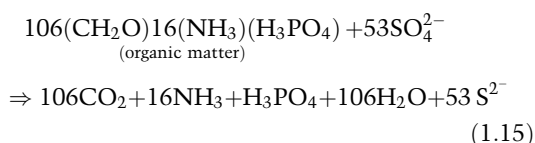
Many metalliferous sulphide, oxide, carbonate and sulphate deposits originate by autochthonous sedimentation following hydrothermal exhalation, precipitation of solutes and deposition of ore particles on the seafloor. *Sensu stricto*, all ores with this origin are “sedimentary”. However, the different process systems that may cause subaqueous exhalation of ore fluids and the prevailing geological setting must be part of the classification. This is why Cyprus type sulphides are

grouped with “Ore Deposits at Mid-Ocean Ridges and in Ophiolites” and Kuroko and Besshi types with “Volcanogenic Ore Deposits”. In this section, only those deposits of exhalative-sedimentary character are discussed, which were formed in a sedimentation-dominated environment and distal from contemporaneous volcanism. This is the class of sedimentary-exhalative (sedex) deposits.

Sedimentation is limited to the surface of the Earth, which is also the realm of life and its biogeochemical cycles (Falkowski *et al.* 2008). Therefore, sedimentary ore formation will almost always have a biogenic component (Southam & Saunders 2005). In some cases this is very obvious, for example in phosphate deposits made of bones and coprolites, or a lignite seam composed of fallen trees. In few ore deposits, however, the biogenic component is immediately visible. This is illustrated by sedimentary sulphide deposits that display a very light, biogenic sulphur isotopic composition, although the metals were introduced by hydrothermal-exhalative systems from below the seafloor. The cause for the light sulphur lies in oxygen depletion of seawater around hydrothermal centres and consequently, massive proliferation of anaerobic sulphate-reducing bacteria such as *Desulphobacter* or *Desulphomaculum* (Boschker *et al.* 1998). In the photic zone, green sulphur bacteria (Chlorobiaceae) thrive by anoxygenic photosynthesis. Sulphate-reducing bacteria often form consortia with archaea, whose role is not yet fully understood. These microbe communities reduce seawater SO_4 to H_2S , using organic matter as an electron donor (eq. 1.15). Simultaneously, carbon is “mineralized” to CO_2 or carbonate. As the microbially mediated reduction of sulphur involves a considerable negative isotope effect, metal sulphides formed from this H_2S contain light, “biogenic sulphur”. However, a minimal sulphate content in seawater of more than 1 mM is a precondition. Low contents of dissolved sulphate in seawater may have several reasons (e.g. the precipitation of evaporite gypsum: Wortmann & Chernyavsky 2007; cf. Section 4.2.2 “Seawater in the Geological Past”). The maximum isotopic fractionation by bacterial sulphate reduction (BSR) is 46‰, but most natural samples have a much smaller spread. Some rare microbial

BSR-communities produce intermediate-valence sulphur species (like S^0 or $S_2O_3^{2-}$) by bacterial sulphur disproportionation (BSD) that results in $\delta^{34}S$ fractionation between sulphate and sulphide approaching 70‰ (Canfield & Thamdrup 1994; Canfield & Teske 1996). Quite often, the involved microbe colonies are fossilized in the form of framboids (microscopic aggregates of pyrite cubes in shale). Earliest evidence for biogenic sulphate reduction dates from ~2.7 Ga. Earlier in the Archaean, bacterial sulphur disproportionation seems to have been the main microbial metabolism (Philippot *et al.* 2007).

Anaerobic microbial (bacterial) sulphate reduction:



Another frequent form of microbial sulphate reduction occurs at diffuse ("pockmark fields") or vent-like locations ("cold seeps") of methane degassing from sediments or from gas hydrate layers beneath the ocean floor (eq. 1.16). The process is very similar to the one described above.

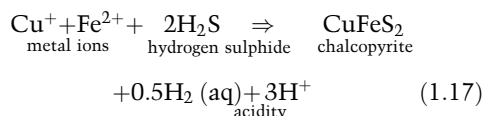
Anaerobic microbial sulphate reduction and concurrent methane oxidation:



The precipitation of metals and other elements from exhalations and seawater depends on the presence of suitable partner ions (e.g. HS^-) and pH/Eh conditions. One mode of precipitation is anion exchange, for example mixing of dissolved chloride-metal complexes with H_2S -rich seawater, resulting in sulphide formation. Note that sulphide precipitation results in lowering the pH (equation 1.17). Where redox-sensitive metals are transported across zones of different Eh, for example from the coast into a euxinic marine basin, the precipitates reflect this by lateral zoning. Zones may comprise oxides near the coast followed by carbonates, silicates and finally sulphides in the most reduced environment. Zoning is most noticeable if the same metal is present through all zones

as in some iron ore districts. In polymetallic ore deposits, several subzones may be distinguished within the major facies zones.

Production of acidity by sulphide precipitation:



1.3.1 Black shales in metallogenesis

Carbonaceous shales are important host rocks of sedimentary ore deposits. They are fine-grained laminated clastic sediments consisting variably of quartz, carbonate and clay with more than 1% of organic matter. Global black shale units may reflect major perturbations of global carbon and climate cycles, which are controlled by endogenous (tectonics, mantle plume break-out) and exogenous processes (Emeis & Weissert 2009). Their sedimentary environment is characterized by low energy, benthic anoxia and often, by euxinic conditions (associated with stable reduced sulphur species in water above the seafloor). As shown earlier, metal cations dissolved in seawater are precipitated by H_2S and HS^- . The mass of metals dissolved in modern seawater is very large: 13,300 Mt molybdenum, 4400 Mt uranium, 2690 Mt vanadium, 690 Mt zinc and 620,000 t lead. Marine anoxic periods in the geological past may have temporarily reduced the concentrations to less than half of these figures (Algeo 2004).

Organic-rich pelites are generally characterized by elevated contents of redox-sensitive trace elements (including U, V, Mo, Ni, Co, Cr, Cu, Pb, Zn, Cd, Au, Ag, As; Morford & Emerson 1999) and phosphate. Many of the enriched elements are essential for life and their changing concentration in seawater through geological history influenced the evolution of life on our planet (Anbar 2008). Some may have been sourced from continents and entered the sea adsorbed on detrital organic particles. The import of a large mass of plant remains into marine black shale basins is often questioned. Yet, many marine petroleum source rocks produce oil with a considerable fraction of paraffins, whose main precursors are waxes and lipids of plants (Hunt 1996). Apart from continental sources, mid-ocean hydrothermal

activity, submarine volcanism and extraterrestrial matter provide parts of the dissolved metal stock. Explanations for preferential metal concentration in marine black shales include:

- Significant metal enrichment may be acquired by the special faculty of marine organic matter to bind trace metals dissolved in seawater (especially Ni, Co, Cu and Zn);
- in contrast to the first group, V, U, Mo and Cr are not fixed by organic species but by reduction;
- elements like Ba, P and Cd are imported from and indicators of a high biological productivity in the upper, oxic layer of the stratified water column.

Manganese (and sometimes even iron) is typically impoverished in black shales relative to ordinary pelites, because it dissolves in the highly reducing bottom sediment pore waters and with increasing consolidation, is flushed out back into the sea. This reduction is in part due to bacterial activity (Kim *et al.* 2004). Low Fe-contents (expressed by low Fe/Ti ratios) inhibit the formation of syngenetic pyrite, favouring the production of significant amounts of H₂S in anoxic pore fluids. This may be an important factor controlling the amount of reduced sulphur available to form ore deposits by capturing metals from migrating fluids.

Accordingly, most black shales have anomalous metal contents, but these are not economically exploitable. The only current profitable use of ordinary black shales is the recovery of the energy inherent in organic matter, either by direct burning or by the production of synthetic oil (cf. Chapter 7.7 "Oil Shale"). The most important economic significance of black shales is their role as the main source of petroleum and natural gas. Similar to the expulsion of hydrocarbons, metals mobilized from black shales during diagenesis or metamorphism can form ore deposits. Some former black shales have been transformed into metamorphic graphite deposits.

Yet, there are many large **sulphide ore deposits hosted in black shales** (with metals such as Cu, Sb, Zn, Pb, Ag and Au), which were typically formed from submarine hydrothermal-exhalative fluids, but precipitation from average seawater without

increased hydrothermal input is a plausible alternative. A current example of this scientific controversy is the Chinese Mo-Ni sulphide ore shales (Shao-Yong Jiang *et al.* 2006, Lehmann *et al.* 2007, Wille *et al.* 2008; cf. Chapter 2 "Molybdenum"). Similarly, the European copper shale and the Central African copper-cobalt shale deposits were for a long time considered to be purely sedimentary formations. Meanwhile, the scientific consensus is that both were formed epigenetically by migrating diagenetic, hot fluids (cf. Section 1.4 "Diagenetic Ore Formation Systems").

The distinction between sedimentary and diagenetic ore deposits is sometimes ambiguous, both in theoretical classification and in practical application. The critical difference is the time of concentration of the considered element: Was it effected during sedimentation of the immediate host rocks (by syngeneses) or during later diagenesis (by epigenesis, for example concentration by migrating formation waters)? Isochemical recrystallization during diagenesis or later metamorphism does not justify a different genetic class, except that the sedimentary ore may be called consolidated, lithified or metamorphosed.

Sedimentary ore deposits are increasingly explored and investigated by methods of dynamic basin analysis, sequence stratigraphy and palaeogeographic reconstructions, that were first developed for oil and natural gas exploration (Einsele 2000). These methods encompass concepts such as distinction between sedex-deposits formed during early rifting of a basin and others that originated during later thermal contraction. If the stratigraphic, facies and tectonic evolution of a basin is well understood, it appears possible to predict prospective localities and stratigraphic positions of potential ore (Ruffell *et al.* 1998).

1.3.2 Placer deposits

Sedimentary placer deposits are mechanically formed concentrations of heavy, durable minerals that may occur in transported soil or regolith (colluvial), in fluvial and in coastal sediments. Aeolian placers (Figure 1.61) and placers in glacial sediments are also known, but rarely of economic



Figure 1.61 (Plate 1.61) Aeolian lag enrichment of magnetite (dark sand patches) at An Kor, Red Sea Hills, Sudan. Note the exploration trench testing the Neoproterozoic primary mineralization in the foreground.

significance. Placer deposits of economic importance are classified as residual, eluvial, colluvial, fluvial and coastal (for the latter, terms also used include marine and beach placer). Geologically young, usually Quaternary placers (Duk-Rodkin *et al.* 2001) are discerned from fossil placers. Residual and eluvial placers were briefly introduced earlier.

Placers are important sources of gold, platinum metals, tin, titanium (rutile, ilmenite), zircon, rare earth elements (monazite) and gemstones (diamond, garnet, ruby). Precondition of the concentration of placer minerals is their mechanical and chemical durability during weathering and trans-

port, and their elevated density compared with the ordinary rock forming minerals (Table 1.4).

Simple washing in a gold pan (Figure 1.62) easily separates light quartz and feldspar from dark mafic silicates, garnet, ilmenite and magnetite. This dark fraction of “black sand” contains the valuable minerals such as flitters of gold. Note, however, that the same term black sand is often used to describe Canada’s giant oil sand resources, which are definitely not placer deposits.

Colluvial placers originate by downslope creep of soil from weathered primary deposits (Figure 1.63). Heavy minerals move to the base of the regolith, whereas lighter and fine-grained

Table 1.4 Density of common placer and gangue minerals (g/cm³)

Feldspar	2.5–2.8	Monazite	5.2–5.4
Quartz	2.65	Magnetite	5.2
Mafic silicates	ca. 3–4	Columbite	5.2–7.9
Diamond	3.5	Scheelite	5.9–6.1
Topaz	3.5–3.6	Cassiterite	6.8–7.1
Garnet	3.6–4.3	Wolframite	7.0–7.5
Corundum (ruby)	3.9–4.1	Cinnabarite	8.1
Rutile	4.2–4.3	Uraninite	7.5–9.7
Ilmenite	4.5–5.0	Platinum metals	12–21.5
Zircon	4.7	Gold	15–19.3

The density of many minerals varies considerably because of chemical variation. Alloys of native metals vary in composition.

fractions are displaced upwards. Orebodies are sheet- or channel-like bodies consisting of ore (e.g. cassiterite) and gangue (quartz) minerals, and of rock fragments. Colluvial ore minerals at the foot of a slope can be eroded by rivers and re-concentrated by alluvial processes.

Fluviatile, or alluvial placers

Fluviatile, or alluvial placers occur in active stream channels and in older river terraces

(Figure 1.63). Heavy mineral concentrations form at morphologically well-defined sites, mainly characterized by changes of flow velocity. Such sites include large boulders, rock bars, gravel beds on the inside bank of river bends, the downstream end of gravel and sand islands (point bars), but also reed patches. Another important trapping mechanism is infiltration of heavy minerals into open pore space of sand-free pebble banks (Hattingh & Rust 1993). This mechanism explains exceptionally high gold grades in the ancient Witwatersrand

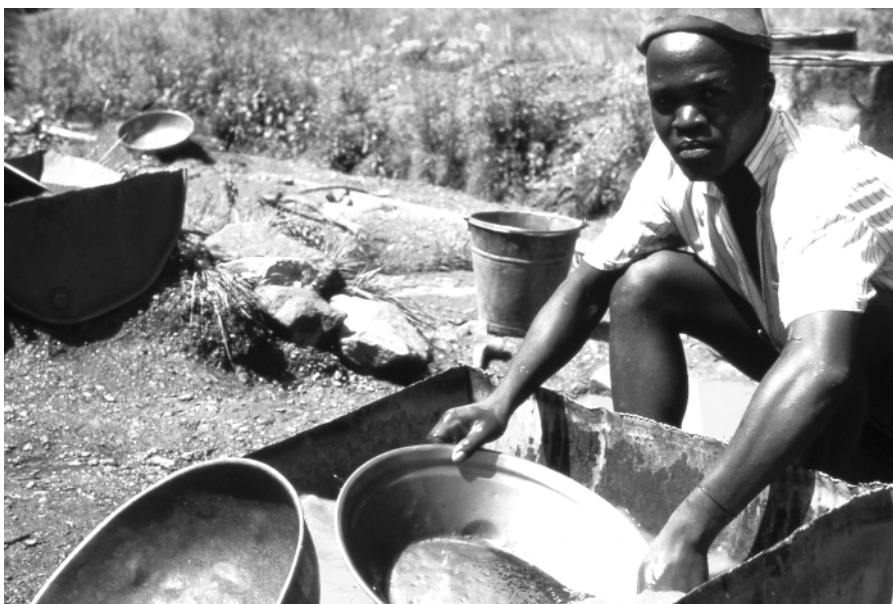
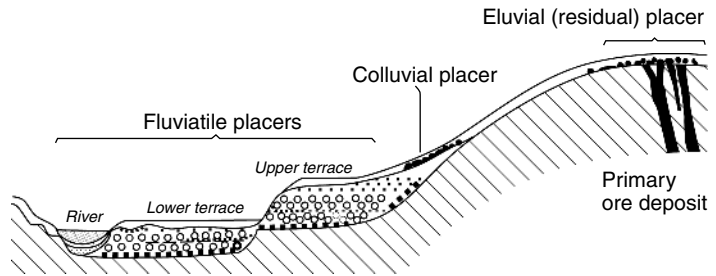


Figure 1.62 (Plate 1.62) Panning cassiterite-columbite ore from Ngara pegmatite, eastern Rwanda. Note the small mass of black ore mineral sand which remains from washing the pan initially filled with ore to the brim.

Figure 1.63 Cross-section of a river valley near an outcropping primary ore deposit, which is the source of residual (eluvial), colluvial and fluviatile placers (black dots).



conglomerates (see below). Saxton *et al.* (2008) confirmed experimentally that high-grade longitudinal pebble to cobble bar systems trap gold during their formation from fast-moving suspension flows. Many alluvial placers in mountain stream valleys comprise the whole volume of the valley fill (Figure 1.64). Downstream, trapping sites, such as those mentioned above, control exploitable grades. Alluvial placers rarely extend for more than several kilometres along a valley, because both concentration and grain size of ore

minerals diminish with increasing transport distance.

Transport, deposition and density sorting of minerals in flowing water are controlled by factors of “hydraulic equivalence”. Originally, this term was used in the sense of “settling equivalence”, which refers to the physical principle that the settling velocity of suspended particles in water depends on diameter and density (Stoke’s Law, eq. 1.4). Hydraulic equivalence *sensu stricto* results in concurrent deposition of small high density



Figure 1.64 (Plate 1.64) Alluvial placer mining near Ruhanga in the tin-tantalum district of Gatumba, Rwanda. After extraction, the devastated valley must be restored. Courtesy B. Lehmann, Clausthal.

grains with larger and lighter ones (e.g. fine-grained gold in coarse alluvial gravel). Meanwhile it has been recognized that concentration of heavy minerals is due to several dynamic processes, which include lag mechanisms: When river sediment is entrained, high density particles tend to remain essentially *in situ*, whereas light particles are removed downstream (this is called “selective entrainment” or, linguistically not quite correct, entrainment equivalence; e.g. James & Minter 1999). Today, the term hydraulic equivalence is usually understood to comprise both settling and entrainment equivalence, and other hydrodynamic factors such as shape, size and surface properties of particles (Carling & Breakspear 2006).

Investigations of fluvial placer formation must include studies of the particular sedimentary system (Fielding *et al.* 2009). Physical models of turbulent mass flow in fast-moving rivers support genetic understanding (“granular physics”, Frey & Church 2009). Extensive pebble to cobble longitudinal bar systems of braided rivers at Witwatersrand, South Africa (gold) and Elliot Lake, Canada (uraninite) are believed to have originated in such an environment. Enrichment of the heavy minerals is caused by their tendency to accumulate near the base of a flow where they are easily trapped (Saxton *et al.* 2008).

Often, the highest concentration is located at the base of the valley fill directly on bed rock, but ore is also found above beds of fine-grained or cohesive ground between pebble beds (“false bed rock”). This may be caused by two different mechanisms:

- 1 The heavy minerals gradually work themselves to the bottom of a pebble bed (this is the hypothesis of an “active bed”, Bilibin 1938); or
- 2 a perpetual and complete reworking of the pebble bed is assumed so that selective entrainment concentrates heavy minerals at the base (“lag deposit”).

The second explanation appears to be more likely, because floods provide the main input of energy into erosion and transport processes of river valleys. When exploring for placer deposits, or sampling river sediments for other purposes, it is always advisable to invoke practical aspects of

hydraulic models. In addition to hydraulics, chemical and biochemical processes in valley sediments mobilize and reprecipitate elements, including native gold (Reith *et al.* 2010). Chemical mobility of gold in placers is suggested by both the occurrence of very heavy nuggets that could hardly be moved by flowing water and by the occasional observation of idiomorphic, undeformed gold crystals in river sediments:

Today, geologically young alluvial placers are mainly exploited for gold. Their economic role is feeble, however, compared to the time of the great gold rushes in California, Alaska and Australia in the 19th century. Among fossil alluvial placers, the Archaean Witwatersrand Basin in South Africa hosts by a wide margin the largest gold resources of the world. Because of the costs of increasingly deep mining, however, its share of world gold production is steadily decreasing. It is one of the world’s most intensively investigated placer districts (for more details refer to Chapter 2.3 “Gold”). One remarkable result of the research is the reconstruction of the palaeohydrologic situation (Figure 1.65a) showing braided streams, pebble diameters and flow vectors of one of the gold conglomerate beds. Figure 1.65b demonstrates that higher gold contents occur in the middle section of the fan, whereas both marginal (entry front) and basinal areas contain less gold. Geological mapping and precise determination of fluvial facies regimes are essential contributions to a rational exploitation of these superdeep deposits.

The source of ore minerals in placers is an exciting question, both for the practitioner posing questions such as “Can we locate the primary source?” and for scientists. One way is to estimate the mass balance between erosion and uplift in the source region in comparison to the depositional system. Application of this approach reveals that the mass of gold in the Witwatersrand District can be explained without invoking exceptionally high gold contents in the former source region (Loen 1992).

Coastal placers

Coastal placers are mainly formed in surf zones. In contrast to typical alluvial placers, both light and

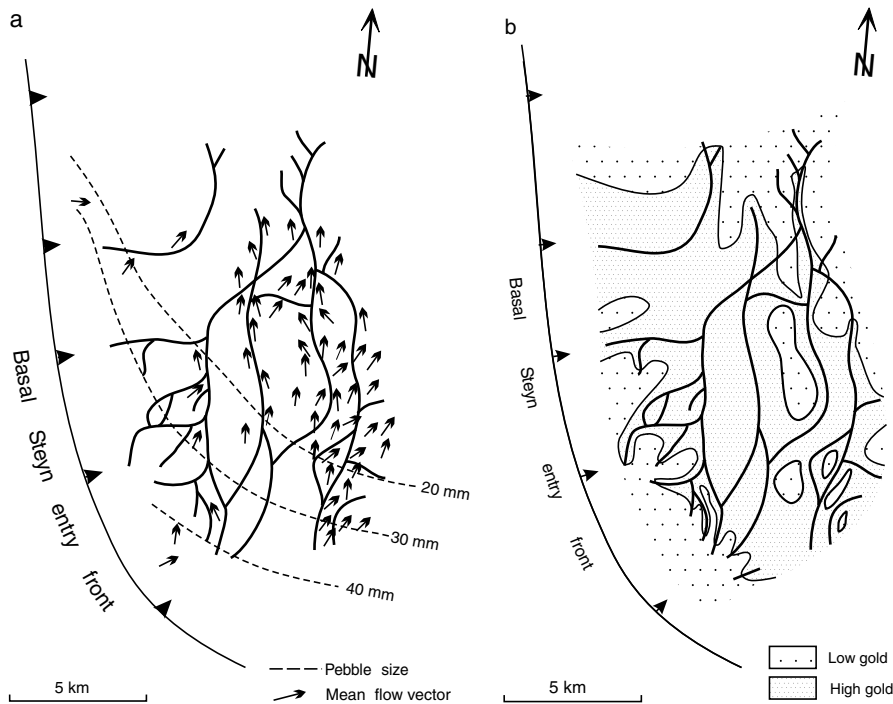


Figure 1.65a,b Facies control of gold deposition in the braided alluvial fan complex of the Basal and Steyn Reefs in the Steyn Mine, West Rand Goldfields, South Africa (after Minter *et al.* 1986). Courtesy Geological Society of South Africa.

heavy minerals occur roughly in the same grain size that is almost exclusively sand. Obviously, the hydraulic equivalence *sensu stricto* has no role in this environment and the critical factor is mainly entrainment equivalence. The incoming surf imposes a turbulent regime that transports suspended sand including heavy minerals towards the beach. When a wave runs out, sand grains settle for a moment. Return flow to the sea is laminar and only light minerals can be entrained. Heavy minerals are enriched in a narrow linear strip along the beach. Other coastal processes may enhance placer formation including tides, lateral currents, wind and especially storms that induce higher waves (Roy *et al.* 2000, Hoefel & Elgar 2003).

Coastal placers are more frequent on stable coasts, because neither strong erosion nor rapid

sedimentation is propitious. Single orebodies are elongated narrow lenses or strips of dark sand that may extend over hundreds of kilometres. In some cases, the connection of placers with a river mouth delivering sediment is obvious, but erosion of older coastal strata may also be a source. Sea level changes produced either submerged placers (e.g. during Quaternary glacial conditions, the sea was >100 m below the present level) or deposits above today's sea level associated with the raised beaches of Pleistocene interglacial and older climate epochs warmer than today. Recently, a major new province of marine placers was discovered in the Murray Basin of interior Australia. The placers occur in 400 km long barrier complexes as beds and narrow "shoestrings", which formed in a very shallow transgressive Pliocene inland sea. The

barriers developed across more than half of the basin. Many promising coastal placer deposits of coarse-grained (90–300 μm) quartz and the heavy minerals rutile, zircon, ilmenite and altered ilmenite (leucoxene) have been outlined. In lower-energy environments, only low-grade and fine-grained (40–80 μm) heavy mineral sands were deposited. The concentration is attributed to large storms and consequent ground swells, which may have eroded pre-enriched underlying Miocene sands (Roy *et al.* 2000).

Coastal placers can consist of up to 80 wt.% heavy minerals. Their contribution of rutile and zircon to world markets is of high economic importance. They are lesser sources of diamond and cassiterite. Gold and platinum are rare in coastal placers. Iron ore breccias ("detrital iron ore") hosted by Early Cretaceous transgressive sediments in Northern Germany constitute a rarely mentioned type of coastal placers. In this region, oxidized pyrite nodules of emerged Jurassic shales were swept by the surf into depressions that developed due to salt diapirism and subsidence. The ores were low-grade and mining ceased with increasing competition by overseas imports.

1.3.3 Autochthonous iron and manganese deposits

Autochthonous iron and manganese ores are chemical, partly biogenic marine sediments. Today, terrestrial iron ores (including recent bog iron ore, or after diagenesis siderite in black coal) are economically insignificant. In the future, manganese nodules and crusts of the deep oceans may become an essential source of metals. For now, the most important raw materials of this group are enriched parts of marine banded iron

and manganese formations (predominantly formed in the Palaeoproterozoic), and ooidal or massive iron and manganese ore beds that are of much younger, Phanerozoic age.

Banded iron formations

Banded iron formations (BIF, including the varieties itabirite, jaspilite, cherty iron formations) are layered, banded (0.5–3 cm) and laminated (<1 mm) rocks containing >15% iron. Essentially, BIF consist of quartz and magnetite layers that form sedimentary units reaching lateral extensions of thousands of kilometres and a thickness of hundreds of metres. Geological setting and associated rocks allow a subdivision of BIF into three types:

- 1 Algoma type in submarine volcanic settings;
- 2 Superior type in marine shelf sediments; and
- 3 Rapitan type, which is closely related to glaciogenic marine sediments (James & Trendall 1992).

Banded iron ores of **Algoma type** are especially common in Archaean greenstone belts, but occasionally, geologically similar deposits formed in younger periods (Figure 1.61). The oldest examples are known in the Isua Belt on Greenland (Whitehouse & Fedo 2007; ~3800 Ma). Host rocks of Algoma ore are volcanogenic sediments such as greywackes, tuffaceous and magmatic volcanic rocks. Typical ore beds are less than 50 m thick and may display a transition from oxide through carbonate and silicate to sulphide facies. Oxide facies iron occurs as magnetite, haematite is rare (Figure 1.66). Algoma type iron formations extend to several thousand square kilometres, which is quite small compared with Superior type basins. In several districts, numerous exhalative centres with sulphides

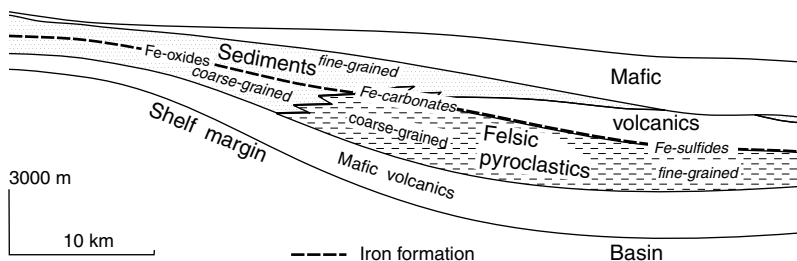


Figure 1.66 Stratigraphical context and facies zones of an Algoma Type volcanogenic iron formation in the Archaean Michipicoten Basin, Canada. Modified from Goodwin, A. M. 1973, Society of Economic Geologists, Inc., *Economic Geology* Vol. 68, Figure 2 p. 919.

and some larger VHMS deposits punctuate Algoma BIF horizons (McClenaghan *et al.* 2009). This observation, and their close association with volcanism, suggest formation on the seafloor by exhalative, hydrothermal-sedimentary processes driven by heat anomalies. Magmatic fluids may also participate in ore formation. Consequently, Algoma type ore is essentially volcanogenic (cf. Section 1.1 “Volcanogenic Ore Deposits”).

Banded iron ores of **Superior type** (Figure 1.67) are hosted in sedimentary sequences that include black, organic-rich and silicic shale, quartzite and dolomite, and transgress older basement. Bimodal volcanic rocks (rhyolite and basalt) may occasionally form part of the country rocks. This indicates a sedimentary environment of stable continental shelves covered by relatively shallow seas with some extensional tectonic strain and associated volcanism. Shallow, coastal and deep basinal facies can be recognized (James & Trendall 1992).

Iron formations of the Superior type are marine sediments of global extension. They are preserved in remnants of marine basins that reach tens of thousands of square kilometres. Banding and lamination are remarkably persistent but not all BIF are strictly autochthonous. Chert-free, massive iron sediments locally replacing bedded BIF are interpreted to reflect synsedimentary sifting and deposition by density currents (Lascelles 2006). Truncated beds, flow ripples and synsedimentary deformation structures are recorded. Commonly, BIF contain iron in oxide, carbonate and silicate phases; sulphides are rare. Iron and SiO_2 were deposited as fine-grained ooze (or as a gel), but ooids, concretions and biogenic textures have been observed. Primary precipitates were probably amorphous SiO_2 , ferric hydroxide $\text{Fe}(\text{OH})_3$ and nontronite (near landmasses, oxic conditions), or precursors of magnetite, siderite and greenalite [$[\text{Fe}]_{2-3}\text{Si}_2\text{O}_5(\text{OH})_4$] (far from land; in deeper,



Figure 1.67 (Plate 1.67) Folded and metamorphosed Superior type banded iron formation near Mt Tom Price mine in the Hamersley Gorge (Karijini National Park, Western Australia) with marine scientists Aivo Lepland and Mark van Zuilen kindly posing for scale. Iron-rich beds black, silica (jasper) red. Photograph by Aivo Lepland, courtesy Geological Survey of Western Australia.

dysoxic-anoxic basins). Diagenesis and common low-grade metamorphism produced the ordinary paragenesis of BIF ore, comprising quartz, haematite, magnetite, siderite, minnesotaite $[(\text{Fe,Mg})_3\text{Si}_4\text{O}_{10}(\text{OH})_2]$, stilpnomelane, asbestiform amphiboles and many other Fe-rich silicates. Primary ores have an $\text{Fe}_2\text{O}_3/\text{SiO}_2$ ratio of 0.98–1.26, typically 25–45 wt.% Fe, <3% each of Al_2O_3 , MgO and CaO, and small contents of Mn, Ti, P and S. This discriminates Superior type BIF from other marine sedimentary iron ores. At sufficiently high

magnetite grades, the primary ores are exploited as “taconite”. Most BIF-based iron ore mines, however, extract parts of iron formations that were enriched either: i) by supergene processes typically resulting in “martite-goethite ore” with 60–63 wt.% Fe; or ii) by hypogene hydrothermal processes forming “high-grade haematite ore”, with 60–68 wt.% Fe (cf. Section 1.2 “Supergene Enrichment”). Martite is a term that denotes haematite pseudomorphs replacing magnetite.

BOX 1.9 The origin of Superior type iron formations – still disputed

Superior type BIF occur exclusively in the Late Archaean and Early Palaeoproterozoic (2.6–1.8 Ga). Apart from the formation of giant iron and manganese deposits, the Archaean-Palaeoproterozoic transition includes other remarkable events of Earth history:

- The Lomagundi-Jatuli carbon isotope excursion (Melezhik *et al.* 2004);
- the Earth’s earliest (Huronian) glaciation;
- the first global appearance of terrestrial “red beds”;
- the earliest abundant calcium sulphate sediments; and
- the Shunga event, a giant accumulation of C_{org} -rich sediments.

The common cause of these changes is probably the rapid expansion of photosynthetic eukaryotes, which was triggered by enhanced nutrient supply and the first formation of an ozone shield in the atmosphere. Most scientists relate the precipitation of the giant mass of iron contained in BIF to the transition of oceans and atmosphere from a reduced to an oxidized state (the “Great Oxidation Event” between 2.45 and 2.2 Ga: Holland 2002, 2005; Anbar *et al.* 2007, Anbar 2008, Kump 2008, Qingjun Guo *et al.* 2009). In the Archaean before oxidation, PO_2 of the atmosphere was <10–5 PAL (present atmospheric level). Other scientists, however, suggest that oxidized seawater existed much earlier (Ohmoto *et al.* 2006, Kesler & Ohmoto 2006).

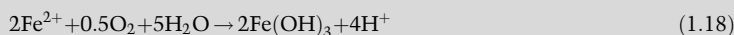
Sources of iron in BIF may have been:

- submarine-exhalative systems (Kimberley 1994, Morris 1993) similar to today’s mid-ocean ridges;
- submarine-exhalative systems associated with intraplate tensional tectonic structures and volcanoes (Bekker *et al.* 2010, Barley *et al.* 1997); and
- continental weathering.

Probably, all these sources contributed iron at different times and locations (Alibert & McCulloch 1993). However, worldwide trace metal contents of Superior type BIF are very low (Morey 1992), arguing against local hydrothermal sources and for homogenized ocean water. Sources of SiO_2 in the chert bands were most probably weathering landmasses (Hamade *et al.* 2003). It is assumed that the ancient oceans were saturated with dissolved silica (as $\text{Si}(\text{OH})_4$), resulting in a steady rain of siliceous matter to the ocean floor. The modern oceans are markedly undersaturated in silica and this may be the main reason for the changing character of iron ores, from ancient BIF to more recent ironstones. The banding in BIF can be explained by diurnal to seasonal cycles of biological activity, to temperature fluctuations (Posth *et al.* 2008), or to episodic depletion of ferrous iron in the water column.

Essential parameters of the formation of Superior type BIF are still discussed, apart from the basic agreement that the ores are chemical or biogenic precipitates from seawater (eq. 18).

Oxidative precipitation of dissolved reduced iron forming banded iron formations:



Many scientists support the following hypothesis: “The atmosphere may have been nearly free of oxygen, while the oxygen in the oceans started to increase. Seasonal blooms of the earliest photosynthetic micro-organisms (cyanobacteria) increased oxygen concentration in seawater that oxidized and precipitated dissolved Fe^{2+} .”

Recently, this was both confirmed (Qingjun Guo *et al.* 2009) and vividly contradicted (Ohmoto 2003a, Ohmoto *et al.* 2006). The latter cast doubt on both a low-oxygen atmosphere and the late appearance of cyanobacteria, and propose a euxinic model, with precipitation of iron at the contact between reduced deep water and O₂-rich surface water. Widespread euxinia is confirmed by sulphur isotope and iron speciation data (Reinhard *et al.* 2009). Under anoxic conditions, BIF deposition may have been catalysed by anoxygenic photoautotrophic bacteria (Kappler *et al.* 2005). A third possible precipitation mechanism is abiogenic UV-induced oxidation (Bekker *et al.* 2010). Iron isotope investigations support the concept of a redox-stratified ocean (Rouxel *et al.* 2005) and of an important role of early diagenetic dissimilatory iron reduction (Johnson *et al.* 2008). The worldwide termination of Superior type BIF deposition at ~1.85 Ga may have been caused by the Sudbury impact: Slack & Cannon (2009) suggest that the bolide's oceanic impact destroyed redox layering in the oceans, which impeded dispersion of dissolved Fe(II) from ocean-floor hydrothermal vents. In their thorough review, Bekker *et al.* (2010) conclude that no single parameter explains BIF formation and suggest a control by multiple environmental changes of earth systems.

Manganese formations

In the Transvaal Basin of South Africa, **marine manganese oxide strata (manganese formations, MnF) of the ca. 2.22 Ma Hotazel Formation** occur interlayered with Superior type BIF, which hosts important iron ore deposits. The outstanding feature is, however, that this province (the Kalahari manganese field: Maynard 2010) comprises about half of the world's manganese resources. The concentration of Mn relative to Fe is believed to have been effected by earlier abstraction of iron from seawater and precipitation of BIF. In consequence, the more soluble manganese was relatively enriched and only when PO₂ continued to rise, Mn²⁺ was oxidized to Mn³⁺ and manganese-rich beds were deposited. Note that similar to Superior type BIF, manganese formations are only exploitable if enrichment processes acted on protore (cf. Chapter "Manganese").

Banded iron formations of **Rapitan type** were deposited immediately following the Sturtian (~730 Ma) and the Marinoan (630 Ma) glaciations, during the Cryogenian System of the Neoproterozoic. The name Rapitan is derived from a Sturtian locality in the Mackenzie Mountains, Northwest Canada. Similar occurrences were found in Brazil (Urucum: Walde & Steffen 2007) and in Namibia (Otjosondou). During these glacial events, land and even oceans were widely covered with ice ("Snowball Earth" hypothesis: Hoffman *et al.* 1998), causing a nearly global anoxia and the presence of dissolved ferrous iron in seawater. Inter- and post-glacial melting of the ice caps resulted in

formation of glacial sediments, re-oxidation of the oceans, and precipitation of ferric iron and manganese oxides. As marine sediments, Rapitan type iron formations are similar to Superior type BIF, but have little economic significance.

Oolitic iron ore

Oolitic iron ore was exploited from approximately 500 deposits worldwide. Formation of this ore type is restricted to Phanerozoic time. Economically outstanding historic mining districts in the Jurassic of western Europe, and those in the Palaeozoic of the northern USA led to the distinction of "Minette type" (limonitic) and "Clinton type" (haematitic). Always, these ores are sediments of shallow epicontinental seas or of shelf-regions and are interbedded with clastic sediments. Ore beds reach a thickness of about 30 m and lateral extensions up to 150 km. This suggests that eustatic highstands are favourable conditions for their formation, as shown by Young (1992) for the Ordovician deposits of the West-Mediterranean province.

Oolitic iron ore (Figure 1.68) is not banded and contains no primary colloidal silica. Textural varieties include mainly the namesake round accretionary bodies called ooids (earlier termed "ooliths") and pisoids, but also fine-grained iron ore particles forming massive "ironstone" *sensu stricto*. Precipitation of ooids in agitated water is indicated by many observations, including intraclasts of oolitic rock in ooidal matrix, fractured and freshly mantled ooids, cores of ooids formed by quartz, phosphorite and fragments of fossils,



Figure 1.68 (Plate 1.68)

Haematitic iron oolite ore formed in a Late Cretaceous marine embayment at Aswan, Upper Egypt.

oblique and cross-bedding. Iron oolite rock of ore grade has closely packed ooids, but host rock bituminous marls of the minette enclose widely disseminated ooids. The ore beds are often connected with rich fossil communities. Fossils are typically replaced and cemented by iron ore minerals. A lateral differentiation of iron facies (e.g. oxide, carbonate, silicate) in oolite beds is rarely clear. Single ooids consist of goethite, haematite, chamosite and siderite (with very little magnetite and pyrite) that alternate in growth zones or in cross-cutting metasomatic zones. Compared to the crustal average, iron and phosphorus are enriched by a factor of 6 (Fe to ~34%, P to 0.6%), similar to Mn, As, V and other elements. An apparent paradoxon is the high percentage of reduced iron in ooids that were formed in oxygen-rich seawater, as proven by the associated fossils.

The coincidence of both sedimentary and diagenetic textures caused very different genetic interpretations. Sorby (1857) thought that originally aragonitic oolitic rock had been replaced by iron ore after lithification. However, many observations favour a synsedimentary supply of iron followed by chemical and biochemical precipitation (Dahanayake & Krumbein 1986). This is supported by many modern submarine studies. Sturgeson *et al.* (2000) observed the formation of iron

ooids on the submerged flank of an island volcano in the Philippines, where local seawater is enriched with dissolved Fe-Al-Si and oxic ooids are formed. The source of the iron could not be determined; the authors think that submarine hydrothermal springs or ash falling into the sea, or leaching of recent lava flows, are equally probable alternatives. In recent marine sediments of the Niger delta, Porrenga (1967) described the presence of goethite pellets in the uppermost 10 m of sediment, underlain by 50 m of chamositic sediment.

The unlithified sediments at the origin of oolitic iron ore consisted of ooids, pisoids and peloids that originated by rolling on the seafloor. The matrix between these larger grains consists of detrital minerals, fossils, organic material and fine-grained iron-bearing kaolinitic clay (Mücke & Farshad 2005). Subsequent diagenesis, mostly under reducing conditions, caused by bacterial decomposition of organic matter, typically leads to transformation of kaolinite into chamosite (an iron-rich chlorite) and neoformation of pyrite and siderite. Finally, many deposits were upgraded by oxidation caused by meteoric seepage waters.

The source of iron in marine oolitic iron ores were probably lowlands experiencing intensive weathering in tropical climates, where humidity

and profuse plant growth produced wetlands discharging river water rich in dissolved organic matter. The Amazon River, for example, annually exports 70 Mt carbon to the sea. Such waters are acidic ($\text{pH} < 5$) and dissolve reduced iron (Fe^{2+}). Oxidized iron (Fe^{3+}) may be adsorbed to organic matter and clay (either in colloidal or particle size) suspended in the water. Transport of siliciclastic sediment in these rivers must have been very limited, because this would have diluted the iron. Mixing of river water with seawater ($\text{pH} > 7$) provokes immediate precipitation of iron oxy-hydroxides. Other possible iron sources that have been considered are coastal submarine groundwater springs (James 1966) and seawater flowing up from a deep CO_2 zone, where iron is soluble, into coastal waters where it will precipitate (Borchert 1960). Even hydrothermal sources rising from great depth have been invoked (Kimberley 1994).

Because of the availability of higher quality and inexpensive BIF ore, few oolitic iron ore deposits are exploited today. In contrast, genetically equivalent manganese ores occupy a central role in the world economy. Nearly one half of the primary manganese supply is produced from this type of deposit, mainly located in the Paratethys seaway of Eastern Europe and in northern Australia.

Oolitic manganese ore

Oolitic manganese ore occurs in seams within sediments of epicontinental seas, mainly associ-

ated with clay, marl and sand (rarely carbonates). The largest province of these ores is the South Ukrainian basin of Eocene-Oligocene age, with many mines around Nikopol. In this region, the sedimentary succession is transgressive, starting with palaeosol developed on Precambrian crystalline rocks, covered by coal-bearing limnic sediments and finally glauconite-rich sands that announce the sea. The manganese horizon occurs within clastic marine sediments (Varentsov and Muzylev 2001, Figure 1.69):

The manganese seam of Nikopol reaches a thickness of 4.5 m and an extension along strike of 250 km. A marginal facies of ooids, concretions and earthy masses of manganese oxy-hydroxides (pyrolusite and psilomelane) gives way to a carbonate facies of rhodochrosite and manganocalcite at deeper basinal levels and finally to bluish-green clay with Mn concretions. Sedimentary manganese deposits elsewhere display a similar zonation, for example those of Cretaceous age on Groote Eylandt, Australia (Bolton *et al.* 1990). Note that the Australian ores have a complicated history, with sedimentary features overprinted by diagenesis and later supergene, lateritic alteration.

Similar to ironstone and oolitic iron ore, the metal source for oolitic manganese deposits may have been continental weathering (Frakes & Bolton 1992) or ocean-floor hydrothermal venting (Maynard 2010). In principle, manganiferous particles may flocculate and form an enriched bed,

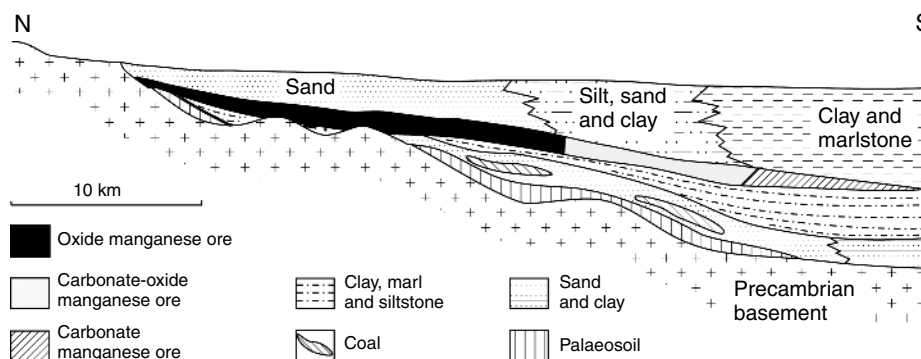
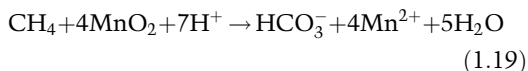


Figure 1.69 Generalized section of facies zones in the Eocene-Oligocene marine-sedimentary manganese horizon in southern Ukraine (adapted from Varentsov & Muzylev 2001).

but a more convoluted path to enrichment is assumed: When the particles settle into the reduced lower section of a restricted sea, they are dissolved, either abiotically or supposedly more often, by microbial anaerobic methane oxidation (Beal *et al.* 2009; eq. 1.18).

Reduction and dissolution of manganese by microbial methane oxidation:



This process leads to enrichment of anoxic deep water with dissolved manganese (Mn^{2+}) while iron and other easily reduced metals are precipitated by hydrogen sulphide. Interaction of the Mn-enriched deep water with oxygen-rich marginal zones induces precipitation of Mn oxides, especially during transgressive phases (Roy 1992). This situation is demonstrated by the recent Black Sea with its high $\text{Mn}^{2+}/\text{Fe}^{2+}$ ratio of deep, highly reduced euxinic water and MnO_2 precipitation in shallow mixing zones with oxic surface water (Force & Maynard 1991). A second viable path to Mn-enrichment is the oxygen minimum zone (OMZ) model; an OMZ develops below high productivity seas but deep ocean water underneath is oxic, not euxinic. Upwelling OMZ water precipitates Mn

(and P: Maynard 2010). Plate tectonics, basin configuration and climate cycles control ocean redox conditions favourable for manganese precipitation (Frakes & Bolton 1992).

Manganese nodules

Manganese nodules (Figure 1.70) occur over wide expanses of deep seafloor below the carbonate compensation depth (CCD). In these areas, pelagic sediment (mainly radiolarian ooze) accumulates at a very small rate. In shape and size, the Mn nodules are compared to potatoes but, of course, smaller and larger specimens do occur. Cobaltiferous manganese crusts cover submarine rock outcrops of mid-ocean ridges and of oceanic intraplate volcanoes. Proximity to submarine hydrothermal fields is not essential, although these are surrounded by Mn-rich sediments (e.g. manganese mud mounds of low-temperature exhalations near the Galapagos Islands, the manganese umbers (brown earthy pigments) and Mn-SiO₂ exhalites of many ophiolites).

Economically prospective manganese nodule fields include the Clarion-Clipperton-Zone in the Pacific, the Peru Basin and the central part of the Indian Ocean. Nodules contain ~29 wt.% Mn, 5% iron, 1.2% copper, 1.37% nickel, 1.2% cobalt and 15% SiO₂ (Lenoble 1996). Minor contents of other

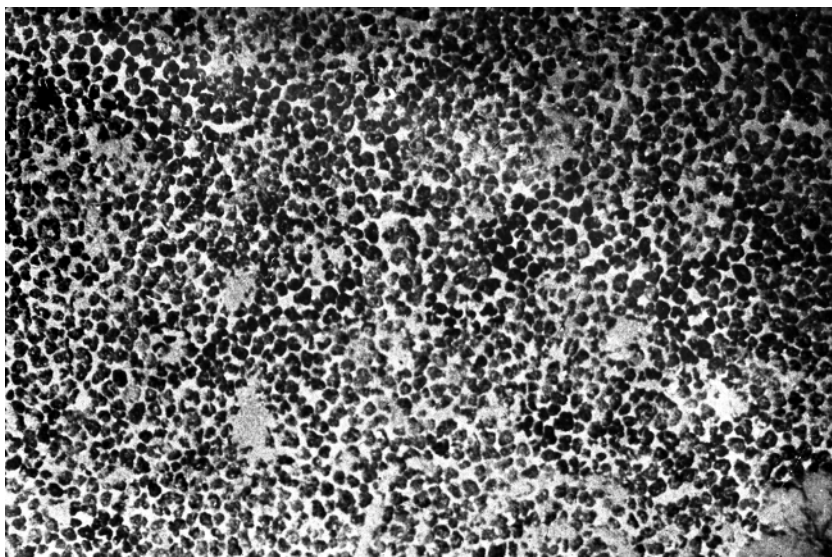


Figure 1.70 Seafloor aspect of polymetallic manganese nodules in the Clarion-Clipperton-Zone (CCZ) of the Central Pacific. The density is here about 20 kg/m². Individual nodules have diameters of 3 to 5 cm, the matrix is radiolarian ooze. Courtesy P. Halbach (FU Berlin).

metals including platinum are potentially recoverable. Mn nodules have a botryoidal or smooth surface and consist of concentric shells of amorphous and crystalline manganese and iron oxides. Formation of the nodules is partly by *in-situ* precipitation from pore fluids ("diagenetic") and partly by attachment of colloidal particles or dissolved matter from seawater ("hydrogenetic"; Hein *et al.* 2005). In both cases, microbial intervention may be essential. Manganese crusts grow mainly by hydrogenetic processes. Nodules and crusts have remarkable contents of valuable metals. The source of these metals are most likely hydrothermal exhalations at mid-ocean ridges, but submarine weathering of Hess Crust serpentinites, extraterrestrial dust and input from land to the oceans may contribute part of the endowment.

1.3.4 Sediment-hosted, submarine-exhalative (sedex) base metal deposits

Sediment-hosted sulphide deposits formed by hydrothermal outpouring on the seafloor compete with porphyry deposits for the role of the largest base metal accumulations on Earth. Clearly, systems forming these ores must be both of large scale and geologically common. Earlier, we have noted that hydrothermal-sedimentary sulphide ores

occur in a continuum from: i) a proximal position to submarine volcanoes; to ii) more distal positions where only sparse ash layers in the sedimentary column point to synchronous volcanism; and iii) to purely sedimentary settings. Only the cases ii) and iii) are referred to as sedimentary-exhalative or short, sedex type ore deposits. The first are volcanogenic (cf. Section 1.1).

Distal to volcanism are the locations of Early Proterozoic HYC-McArthur River, Australia and of the Devonian Rammelsberg deposit in Germany (Large & Walcher 1999). Some of the giant Mississippian Zn-Pb-Ag deposits of the Red Dog district, Alaska, are close to igneous rocks but genetically unrelated (see below). Mesoproterozoic Sullivan, BC, Canada, was earlier thought to be purely sedimentary without any magmatic influence ("Sullivan type sulphide deposits"). The choice was not opportune, however, because deep magmatic bodies may have controlled ore formation at Sullivan and the discussion appears to be still open (Slack *et al.* 1998). Hardly any traces of volcanism occur near the Pb-Zn-Ag orebodies within Palaeoproterozoic carbonatic-evaporitic black shales of Mt Isa, Australia, and in the Early Carboniferous carbonate host rocks of Irish deposits.

Sedimentological investigations indicate that the sulphides were deposited in a geologically very short time. The clastic sedimentation rate in the host basins was certainly not exceptionally low,

BOX 1.10 Submarine-exhalative (sedex) base metal deposits

The term sedex implies syngenetic origin of ore and host rocks. Because this cannot always be clearly established, "clastic-dominated lead-zinc ore" was instead proposed by Leach *et al.* (2010). The characteristic setting of these deposits is submarine rifting within epicontinental seas. Orebodies are typically related to faults, synsedimentary tectonic activity and the formation of local subbasins. Pluriphase extensional strain, reefs, sediment-starved restricted basins and distal volcanic centres may be part of the environment (Figure 1.71). Many hydrothermal-sedimentary sulphide ore deposits are close to or enclosed in black shales indicating a state of partial (dysoxia) or severe oxygen depletion (hypoxia to anoxia) of bottom waters. The correlation may be caused by incidental outpouring into a euxinic environment (i.e. anoxic, highly reduced, H₂S stable), or by "poisoning" of a marine sub-basin by profuse amounts of hydrothermal metalliferous fluids. Some sedex ore deposits are hosted by carbonatic silt- and claystones. Cherts are often part of the host sediments.

Sedex orebodies are stratiform and stratabound, and consist of massive, laminated or banded sulphides (Figure 1.72), with varying admixture of clastic matter, barite and other exhalites (SiO₂, haematite, etc.). In appearance they are very similar to volcanic-hydrothermal exhalative (VMS) orebodies; the decisive difference is the sedimentary as opposed to the volcanic genetic setting. Whereas the first are principally controlled by volcanic point heat sources, sedex ore is commonly localized by extensional faults (e.g. basinal growth faults). Single ore beds are either monomineralic or simple

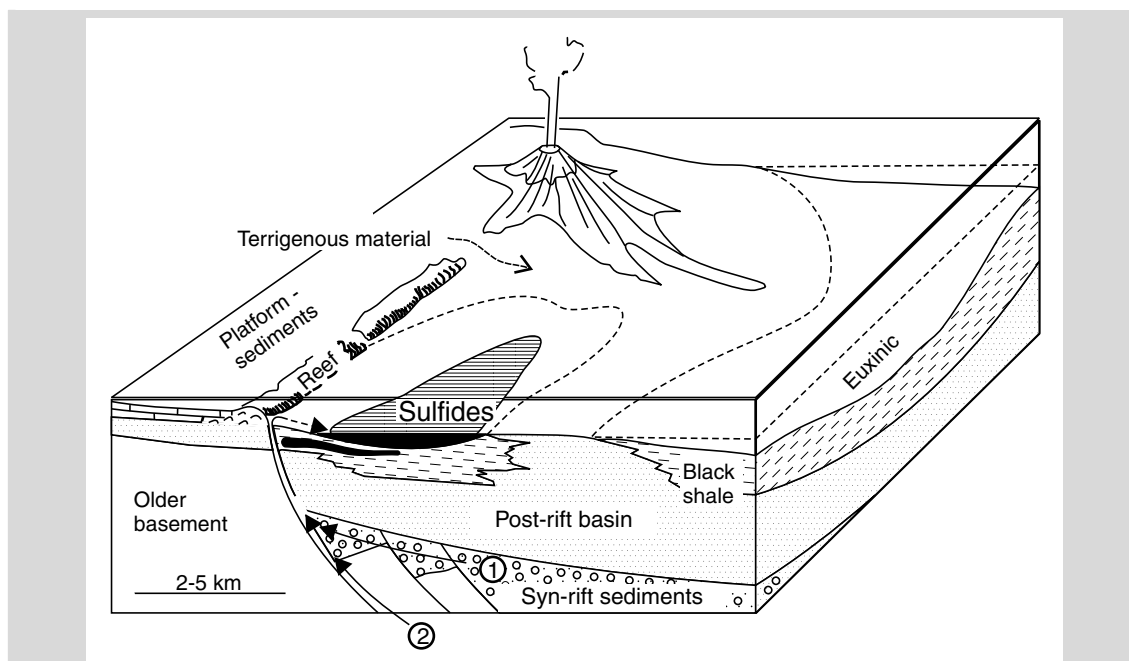


Figure 1.71 Schematic sketch of the geological setting of an exhalative-sedimentary (sedex) sulphide (-barite) ore deposit in a black shale basin. Note distal rift-related basaltic and felsic volcanic centres.

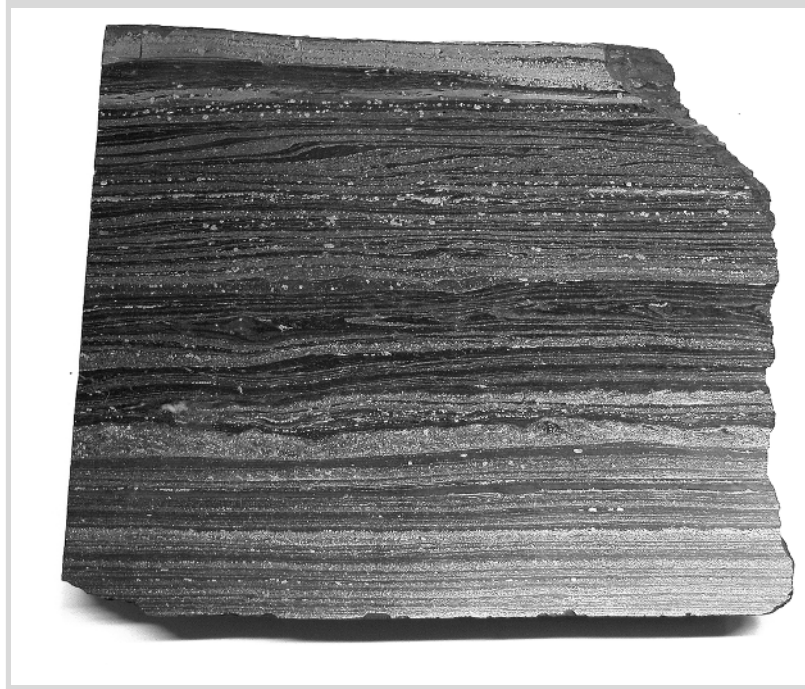


Figure 1.72 (Plate 1.72) Undeformed shale-banded copper-zinc dominated sulphide ore from Rammelsberg sedex deposit (Germany) displays ductile soft-sediment deformation and cross-lamination. Width of image ~20 cm. Courtesy B. Lehmann, Clausthal.

mixtures of galena, sphalerite, pyrite and pyrrhotite, rarely including more than traces of arsenopyrite and copper sulphides. Beds display sharp boundaries with each other, whereas in the same bed, lateral facies changes include decreasing metal grades and often, a metal zonation (e.g. copper in the centre, surrounded by annular zones of Pb, Zn, Ba and Mn). Elevated pyrite contents and geochemical manganese enrichment are found in a wide perimeter of the deposit. Initial ore precipitates were extremely fine-grained ($<5\ \mu\text{m}$), often with colloidal organo-metallic phases. Coarser grain size required for economic ore processing is a consequence of diagenesis, orogenic deformation and metamorphism. The unmetamorphosed Palaeoproterozoic HYC deposit, McArthur River district in northern Australia, provides an interesting case history. First reported in 1880, the high-grade but very fine-grained mineralization was technically not exploitable. Serious exploration was only done 80 years later (Logan *et al.* 1990). Total resources of $\sim 125\ \text{Mt}$ of ore with 13% Zn and 6% Pb were defined. Again, 30 years later in 1992, a mine was established. New milling and metallurgical methods allow profitable exploitation of reserves comprising 27 Mt at 14% Zn, 6.2% Pb and 63 g/t Ag.

Structures and textures of sedex ores confirm the syngenetic formation by fluids emanating from the seafloor. They include fine lamination, graded bedding, the frequent presence of framboidal pyrite, colloform banding, soft sediment deformation and mass transfer by submarine mudflows (as at HYC: Ireland *et al.* 2004). Fossil hydrothermal vents resembling those of black smokers were found at Silvermines and Tynagh in Ireland providing further proof for exhalative processes. Below the soft sediment surface, early diagenetic replacement and zone refining may take place simultaneously, as at HYC (Ireland *et al.* 2004) and the Red Dog district (Kelley & Jennings 2004). This leaves features of epigenesis that must be weighed against arguments for syngenes and interpretations may differ as at HYC (Symons 2007). Hydrothermal alteration is only visible where footwall rocks with advection flow paths are exposed (e.g. the “Kniest” at Rammelsberg, Germany, or vein breccias below the Red Dog orebodies, Figure 1.73). If subjacent flow channels cannot be found, heavy hot metalliferous brines may have flowed from elevated outflow points into nearby depressions on the seafloor (Sangster 2002).

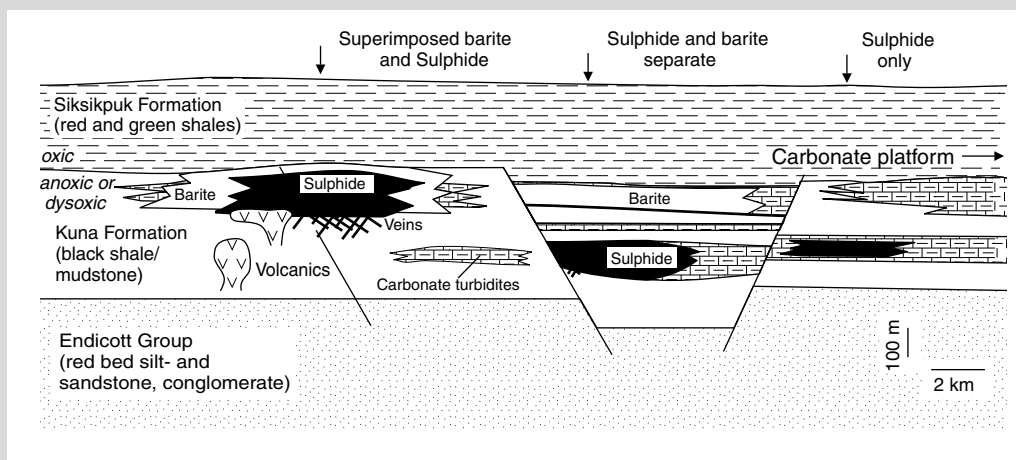


Figure 1.73 Horst-and-graben architecture of the Late Mississippian Brooks Range Basin, Alaska, hosting the giant Red Dog Zn-Pb-Ge-Ag massive sulphide (and barite) sedex deposits. Modified from Kelley, K.D. & Jennings, S. 2004, Society of Economic Geologists, Inc., *Economic Geology* Vol. 99, Figure 4 p. 1270.

but the sulphide deposition rate was very high. Only this allowed the formation of massive sulphide rocks that are common in this environment.

The source of metals in sedex ore deposits is sought in either the sedimentary basinal rocks (diagenetic) or in the basement underneath (retrograde-metamorphic). Different ratios of

Pb-Zn-Cu in mining districts indicate varying lithochemical source material, but also different processes or conditions of metal leaching. Lead isotope data may help to identify the source rocks of metals. Fluids involved in ore formation include:

- deeply convecting seawater and evaporitic brine;
- occluded formation fluids (Slack *et al.* 1998);

- diagenetic water of basinal sediments; and
- fluids mobilized from a deep source (e.g. elevated heatflow from the mantle).

Rising mantle fluids were invoked for giant Broken Hill, Australia by Plimer (1985). Most sedex deposits were generated by migrating formation fluids and seawater or brine fed into convection cells. Convection cells may reach many kilometres downward below the floor of a basin. The metalliferous fluids are either oxidized (SO_4 -rich) or reduced (H_2S -rich), depending on the nature of the basin fill. Oxidized, neutral or weakly acidic fluids originate in sediments that are dominated by carbonates, evaporites and haematitic sandstones (e.g. McArthur River, Red Dog), whereas dark shale and sandstone produce reduced and acidic fluids (Rammelsberg, Cooke *et al.* 2000).

The geodynamic environment of submarine, hydrothermal sediment-hosted sulphide deposits is different from Kuroko and Cyprus types, which form near plate boundaries. Sedex deposits occur typically at within-plate locations, such as sedimentary epicontinental shelf regions grading into passive continental margins. This environment combines tensional tectonics and crustal thinning with high heat flow and thermal basin subsidence that all favour fluid convection (Betts *et al.* 2003). The giant Alaskan Red Dog sedex deposits with approximately 40 Mt of contained lead and zinc illustrate these observations (Figure 1.73). The Kuna formation hosting the orebodies is intruded by igneous rocks including mafic sills and rhyolite plugs. Yet, the source of the hydrothermal ore-forming fluids was not magmatic, but brine from evaporating seawater. Sources of the metals were probably fluvial-deltaic red beds of the subjacent Endicott group (Kelley & Jennings 2004).

Because sedex ore deposits are geologically common, both in space and time, numerous members of the group were metamorphosed. Low-grade metamorphism is the most frequent state found (Red Dog, Mt. Isa). Very high-grade metamorphic deposits such as Gamsberg, South Africa (amphibolite facies) and Broken Hill, Australia (granulite facies) are of special scientific interest (cf. Section 1.5 "Metamorphic and Metamorphosed Ore Deposits"). Often, metamorphosed ore displays signs of local mobilization (e.g. cross-cutting

coarsely crystalline sulphide veins). In the past, observations of this kind have occasionally caused erroneous epigenetic interpretations of sedex ore formation.

1.4 DIAGENETIC ORE FORMATION SYSTEMS

Diagenesis is "the sum of all chemical, physical and biologic changes undergone by sediment after its initial deposition, and during and after its lithification, exclusive of surficial alteration (weathering) and metamorphism" (Neuendorf *et al.* 2005). The role of diagenesis in the formation of petroleum and natural gas deposits has been known for a long time. Metallogenesis by diagenetic processes was suspected, but decisive evidence could only be assembled in more recent times. Examples of ore deposit types that illustrate the diagenetic realm include the European Copper Shale, many deposits of the Central African Copper-Cobalt Belt, Mississippi Valley type lead-zinc (barite-fluorite-celestite) deposits, and orebodies that originate from brines derived by interaction with salt rocks (e.g. lead-zinc and siderite in Northern Africa). Note that brine *sensu stricto* is defined by a salt content of more than 10% (Table 1.5). Saturation of NaCl in water is reached at a concentration of 26.4% (25°C).

The salinity, or more precisely, the total dissolved solids concentration (TDS) of brines is measured and expressed in two different forms, ppm (g/t) or mg/L (eq. 1.20). In oceanography, "practical salinity units" (psu) are used, which

Table 1.5 What exactly is a brine? Terms for water with different salinities (Davies & DeWiest 1966)

Term	Concentration of total dissolved solids (TDS) in ppm (parts per million) and weight percent	
Fresh water	0–1000	<0.1%
Brackish water	1000–10,000	<1%
Seawater	31,000–38,000	3.1–3.8%
Saline, or salty water	10,000–100,000	<10%
Brine	>100,000	>10%

represent the conductivity ratio of a seawater sample relative to a standard KCl solution.

Contents of total dissolved solids in water and brine:

$$\begin{aligned} &\text{ppm (parts TDS per million TDS+H}_2\text{O)} \\ &\text{mg/L (milligrams per litre)} \\ &= \text{ppm/density (mg/cm}^3\text{)} \end{aligned} \quad (1.20)$$

In order to determine the origin of salinity in basinal brines, formation water and hydrothermal fluids, mole ratios of halogens and electrolytes are measured (Botrell *et al.* 1988). Because of its conservative behaviour and small coefficient of partitioning from brine into halite, bromine (Br) is an ideal discriminator between two main solute sources: i) subaerial evaporation of seawater; or ii) dissolution of evaporite salts (mainly halite). Seawater has a characteristic Cl/Br molar ratio of ~655. When seawater evaporates and deposits halite, Br content relative to Cl and Na of the residual brine dramatically increases along the "seawater evaporation path". Consequently, precipitated halite contains little Br (Cl/Br >655, Hermann 1980, Holser 1979). Thus, the congruent dissolution of halite results in high Cl/Br and Na/Br molar ratios and Na/Cl of ~1, very different from the seawater evaporation array. Brines resulting from seawater evaporation have Cl/Br molar ratios distinctly <655. Although halogen ratios appear to be quite conservative (Nahnybida *et al.* 2009), several processes do induce changes, for example leaching of bromine from organic matter (Collins 1975). As a highly organophilic element, iodine (I) is strongly enriched by organisms and an elevated I/Cl ratio is a useful indicator of the passage of solutions through organic-rich sediments (Kendrick *et al.* 2001).

The core of a diagenetic ore formation model is the argument that most sediment includes a large mass of water at the time of deposition ("connate water"). During diagenesis, most of this initial water is expelled by mechanical compaction, with a minor contribution by chemical liberation. When newly deposited, sand may contain 40 vol. % of water, clay 90%, and carbonates ~50%. By diagenesis, the pore space occupied by water is reduced to <1 vol. % at pressures and temperatures approaching the transition to metamorphism. Obviously, all this water must leave the system

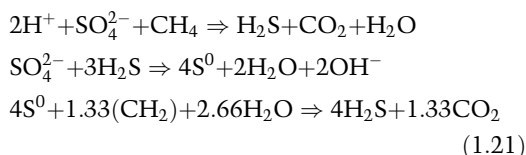
by flowing upwards and to the margin of sedimentary basins. Drilling for hydrocarbons revealed that water in sediments frequently attains temperatures of more than 100°C and reaches a maximum of about 300°C. By reacting with rocks, the "formation water" acquires a high content of dissolved matter. Where large masses of such fluids pass through geochemical or physical "traps", minerals may be precipitated which concentrate useful elements. Ore deposits that are formed as a result of these processes are hydrothermal and epigenetic.

Stable isotope data prove that part of the water in sediments can have a meteoric origin (precipitation infiltrating basin aquifers), but most is initially occluded seawater. Both the rocks and the pore water chemistry change as diagenesis progresses ("diagenesis of formation water"). Typical formation waters are brines (Table 1.5) dominated by Na-Ca-Cl and with elevated traces of HCO₃, K, I and Br. Compared with seawater, iron, manganese, copper, zinc and many other elements are enriched. Magnesium and sulphate are depleted; the first by neogenesis of dolomite and chlorite, the second by bacterial (eqs 1.15 and 1.16) or thermochemical sulphate reduction to H₂S. In the geological past, however, seawater composition was not constant (cf. Chapter 4.2.2 "Seawater in the Geological Past"). In the Early Palaeozoic, the Jurassic and the Cretaceous, seawater had low concentrations of magnesium and sulphate. Therefore, some basinal brines were dominated by Na-Ca-Cl already at the time of occlusion (Lowenstein *et al.* 2003).

Recently, the presence of **live microbes** was substantiated to a depth of several kilometres below the surface and to temperatures of ~140°C (Schippers *et al.* 2005). Microbes convert organic matter to CH₄ (and CO₂) and produce the methane of biogenic gas deposits. In the near-surface realm of early diagenesis, methanogenesis and sediment dewatering combine to cause methane-rich cold seeps that are sites of submarine barite deposit formation (Torres *et al.* 2003). Many microbes have a role in diagenesis. *Geobacter metallireducens*, for example, catalyses Fe(III) reduction and decomposition of organic substance to CO₂ (Childers *et al.* 2002). In the absence of microbes,

for example at higher temperature ($>80^{\circ}\text{C}$: Thom & Anderson 2008) and greater depth, abiotic sulphate reduction based on destruction of organic matter (here represented by CH_4 and CH_2) is possible (eq. 1.21).

Thermochemical sulphate reduction (TSR):



By disintegrating anhydrite, this process can cause a relative enrichment of CaCl_2 in the fluids. NaCl may be retained and concentrated by clay beds acting as a semi-permeable membrane. Probably more often, NaCl brines originate by evaporation at the surface or by dissolution of salt rocks in the basinal sediments. Mature, commonly deep formation waters are mostly concentrated NaCl brines. Maturation and decomposition of organic matter in sediments results in dissolved CH_4 , CO_2 , H_2 , N_2 and higher hydrocarbons (e.g. petroleum). Oxygen induced by infiltrating seawater and meteoric water, and oxygen produced by disproportionation of formation waters is quickly consumed by oxidation of Fe(II) or of organic matter. Therefore, most formation waters display a low redox state, favouring high solubility of many metals. In solution, some metals may occur in the form of organo-metallic complexes (Ni , V , part of Zn and Cu), while others such as Pb , Fe and most Cu and Zn are dissolved as simple ions. The important metallogenetic role of basinal NaCl -brines extends into the realms of metamorphism and even to magmatic ore formation (e.g. iron oxide Cu-Au deposits: Barton & Johnson 1996).

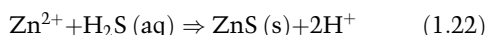
Not all basinal fluids are reduced, and oxidized formation waters are commonly enriched in SO_4 . This is possible when the source rocks include predominantly haematitic sandstone and mudrock, limestone, anhydrite and halite, for example in the Rotliegend (Permian) desert and salt lake sediments of Northern Germany. Oxidized fluids are able to dissolve Cu , Pb and Zn , to transport the metals over wide distances and to precipitate ore at

suitable traps such as redox fronts established by organic-rich shale (e.g. the European Copper Shale). Barium and iron, in contrast, are insoluble in oxidized fluids and are not part of the resulting ore paragenesis.

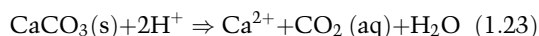
Metal uptake in the source region (reaction zone) or along flow paths is a function of kinetic and thermodynamic factors, including rock and water chemistry, T , P , Eh and pH . In contact with formation waters, several common minerals are unstable, including amphibole, pyroxene, olivine and epidote. Their alteration releases trace metals into the aqueous phase. Other mechanisms of liberating metals include ion exchange with clay minerals and simple diagenetic transformation of clays. An example is lead that is often adsorbed on kaolinite, but is released into solution when illite replaces kaolinite.

The flow paths of expelled deep fluids are determined by hydrogeological parameters such as permeable rock units, tectonic disaggregation and the general pressure gradient. Petroleum and gas deposits in crystalline and magmatic rocks clearly demonstrate that diagenetic flow may encompass basement underlying basins. The norm is probably a slowly moving, diffuse compaction flow that loses its dissolved matter by forming pore-cement in sediments or by discharge into seawater. Ore formation will only occur where a large mass of hot brine is focused into preferential flow paths, which may be envisaged as streams within permeable rocks or tectonic structures. In these channels, a rapid drop of temperature or pressure, reaction with host rocks, and mixing with chemically different water may precipitate solutes in a small rock volume. Because of their high permeability, near-surface faults, reefs or karst cavities at the margins of sedimentary basins or basement islands often locate ore deposit formation. Note that traps of diagenetic ore deposits are quite the reverse of petroleum and gas deposits; the first are open flow systems with hydrostatic pressure, whereas the second are closed and often overpressured. The origin of secondary porosity and of caves in carbonate rocks may be caused by metal sulphide precipitation, which produces hydrogen ions (eq. 1.22) that maintain limestone dissolution (eq. 1.23).

Precipitation of metal sulphides by reaction with H_2S :



Dissolution of calcite:



Intracratonic basinal hydrothermal flow systems

There are many variations to the theme of intracratonic basinal hydrothermal flow systems. Some of the more frequent geological driving agents of basin dewatering and fluid migration are the following:

- standard diagenetic dewatering by compaction of pore space (consolidation: Terzaghi *et al.* 1996, Noble 1963), in a slowly progressive process, mainly caused by continuing sedimentation and subsidence in the basin;
- episodic expulsion of brine by increasing overpressure in sand lenses that are enveloped by clay beds of low permeability (Fowler & Anderson 1991); this can be observed as mud-eruptions in the Mississippi delta, although without leading to mineral deposit formation;
- displacement of deep, hot and therefore relatively light brines by cold, heavy groundwater infiltrating from topographically elevated basin margins; this hypothesis assumes that permeable rocks or active extensional faults provide linked-up flow paths (Daubrée 1887);
- tectonic expulsion of formation fluids by a moving nappe pile, causing flow of diagenetic and metamorphic fluids towards the foreland, where transported heat and dissolved matter result in mineral deposit formation (Oliver

1986, Figure 1.74); a present-day analogue are methane-rich hot fluids ejected from the accretion wedge at many subduction fronts;

- fluid overpressures can also be induced by pulses of hydrocarbon generation caused by a rapid thickness increase of cover sediments and consequently of rock temperature; or by a rapid fall of sea levels (Eisenlohr *et al.* 1994);
- Expulsion of formation waters by deep heatflow (e.g. cryptic intrusions, underplating) imposing a wide halo of higher-grade diagenesis; this may trigger submarine venting of fluids resulting in synsedimentary sedex type deposits (Figure 1.71) or of epigenetic ore.

Several of these hypotheses have been tested by Oliver *et al.* (2006), who showed that tectonic extension alone is insufficient for inducing fluid upflow and the main drive is a favourable thermal field. The precise causes, timing and mode of fluid generation and flow in sedimentary basins are a long-standing subject of applied research in the oil and gas industry. Concepts and approaches similar to modelling petroleum systems (Magoon & Dow 1994) considerably advance investigations concerning diagenetic ore formation.

Many diagenetic mineral deposits display strikingly banded textures of newly-formed precipitates that have been called “diagenetic crystallization rhythmities” (DCR) or “zebra textures”. The thickness of the bands varies between millimetres and decimetres. They occur in dolomite, evaporite, in sparry magnesite, in siderite and most typically, in stratabound Pb-Zn-Ba-F deposits hosted by platform carbonates. Their formation is attributed to coupling of

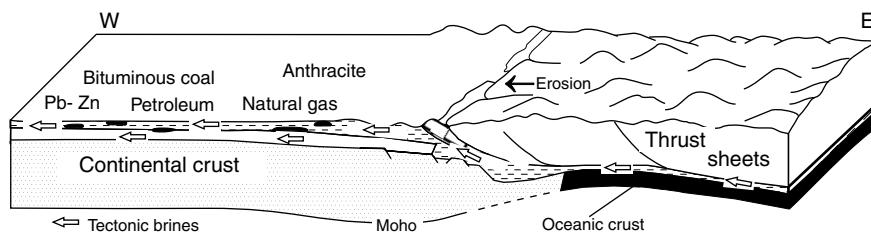


Figure 1.74 Expulsion of fluids (“tectonic brines”) towards the foreland from underneath the west-moving nappe pile of the Appalachian Mountain Belt (modified from Oliver 1986).

diffusion with precipitation reactions (Kapral & Showater 1995).

1.4.1 The European Copper Shale

Diagenetic mineral deposits may display properties that resemble synsedimentary features and in a number of cases, only persistent investigations revealed an epigenetic origin from diagenetic solutions. The ambivalence is clearly illuminated by the research history of the European Copper Shale (in German: Kupferschiefer).

In the Central European Permian rift basin, the Copper Shale is a thin stratum that forms the base of the post-Variscan transgressive marine sedi-

ments (consult Chapter 4.2.2, “The Zechstein Salt Formation in Northern Europe”). Copper shale is known over an area of more than 600,000 km². Basinal Copper Shale intersected in hydrocarbon drillholes displays very low base metal values (Pašava *et al.* 2010). Exploitable metal grades are restricted to southern basin margins (in Germany the Harz District with Mansfeld and Sangerhausen; Silesia in Poland). The Copper Shale of the mining districts is a euxinic sediment deposited in a shallow sea of only a few hundred metres water depth. Ubiquitous fossils of fish and brachiopods indicate that the upper water column was well aerated, whereas deep water was poisoned with H₂S. Continent-derived clastic sediment import was very

BOX 1.11 Copper Shale mineralization

Petrographically, the Copper Shale is a black laminated marly claystone formed from illite, montmorillonite, dolomite, less than 30% organic matter (kerogens include bituminite, vitrinite, fusinite and liptinite: Koch 1997), sulphides, anhydrite or gypsum, phosphates and little quartz. Its footwall is mostly Rotliegend (literally “red footwall” in German) sand or conglomerate, but in some marginal exposures Copper Shale rests directly on folded Variscan basement. The time when Rotliegend sediments experienced reddening (Fe²⁺ oxidized to haematite) is a critical point for a detailed understanding of copper ore introduction (Brown 2009). One obvious possibility is that iron oxide (desert varnish) originally coated the sand grains; palaeomagnetic and illite ages seem to support this assumption (Nawrocki 2000). Hanging wall rocks are lowermost Zechstein carbonates overlain by anhydrite and salt rock. In the North Sea and central Polish basins, the Copper Shale is downwarped to more than 7000 metres below surface. The Copper Shale is not folded but dissected by faults. Fissures and fault intersections are notably mineralized. The bulk of the extracted ore, however, is from stratiform bodies.

As a result of basin palaeomorphology, the Copper Shale horizon occurs in different sedimentary facies: In marginal sub-basins it is quite thin (0.3–0.4 m), rich in Fe, Al₂O₃ and organic substance. Contents of carbonates and quartz as well as thickness increase where shale approaches sills and sand bars. Sills are not mineralized and strikingly red (because of haematite). Miners used to call this barren rock “Rote Fäule” (German for “red rot”). Rich chalcocite orebodies occur at reduction fronts adjacent to Rote Fäule (Figure 1.75; Rentzsch *et al.* 1997).

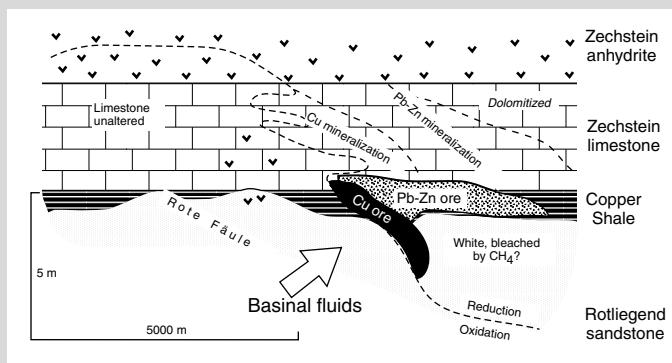


Figure 1.75 Schematic section of a Copper Shale deposit in Northern Germany and Poland (modified from Jowett 1992 with permission from Elsevier).

The sulphides in Copper Shale are of major interest, because they contain the valuable metals. Textural variations from early to late parageneses include (Wodzicki & Piestrzynski 1994):

- Very fine (0.02–0.06 mm), disseminated grains and aggregates, framboids (“mineralized bacteria”, Schneiderhöhn 1962) and crusts on organic particles; sulphides consist mainly of pyrite, with occasional traces of chalcopyrite, bornite, chalcocite and marcasite; copper concentrations of a few 100 ppm are considered to have a purely sedimentary origin.
- Spindles, lenses, concretions and thin lenticular bands of sulphides that are parallel to bedding planes; these features reflect diagenetic remobilization within the rock; copper concentrations reach 2000 ppm.
- The main mass of the sulphide ore paragenesis (with base metal contents reaching 3%) replaces rock forming minerals; ore samples may contain 90% chalcocite; microscopic veinlets of different spatial orientation appear in the ore; ore minerals include mainly silver-rich chalcocite, with some digenite, covellite, bornite, chalcopyrite, sphalerite, galena, pyrite and haematite.
- Where no shale is developed on sills, zones of anhydrite pore cementation finger down into bleached footwall sandstone; these zones are mantled by rich chalcocite ore replacing carbonate and clay minerals.
- Thin and cross-cutting veinlets of coarsely crystalline sulphides (bornite, chalcopyrite, tennantite, galena, sphalerite, Fe-Ni-Co sulphides and arsenides) with a gangue of barite, calcite and anhydrite are the latest phase of ore formation; they represent less than 1% of ore produced.

The metals Cu-Pb-Zn display a distinct zonation, both horizontally around oxidized sills and vertically from copper in sandstone and shale to lead and zinc in hanging wall carbonates that are dolomitized (Figure 1.75). However, some copper orebodies extend from bleached footwall sandstone through shale to hanging wall carbonate. Metal contents in exploited Copper Shale deposits in Poland are reported at 1.2–2.8% Cu and 30–80 g/t Ag. Thickness of stratiform orebodies varies from 1.2 to >20 m. Exploitation takes place underground between 600 and 1200 m below the surface. Metals produced include copper, lead, silver, nickel, gold (Piestrzynski *et al.* 2002), palladium, platinum, rhenium, selenium and sulphuric acid. Until 1970, when mining in the Mansfeld District in Germany was terminated, ~1.5 Mt copper had been produced. The nearby Sangerhausen mines were closed in 1990. Economic reserves in Poland are reported as 2.4 Gt of ore; 50% of this occurs in footwall sandstone, 20% in shale and 30% in limestone. The figures underline that a large mass of copper is concentrated within a very small area of the Copper Shale basin.

small and the fine lamination indicates extremely tranquil conditions in the bottom waters.

Genetic interpretations of Copper Shale ore formation have always been dominated by the controversy between syn- and epigenetic models. The difficulty was essentially to determine the time of metal concentration, during sedimentation, or later? Of course, diagenetic ore textures and veinlets were observed, but were they only caused by local remobilization of a metal stock imported earlier? Meanwhile, modern technologies have refined data to a level where epigenetic ore formation during late diagenesis is strongly supported. One of the few mappable characteristics of Copper Shale orebodies supporting epigenesis is their cross-cutting relations with the Copper Shale stratum. In Figure 1.75, this is emphasized by drastically different vertical and horizontal scales revealing the cross-cutting geometry and metal zoning. In underground exposures, Copper Shale orebodies appear to be perfectly stratiform. Epi-

genesis is also suggested by rings of high-grade ore surrounding red sandstone hills that protrude through the shale. This pattern can hardly be of syndimentary origin.

Elements of today's diagenetic model of Copper Shale ore formation include hot, oxidized (e.g. sulphate-bearing) Ca-Mg-K-Cl formation waters flowing up from deeply buried Permian molasse red bed sediments and volcanics where they acquired their metal contents (Oszczepalski 2000). Increasing compaction and the low permeability of Zechstein evaporites acting as a seal focused the flow towards basin margins where the metals were precipitated. Possible agents of precipitation include decreasing T and P, mixing with cool, alkaline, meteoric (or sea-) water and most importantly, reduction of fluids by contact with organic matter and sulphides of the shale (Wodzicki & Piestrzynski 1994), and methane in the sandstone (Jowett 1992). The metal zonation of Cu-Pb-Zn is consistent with

this model and conforms to the relative solubility of the sulphides (Figure 1.75). To a certain extent, the Copper Shale bed may have acted as a semi-permeable, reactive membrane. The question when exactly the epigenetic Copper Shale mineralization took place is still not satisfactorily answered (Pašava 2010). Evidence has been offered for early diagenetic, Permian (Wedepohl & Rentzsch 2006), to late diagenetic metal introduction during the Triassic (Nawrocki 2000). It appears unlikely that steady-state consolidation of sediments in the Zechstein basin was the driving force. More probable agents are large-scale events, such as the giant mantle plume (Marzoli *et al.* 1999) at ~200 Ma and Triassic-Jurassic rifting phases that punctuated the initial break-up of Pangaea.

Isotope geochemistry supports the diagenetic model of Copper Shale ore formation. Generally, mineralized Copper Shale is isotopically different both from ordinary shale and from red rot. ^{13}C in organic substance is clearly enriched, probably because light carbon was preferentially oxidized and expelled from the system. Sulphide sulphur with $\delta^{34}\text{S}$ between -40 and -25‰ implies bacterial reduction of seawater sulphate. Early pyrite contains the lightest, later sulphides heavier sulphur. This suggests: i) a closed system with a restricted mass of available sulphate; ii) later fluids with higher ^{34}S -contents (Jowett *et al.* 1991); or iii) late thermochemical sulphate reduction (Sun & Püttmann 1998). Oxygen and hydrogen investigations of clays resulted in confining the mineralizing fluids to $\delta^{18}\text{O}$ between 3 and 6‰, and δD from -10 to $+3\text{‰}$, at probable temperatures of 130°C (Bechtel & Hoernes 1993). These characteristics conform to properties of diagenetic formation waters (Figure 1.23).

The copper province of White Pine, Michigan, USA and the African Copper Belt of the Democratic Republic Congo and Zambia are comparable but not identical to the European Copper Shale (cf. Chapter 2.2 "Copper"). All three are included in the non-genetic term of "stratabound and/or stratiform sediment-hosted Cu deposits".

1.4.2 Diagenetic-hydrothermal carbonate-hosted Pb-Zn (F-Ba) deposits

Lead and zinc ore deposits hosted by marine carbonate rocks are a large and heterogeneous group.

Single deposits and districts display end member characteristics of syngenetic as opposed to epigenetic hydrothermal ore emplacement. The first are sedimentary-exhalative or volcanogenic (cf. Sections 1.1 and 1.3), whereas the second may have been formed by igneous, metamorphic and diagenetic process systems. In the following discussion, the subject is epigenetic deposits formed by essentially diagenetic fluids. Let us note here that passage of the fluids through igneous intercalations and deeper crystalline basement is not rare. Host rocks are not restricted to carbonates, but world-class deposits in siliciclastic sediments are rare compared to carbonate-hosted deposits (Chapter 2 "Lead and Zinc").

Several provinces or districts with a more homogeneous subset of traits are commonly designated as "types" for discussion. Well-studied types include the "Alpine" (Middle to Late Triassic in Austria-Italy-Slovenia, Figure 1.76), "Silesian" (Mid-Triassic in Poland), "Irish" (Early Carboniferous in Ireland) and "Mississippi Valley" (Pennsylvanian-Permian of the mid-continental USA). Similar deposits occur worldwide, for example in Australia, in several provinces of China and in Mexico. Here, we shall mainly refer to the Mississippi Valley type (MVT) province, because it hosts the most intensively investigated deposits.

The paragenesis of diagenetic-hydrothermal carbonate-hosted deposits is usually very simple, comprising galena and sphalerite, with a gangue of barite, fluorite, pyrite, marcasite, calcite, dolomite, aragonite, ankerite, siderite, quartz, colloform silica (chert) and occasionally, bitumen. Sphalerite appears mostly in colloform-banded texture (sphalerite-wurtzite banding). Low iron and elevated trace contents of cadmium are characteristic. Galena contains little silver. Copper contents are negligible and there are no copper ore deposits of this type. Often, a wide halo of dolomitization due to the passage of brines envelops the ore and many deposits occur at dolomitization fronts (Harper & Borrok 2007). Lead isotopic compositions of districts vary widely and include ordinary (Silesia, Pine Point, Canada) or anomalous lead (southeast Missouri: Goldhaber *et al.* 1995). Sulphur is in part quite heavy and in that case not

BOX 1.12 Mississippi Valley type Pb-Zn deposit characteristics

Large to giant MVT deposits contain 1–20 Mt combined zinc and lead, with an average Zn:Pb ratio of ~ 3 . Even within the type region, a considerable variance of ore-forming processes and modifying factors is observed. This results in variable proportions of metals and minerals in different districts of the Mississippi province. Generally, orebodies are stratiform or at least stratabound, and include tectonic or karst cavity breccias that were cemented by ore and gangue minerals; replacement bodies and cross-cutting veins are not rare (Leach *et al.* 2010). Some ores fill open cavities in carbonate and DCR textures are very common.



Figure 1.76 (Plate 1.76) Banded and breccia cave ore of brown sphalerite in the historic Lafatsch mine, Karwendel, Tyrol. This is one of the outliers of the Triassic Alpine type carbonate-hosted Pb-Zn deposits. Courtesy B. Lehmann, Clausthal.

World-scale lead deposits were discovered in 1955 in the Viburnum Trend, Missouri, USA. Together with the “Old Lead Belt” nearby, the Viburnum Trend forms a horseshoe-like belt around the Precambrian St Francois Mountains, which are surrounded by Palaeozoic sedimentary basins. During marine transgression in the Cambrian, the mountains were islands with surrounding algal reefs and lagoons, partly of evaporitic facies. The basement is overlain by quartzitic sandstone (Lamotte Sandstone), followed by the carbonatic Bonnetterre Formation and dolomites with shale beds.

Most orebodies occur in the Bonnetterre Formation within an offshore stromatolitic reef that separates a micritic-clayey basal facies from coastal oolites. Oolites also fill channels in the reef, form its hanging wall and detrital cones outside of the reef. In the oolitic calcite arenites, long tubular collapse channels are aligned parallel to the coast. Stratabound orebodies occur in these karst-like collapse structures and along faults (Figure 1.77). Both were channels of higher permeability that focused the solutions flowing up from the Lamotte aquifer where it thins out towards the coast.

Apart from galena, the Viburnum ore contains sphalerite, marcasite and rather untypically for MVT deposits, more than traces of chalcopyrite, bravoite and siegenite. Main gangue minerals are quartz and dolomite. Mineralization took place in cyclic pulses that were controlled by mixing of at least two fluids. A weak zoning of Cu-Pb-Zn is compatible with the assumed hydrothermal flow vector.

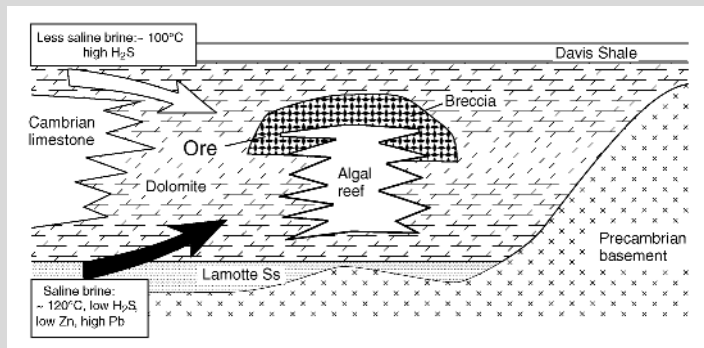


Figure 1.77 Simplified genetic model of the Pb-dominated deposits of Mississippi Valley Type (MVT) in the Viburnum Trend, Missouri. After Plumlee, G.S., Leach, D.L., Hofstra, A.H., Landis, G.P., Rowan, E.L. and Viets, J.G. 1994, Society of Economic Geologists, Inc., *Economic Geology* Vol. 89, Figure 18 (C) p. 1379.

Another important mining area in the MVT province was the Tri-State district, which straddles adjoining parts of the states of Oklahoma, Kansas and Missouri and covers an area exceeding 1200 km². This region hosts some MVT deposits, which are characterized by anomalous and highly radiogenic lead (cf Section 1.1 "Isotope Geochemistry"). From 1850 to 1965, Tri-State mines processed an estimated 500 million tonnes (Mt) of ore at a grade of ~3% Zn and 0.5% Pb. Today, the MVT province is past peak production but paradigmatic for environmental remediation of the mining heritage.

In the mid-western USA, different fluids were involved in MVT ore formation. Viburnum District fluids are marked by reactions in the basal sandstone aquifer, whereas Tri-State district fluids display properties of equilibration with marine clay and carbonate (Viets *et al.* 1992). From a southern source, magmatic fluids rich in fluorine were mixed into the diagenetic fluids (Rowan *et al.* 2002). Metal-bearing brines of Mississippi Valley type deposits display the following general characteristics (Roedder 1984, Kendrick *et al.* 2002):

- Salt concentrations above 15 and often >20 % and accordingly, the fluids are brines (Table 1.5); Br/Cl ratios indicate variable fractions of evaporated seawater and salinity derived from halite dissolution.
- General composition is Cl > Na > Ca ≫ K > Mg; dissolved salts are predominantly NaCl and CaCl₂; sulphur concentrations are low, metal contents reach several thousand ppm (Wilkinson *et al.* 2009).
- Brines are usually reduced and moderately acidic.
- Density is always >1 and often >1.1 g/cm³.
- Temperatures vary from ca. 80–200°C.
- Formation pressures were generally low but above vapour pressure; fluid inclusions evidence of subcritical boiling is hardly ever observed.
- CH₄ in gas bubbles and oil in unmixed droplets are both common, and dissolved hydrocarbons occur in the liquid part of fluid inclusions; often, the fluids are compared to oil field brines.

Precipitation of ore and gangue was probably induced by mixing with near-surface waters that contained reduced sulphur. Some of the latter originated by bacterial sulphate reduction and consumption of organic matter of the carbonate rocks (H₂S-fluids: Plumlee *et al.* 1994, 1995; Figure 1.77). Note the characteristic focusing of ascending fluids into permeable reef carbonates. Reduction may also have been induced by methane and petroleum generated in the heated wallrocks (Anderson 2008).

Rb/Sr ages of Upper Mississippi Valley district sphalerites fall to ~270 Ma (Mid-Permian), the time of Alleghenian/Ouachita orogenesis in the Appalachian Mountain Belt (Brannon *et al.* 1992). Crustal shortening in the east and westward nappe movement are thought to have intensified diagenesis in foreland basins, causing fluid liberation and migration (Figure 1.74).

biogenic but probably due to thermochemical sulphate reduction (TSR, eq. 1.21). As a function of time, strontium isotope ratios of gangue carbonates display higher concentrations of radiogenic ⁸⁷Sr. This is probably due to an increasing share of strontium derived from clays and other silicates of basinal sediments while diagenesis progresses (Brannon *et al.* 1991).

Diagenetic-hydrothermal carbonate-hosted Pb-Zn (F-Ba) deposits are common in most of the world's marine carbonate platform sequences of Phanerozoic age. This is evidence that the specific metallogenetic process systems leading to this mineralization class are integral to basinal evolution. Although orogenic foreland basins, such as the MVT province, are favourable geodynamic

settings, relations to orogeny are not general. Other type regions are related to submarine shelf rifting, to large-scale lithospheric flexure, or to enhanced heat flow and elevated permeability of the crust induced by major plate reorganizations (such as the break-up of Pangaea in Western Europe).

1.4.3 Diagenetic-hydrothermal ore formation related to salt diapirs

In the preceding discussion of diagenetic ore formation, the role of oxidized saline fluids in Copper Shale mineralization and of reduced brines in MVT lead-zinc deposits, were discussed. Also, giant high-grade haematite orebodies derived from BIF were preconcentrated by basinal brines, although the last transformation to economic ore is due to supergene enrichment (Figure 1.52, Thorne *et al.* 2004, 2009). Basinal brines and salt rocks, which are assimilated by magmatic intrusions and consequently leach metals from pervaded rocks, may be the key for understanding the iron oxide-copper-gold class of deposits (Cox & Singer 2007). Of course, the essentially magmatic-hydrothermal IOCG class can hardly be considered as part of the diagenetic process system. In this chapter, brines formed by dissolution and/or dehydration of salt-rich evaporites within basinal sediments shall be singled out for their specific origin.

Most sedimentary basins contain common evaporitic rocks such as anhydrite and rock salt. Dehydration water from evaporites and formation water in contact with these rocks must acquire the character of a saline brine (Table 1.5, eq. 1.20). Other sources of brines in sedimentary basins include evaporated seawater, terrestrial saline lakes and mature formation water. The source of salinity is discerned by determination of halogen and electrolyte ratios (Botrell *et al.* 1988).

Metallogenic action of brines is especially obvious when salt and epigenetic hydrothermal ore deposits are closely related, in space and time. The best sites for studying this relationship are salt diapir related ore deposits. Salt structures induce peculiar geochemical, hydraulic and thermal conditions in their host sediments (Rouvier *et al.* 1985, Kyle & Price 1986, Pohl *et al.* 1986).

Deposits of petroleum and native sulphur in salt diapir cap rocks resulting from the passage of basinal hydrocarbon fluids are known for more than 100 years. However, in addition to oil, some salt diapirs are intimately related to ore deposits (Pb, Ag, Zn and Fe in North Africa), and to non-metallic mineral deposits (barite, fluorite, strontianite; emerald in Colombia).

The southern foreland of the Atlas Orogen in Tunisia and Algeria is underlain by a basin with thick Mesozoic sediments. The package starts with ~1000 m of Triassic evaporites that resemble the Haselgebirge of the Eastern Alps (a melange of salt, anhydrite, clay, dolomite and basalt: cf. Chapter 4.2). Very high subsidence in the Cretaceous reached a total of 8000 m and initiated syn-sedimentary diapirism that continued into the Eocene, when orogenic folding encompassed the basin. Several large metasomatic siderite and numerous small lead-silver-zinc deposits are found in Triassic cap rocks and in Early Cretaceous limestones where these are in contact with apical parts of the diapirs:

The largest diapir-related ore deposits in the region are the massive siderite bodies at Ouenza and Jerissa. The siderite replaces Aptian limestone that is in direct contact with salt rock. The limestones are extremely fine-grained (lithographic) and contain numerous rudist (*Hippuritoida*) fossils, typical for the "Urgonian" facies of Western Europe. Orebodies are stratabound and ore boundaries show marvellous examples of metasomatic fronts. Siderite near the boundaries faithfully preserves bedding, stylolites and fossils of metasomatized limestone and contains large druses of coarse calcite, quartz and tetrahedrite. Figure 1.78 illustrates the margin of a large orebody. Epigenesis of ore is clearly visible as sedimentary textures of host limestones are erased. Antimony fahlore (tetrahedrite), quartz, calcite and aragonite only occur in marginal parts of the ore and are controlled by joints and faults. Within the siderite mass the ore is a nearly monomineralic crystalline rock, with occasional small druses of calcite and dolomite. Ore and host rocks are traversed by rare veins of barite, fluorite and carbonates.

The origin of these deposits is not fully elucidated. It is believed to represent a complex interplay of halokinesis (cf. Chapter 4.3.3) with fluid generation

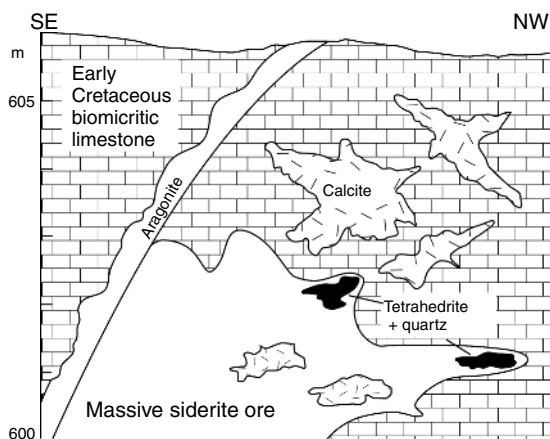


Figure 1.78 Metasomatic front of massive siderite ore replacing bedded limestone at Douamis mine, Ouenza, Algeria (For location, refer to Figure/Plate 1.89.)

by diagenesis of evaporites and host rocks. Mass estimates imply that most of the water of the fluids must have been derived from basinal sediments (Bouzenoune & Lecolle 1997). Partial admixture of meteoric or seawater and dehydration brines sourced from the diapir are all possible. At elevated temperature, iron is extremely soluble in reduced, acidic and highly concentrated brines. Precipitation of siderite is induced by drastic pH-change in contact with the carbonates and by sudden lowering of pressure and

temperature. In this model, the diapirs and their solution breccia envelope are preferred channels for upflowing deep diagenetic brines (Figure 1.79). In active halokinetic phases diapir salt is permeable.

Many diapirs grow in short spurts of active halokin-esis (or halotectonics) that interrupt steady-state pas-sive quietude. During the active phase, major fluid flow may take place. Mineral deposits related to diapirs include petroleum, natural gas, iron, lead,

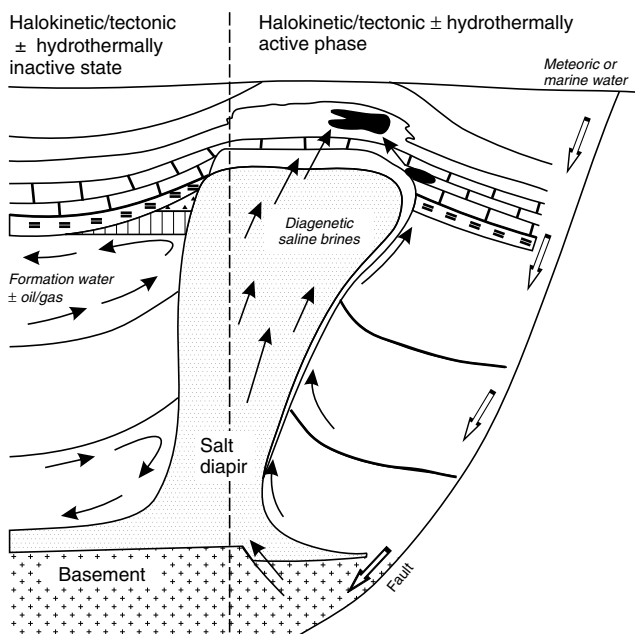


Figure 1.79 Diagenetic metallogenesis related to brines released from salt diapirs, based on observations in the Maghreb region in North Africa (adapted from Pohl *et al.* 1986).

zinc, sulphur, barite and fluorite (apart from salts, cf. Chapter 4). Arsenic, antimony, mercury, silver, copper, manganese and strontium mineralization is rarely economically exploitable.

Occasionally, a pre-enrichment of metals in evaporites is invoked. Of course, many terrestrial salt lake brines do contain anomalous and in part exploitable metal concentrations, for example of lithium, tungsten and magnesium. Sabkhas are believed by some to trap metals and elements such as fluorine and barium that are delivered by inflowing groundwater. Later diagenesis may remobilize the pre-enriched elements and produce ore deposits. As yet, the metallogenetic significance of these hypotheses remains untested.

1.5 METAMORPHIC AND METAMORPHOSED ORE DEPOSITS

Ore deposits in metamorphosed terranes may have been formed before, during or after metamorphic processes. This chapter deals mainly with the first category, which are of premetamorphic origin independent from later metamorphic overprinting. This is the class of "metamorphosed" ore deposits.

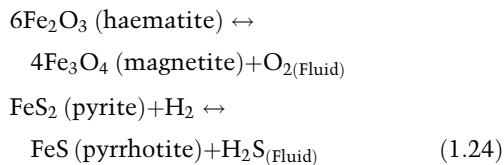
It is possible to distinguish another class of mineral deposits from metamorphosed ores and minerals, a class that owes its economic interest to largely isochemical metamorphic re-equilibration and recrystallization of pre-existing material which had no use in its original state. Examples provide alumina-rich claystones that were transformed into kyanite or sillimanite deposits, or graphite flakes formed from dispersed bitumen. Among ore deposits, gold may be recrystallized from unrecoverable dilute traces and so turn into recoverable economic ore. In allusion to the term metamorphic rocks, this class may be called "metamorphic" ore deposits (Pohl 1992).

Orogenic (regional) and contact (local) types of metamorphism are most common (Bucher & Frey 2002). In the context of this chapter, ocean floor and dynamometamorphism (due to shearing or cataclasis), extraterrestrial impacts and metasomatic changes to rocks will not be further discussed. Ore

deposits that have originated in collisional plate tectonic settings (e.g. island arcs) are most likely affected by later orogenesis and metamorphism. The reverse applies to anorogenic orthomagmatic deposits (e.g. layered mafic intrusions, carbonatites), post-orogenic granitic deposits (tin, tantalum) and superficial alteration deposits (bauxite) which are rarely metamorphosed.

Contact metamorphism of ore in the heated zone around magmatic bodies is usually static (i.e. in the absence of dynamic deformation). Exposure to high temperatures (with a maximum of $\sim 750^\circ\text{C}$) affects fabric, mineralogy and mineral chemistry (e.g. by driving off water and other volatiles). Fabric changes are confined to a general increase in grain size with rising temperature. Monomineralic ores recrystallize by annealing to "foam" textures (Stanton 1972) that are characterized by triple grain boundary junctions at angles of 120° . Instructive observations can be made at magmatic dyke contacts, where changes affect very narrow zones. The contact zone around the Bushveld Complex reaches hundreds of kilometres. Sulphur release (e.g. from pyrite, eq. 1.24) may induce formation of metamorphic pyrrhotite or even magnetite. Because pyrrhotite (like most sulphide minerals) has a pronounced non-refractory behaviour, retrograde cooling will always bring about equilibration at lower temperatures (Vokes 2000). This is the reason why sulphides have a limited role as geological geothermometers or geobarometers. Iron oxide ore at contacts may recrystallize to a different oxidation state (e.g. haematite to magnetite, eq. 1.24) controlled by the oxygen activity imposed by magma or by heated country rocks.

Oxidation/reduction and sulphidation/desulphidation reactions during metamorphism:



Orogenic metamorphism of ore deposits is common. Temperatures may reach 1100°C and

pressures 30 kbar for crustal rocks. Ore metamorphosed in the zeolite, greenschist and amphibolite facies is quite frequent, whereas granulite facies ore is rare (e.g. Broken Hill, Australia). Surprisingly, subducted and high-pressure metamorphic oceanic crust seems to lose mid-oceanic sulphide concentrations: Orebodies hosted in exhumed eclogites and glaucophane schists of subduction zones are very rare (Laznicka 1985). This observation supports assumptions that a part of supra-subduction zone metal concentrations may be mobilized oceanic mineralization.

Orogenic metamorphism is the result of penetrative deformation, while minerals re-equilibrate to new assemblages at geologically elevated temperature and pressure. Volatiles (water, etc.) are partly to wholly (at very high metamorphic grades) removed from the system. Metamorphic rocks exhibit grain coarsening, preferred orientation of minerals and a penetrative fabric (e.g. schistosity, foliation). Ordinary metamorphic rocks display a

number of typical deformation styles, including folding, thinning and rupture of fold limbs, thickening of certain rock types in fold hinges and stretching fabrics that produce elongate shapes. Metamorphosed massive sulphide orebodies (and other metallic and mineral deposits) have been shown to react in the same way as common rocks. Generally, sulphides tend to be more ductile than most host rocks, so that fold hinge thickening and thinning of limbs is very characteristic (Figure 1.80 and Figure 1.81). Of course, sulphide layers in ductile rock, such as black shale or migmatite, may exhibit brittle response, for example boudinage. Extreme elongation leads to orebodies shaped like rods, pencils or spindles. Original spatial relations between ore and alteration zones are often severely disturbed and cannot be reconstructed. This is a serious impediment to geological studies and to exploration of these deposits. Also, it explains why a satisfactory understanding of metamorphosed volcanogenic

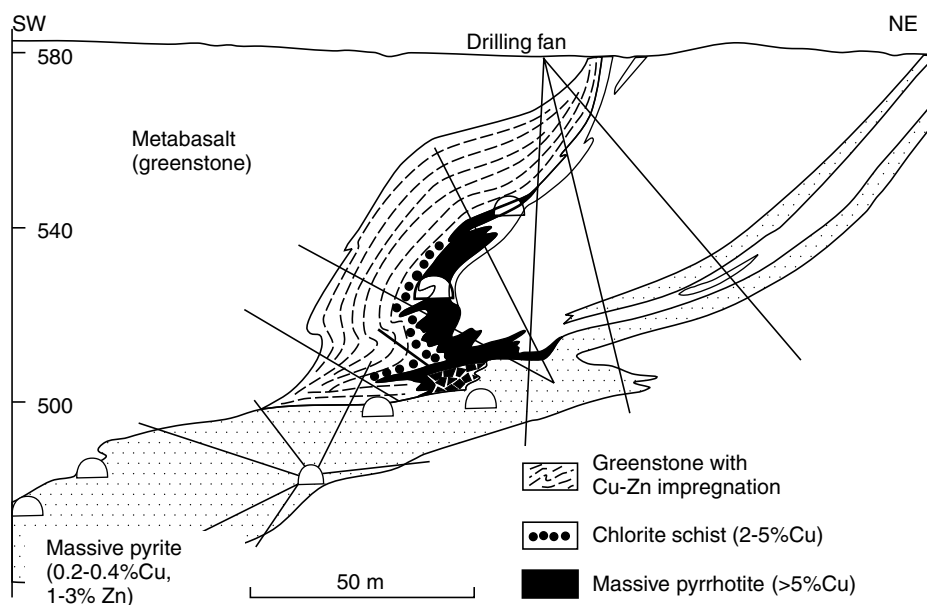


Figure 1.80 Section of Joma Cu-Zn mine in metabasalt northeast of Trondheim, Norway (Bowie *et al.* 1978).

Reproduced with permission of The Institution of Mining and Metallurgy, the Mineralogical Society of Great Britain & Ireland and Maney Publishing www.maney.co.uk. This is an instructive example of orogenic, synmetamorphic deformation of massive sulphide orebodies. Note the drill pattern collared from the surface and from underground mine adits.

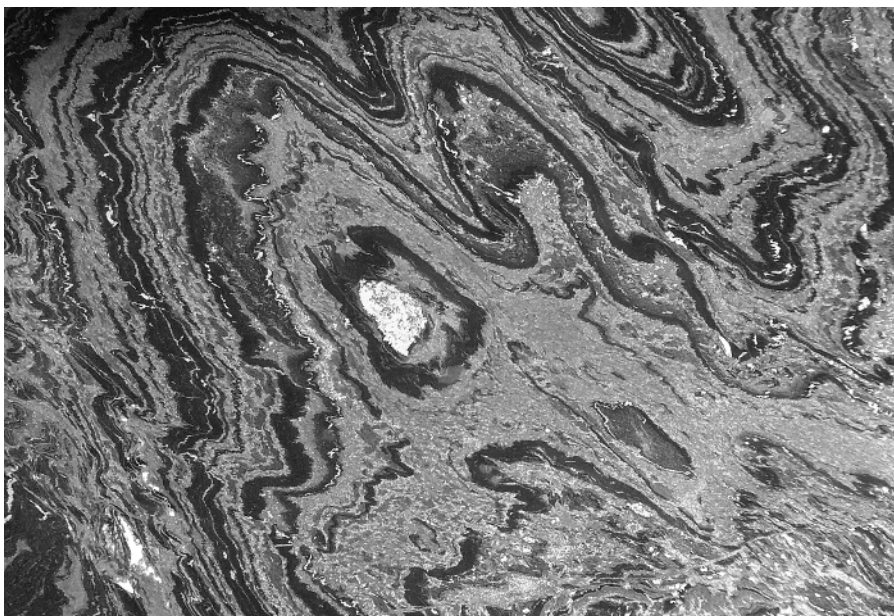


Figure 1.81 (Plate 1.81) Ductilely folded sedimentary bedding in very-low-grade metamorphic shale-banded Fe-Cu-Zn sulphide ore with wispy white dolomite laminae. Note the diffuse axial plane cleavage. Sample from the closure of the orebody synform, Rammelsberg, Germany. Width of image ~20 cm. Courtesy B. Lehmann, Clausthal.

and sedex ore deposits was only recently achieved (Vokes 2000).

An important aspect in studies of metamorphosed ore deposits is the identification of rocks with unusual mineral composition as premetamorphic exhalites or hydrothermally altered rocks (Spry *et al.* 2000b). Quartzites, with or without iron-manganese oxides, are easily identified as former chert, jasper and siliceous sinter. Sillimanite-corundum rock may be metamorphosed alunite alteration; kyanite-andalusite rock might have been advanced argillic alteration and cordierite-anthophyllite schist originally propylitized andesite or basalt (Roberts *et al.* 2003). A pre-metamorphic potassic alteration and sulphidation halo at the Hemlo gold deposit was transformed by upper amphibolite facies metamorphism into microcline and muscovite-quartz schist, apparently of lower metamorphic grade than the kyanite-bearing host formations (Heiligmann *et al.* 2008).

Oxide ore minerals, especially of iron and manganese, react readily with carbonate and silicate

minerals. This caused, for example, formation of the diagenetic-metamorphic skarn rocks in Sweden. Precambrian banded iron formations exhibit many interesting metamorphic features (Stanton 1972). For instance, if alternating magnetite and haematite laminae remain stable, oxygen (and fluid) mobility must have been very restricted. During deformation, haematite typically recrystallizes to micaceous specularite so that the result is a rock similar to biotite schist. Iron silicates and siderite are quite reactive, too. At higher metamorphic grades, siderite loses CO₂ and converts into magnetite or, in the presence of silica, to fayalite (Fe₂SiO₄).

Like iron, manganese is a redox-sensitive and reactive element. During prograde reactions, manganese enters a number of metamorphic minerals, most often spessartine, Mn-rich almandine, rhodonite and rhodochrosite. Rocks of this composition are favourable material for the formation of supergene-residual manganese ore deposits. Elevated Mn-contents of metamorphic silicates (garnet, pyroxene, stilpnomelane, etc.) conserve

the geochemical halos of sedex ore deposits and are useful prospecting tools.

Sulphide ore is chemically less reactive, but allows important deductions concerning deformation and heating history. Increase of grain size by metamorphism is important in practice, because processing of coarse ore is less energy-intensive. Controls on recrystallization and deformation of sulphides include pressure, temperature, synchronous penetrative deformation and the presence of fluids. Ductile deformation by creep along certain lattice planes characterizes galena, stibnite ($>250^{\circ}\text{C}$) and chalcopyrite ($>300^{\circ}\text{C}$), whereas pyrite (Craig *et al.* 1998), magnetite and arsenopyrite display nearly always brittle deformation. The brittle textures, however, may conceal plastic strain during peak metamorphic conditions (Barrie *et al.* 2010). Banded ores typically display folds and injections formed by galena, while pyrite exhibits boudinage culminating in “augen” (eye) structures. Sulphides may be foliated so that ore textures resemble gneiss. In many cases this is due to pressure solution according to Riecke’s principle. If the temperature peak follows well after strain, traces of deformation may be erased by recrystallization to foam textures. The presence of fluids favours recrystallization and local mobilization of sulphides, resulting in the formation of pegmatite-like ore veins in fractures within the orebody or its immediate host rocks.

In contrast to most silicate minerals, sulphides are stable over wide metamorphic P-T conditions. Mineralogical and chemical changes are inconspicuous. Typically, metamorphic recrystallization causes little more than homogenization of pre-existing sulphide minerals and as a consequence, mobilization of trace elements or neogenesis of mineral phases of these elements (Craig & Vokes 1992). Stable isotope systems of the sulphides may be reset by metamorphism. Crowe (1994) reports that sulphur isotopes in chalcopyrite-pyrrhotite assemblages were equilibrated by metamorphism, whereas grains isolated in quartz retained premetamorphic ratios. Orogenic metamorphism may cause a loss of sulphur and formation of pyrrhotite or magnetite from pyrite (“desulphidation”). Sulphur is abstracted by dissolution in prograde dehydration fluids (e.g. water

from breakdown of chlorite), mainly in the form of H_2S . These fluids may mobilize metals such as gold and silver that were hosted in the original pyrite/arsenopyrite because they complex with H_2S . Precipitation commonly takes place in the immediate wall rocks, where the fluids encounter minerals with reduced iron. In this way, metamorphic pyrrhotite, gold and silver ores can be formed (Tomkins 2007), for example, in the Bergslagen district, Sweden (Wagner *et al.* 2005, 2007). In the Brunswick No. 12 volcanic-hosted massive Fe-Cu-Zn-Pb sulphide deposit in Canada, however, gold was not upgraded and mobilized, in spite of upper greenschist metamorphism and intensive deformation (McClenaghan *et al.* 2009).

Beginning at low amphibolite facies metamorphism, the formation of sulphide melts from pre-existing ore is possible (Frost *et al.* 2002). Metals prone to melting include Au, Ag, As, Sb, Bi, Hg, Te and Tl, some of which are low-melting-point chalcophile elements. Until now, this has only been confirmed at a small number of localities. At Broken Hill, Australia, for example, argentiferous galena fills veins in the sillimanite-facies host rocks near stratiform orebodies (Mavrogenes *et al.* 2001). At the large lode gold deposit of Hemlo, Ontario, Canada, premetamorphic disseminated ore was mobilized as a sulphosalt melt within amphibolite facies host rocks. The melt concentrated into dilatational domains such as boudin necks and fractures (Figure 1.40). Sulphide melts have low viscosities close to those of water and therefore, are highly mobile. During metamorphism and deformation, they migrate like other fluids into structurally favourable traps, although in a limited perimeter.

Note that the observations reported in the last two paragraphs demonstrate the passage from metamorphosed ($\pm$ *in situ*) to metamorphogenic (metals are dissolved, transported and reprecipitated) ore deposits, which are described in the next chapter.

Generally, most studies of metamorphosed ore deposits confirm that the concept of an essentially isochemical nature of metamorphism is appropriate. Mobilization of matter affects almost exclusively volatile elements and compounds (H_2O , CO_2 , O_2 , H_2S). As mentioned above, only local

remobilization of very small parts of a deposit's total metal stock is observed (Marshall *et al.* 2000, Vokes 2000, Wagner *et al.* 2005, 2007). Therefore, earlier hypotheses are refuted, that metamorphic "regeneration" of pre-existing ore deposits by dissolution-transport-reprecipitation is both ubiquitous and of more than occasional economic significance. It is yet uncertain whether anatexis partial melting induced by metamorphism may be a path to the formation of ore deposits, although selective enrichment of certain metals in the melt fraction is possible (Tomkins *et al.* 2009). In fact, these authors suggest that pre-existing gold mineralization may be recycled through partial melting to form intrusion-related (magmatic-hydrothermal) gold systems. Proven examples for this connection have yet to be found, because the source of fertile igneous rocks is deep crust, whereas the deposits occur rather in the middle and upper crust. The Challenger gold prospect in South Australia seems to represent such a source of felsic auriferous melt. There, exploration drill core displays leucosomes in migmatite, which contain ~8 g/t Au. Round droplets consisting of native gold and sulphides are thought to be frozen ore melt (Tomkins & Mavrogenes 2002).

1.6 METAMORPHOGENIC ORE FORMATION SYSTEMS

Clearly, skarn and contact-metasomatic ore deposits are intimately related to thermal aureoles of magmatic intrusions. They may be said to be products of contact metamorphism, but the causal agent is the interaction with magmatic fluids and not simple change by heating. Therefore, we discussed this group in the magmatic domain (Section 1.1). The formation of ore deposits by regional (most often orogenic) metamorphism, although suspected earlier (Schneiderhöhn 1932), is only now generally accepted. Consequently, "metamorphosed" and "metamorphogenic" ore deposits must be distinguished (Pohl 1992, Spry *et al.* 2000a). Examples of mineral deposits that are members of the metamorphogenic class include orogenic gold (Groves *et al.* 2003), the graphite veins of Sri Lanka, ruby in the Himalayas, several

large talc deposits (Rabenwald, Luzenac), certain metasomatic siderite deposits (Erzberg, Austria and Bakal, Russia) and metallic ores (e.g. silver and cobalt in Bou Azzer, Maroc; silver, lead and zinc in western Canada: Beaudoin & Therrien 1999; iron oxide-copper-gold in Australia: Fisher & Kendrick 2008). Generally, deposits of this genetic class were formed from passing hot aqueous fluids and are therefore hydrothermal and epigenetic. Rarely, metamorphic sulphide melting may have been the means of metal migration and concentration, as possibly at Hemlo (Ontario, Canada: Tomkins *et al.* 2004).

In the preceding section, it was argued that apart from devolatilization, regional metamorphism is commonly an isochemical process. Here, this statement must be qualified, in recognition of the mass transfer caused by metamorphic fluids. Orogenic metamorphism induces a large-scale outward flow of heat and fluids (Masters & Ague 2005) that may continue over geological time-scales (e.g. 70 million years in the case of the Palaeoproterozoic Ophthalmia orogen, Pilbara, Australia: Rasmussen *et al.* 2005). The metamorphic fluids can be considered as solutions that are in equilibrium with host rocks, and although they are dilute, their sheer mass allows significant transfer of dissolved matter. Even simple field observations of metamorphic rocks provide clues, such as the ubiquitous quartz or carbonate veinlets of epizonal rocks, the unidirectional dissolution of fossils and detrital grains, and the solution schistosity that forms parallel to axial planes. Using these criteria, a loss of ~20% of the original rock mass may not be rare, even at low metamorphic grades. The mass loss of high-grade rocks is probably even higher, but its determination is rarely possible. In cases where identical rocks can be sampled at different metamorphic grades, the mobility of major, minor and trace elements can be quantified. In New Zealand, ore-forming elements (Au, Ag, As, Sb, Hg, Mo and W) are depleted in metamorphic rocks relative to unmetamorphosed protolith samples; the same elements are enriched in the orogenic gold deposits of the region (Pitcairn *et al.* 2006). Some data suggest that even "immobile" elements (e.g. Ti, Zr, Y, Ta) are not reliably conserved, although they are commonly

used for petrogenetic and geodynamic investigation of magmatic rocks (Pearce *et al.* 1984, Winchester & Floyd 1977).

Lateral secretion

Lateral secretion is different from the metamorphic model. It is best exemplified by the extremely common and ubiquitous generation of quartz and carbonate veinlets from host rocks at low metamorphic grades and of pegmatitic mobilizes at high grades. This interpretation is confirmed by the observation that the paragenesis of these veins depends on the chemistry of the enclosing rocks. Quartz mobilizes, for example, occur in siliceous metasediments, whereas calcite veinlets form in limestone marble and in mafic metavolcanic rocks. In the latter case, veinlets include epidote, chlorite and sulphides. Lateral secretion veins are mostly tensile structures that originate in syn- to late-metamorphic stages. They

may contain large crystals of both common and rare minerals, such as the famous Alpine fissure veins (Figure 1.82; Mullis 1996) and many gemstone deposits. Lateral secretion should result in a balanced mass exchange between host rocks and veins. Mobilized elements in the first decrease with proximity to the veins. Because of the chemical equilibrium between fluids and rocks, lateral secretion imprints no hydrothermal alteration on host rocks and stable isotopes reflect equilibrium: The fluids are of a local derivation. A transient pressure gradient induces movement of fluids, which were originally dispersed in the rocks, to the opening fissure. Flow may be along grain boundaries or by diffusion. This system is spatially limited and essentially closed. In its pure form there should be no inflow from beyond its boundary and little outflow. In tectonically quiescent times, temperature and pressure in the fissure and the country rocks are equal, but pressure drops when active extension takes place (Figure 1.83).



Figure 1.82 Alpine fissure with large quartz crystals encountered in 1974, in Aar granite gneiss (Switzerland) during excavation of an access tunnel to the Grimsel II power station. Courtesy Nagra, Comet, Weisslingen. The crystal cave is now a national geological monument, accessible from Nagra's underground laboratory Grimsel. The fissure formed at ~16 Ma from fluids >400°C. Width of image ~1 m.

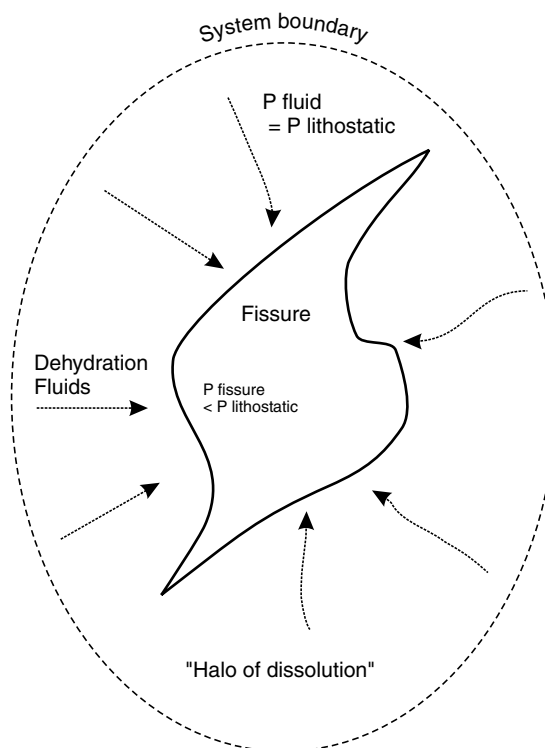


Figure 1.83 Principles of lateral secretion. Changes in the orogenic stress field lead to opening of a fissure. The resulting pressure gradient ($P_{\text{fissure}} < P_{\text{lithostatic}}$) enforces flow of metamorphic fluids into the fissure where minerals precipitate. The system is closed within narrow limits ("halo of dissolution"). The fluids are "dilute solutions" of the surrounding host rocks.

Generally, fluid pressure is lithostatic. Because of the limitations concerning the mass of participating fluids and dissolved matter, a lateral secretion system is not expected to form economic metallic or mineral deposits (apart from pockets of rare mineral specimen). Lateral secretion veinlets demonstrate the retention of metamorphic fluids in a dehydrating rock body. Synchronous shearing is the key to outflow of metamorphic fluids and eventual formation of metamorphogenic ore deposits.

Fluid systems that produce sizeable mineral deposits are open, in contrast to the closed or low flow systems of lateral secretion. In shallower parts of metamorphic complexes, the passage of large masses of deep metamorphic fluids may leave conspicuous clues in the form of regional import of matter (e.g. potassium in the Caledonides: Mark *et al.* 2007). Less visible, oxygen isotope systematics of rocks are changed by the passing fluids (Beaudoin & Therrien 1999). Flow channels of the fluids (e.g. veins) are marked by

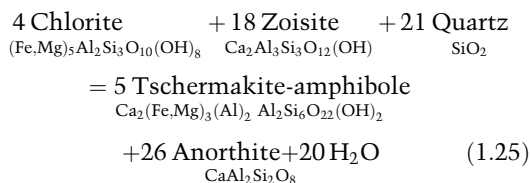
hydrothermal alteration of the wall rocks. Also, veins are surrounded by trace-metal halos with contents increasing as the vein is approached. Changes of this kind can only be explained by the influence of migrating fluids that have passed through the system. They originated in deeper parts of the orogenic body, where metamorphism was active. Prograde metamorphism liberates large amounts of water by endothermic reactions. This can be substantiated both by simple calculations and by comparative analyses of metamorphic rocks (Hanson 1997).

Metamorphic fluids

Metamorphic fluids originate primarily by chemical release (devolatilization), different from diagenetic fluids. Increasing metamorphism, from sub-greenschist facies to anatexis, produces a steady flow of metamorphic dehydration fluids and a decrease of volatiles in the respective metamorphic rocks. The dehydration reactions (eq. 1.25) are

strongly endothermic and consume a heat energy of ~ 90 kJ per 1 mol H_2O (Bucher & Frey 2002). Shales contain ~ 4 wt.% water in contrast to mica schist with $\sim 2\%$. By exothermic reactions, basalt assimilates water during the formation of greenschists to a maximum of $\sim 13\%$, but only 2% H_2O remain in amphibolite. Siliceous carbonates lose CO_2 due to generation of metamorphic calc-silicate minerals. Decomposition of organic substance in sediments liberates H_2 , CO_2 , CH_4 , N_2 and water. During prograde metamorphism, the “mineralic” NH_4^+ that often partially replaces K^+ in diagenetic silicates (clay, mica, K-feldspar) is expelled into the fluid phase. Consequently, total nitrogen decreases in metamorphic rocks and the remaining nitrogen becomes isotopically heavier (Bebout & Fogel 1992). Salt and anhydrite are usually dissolved and leave the system. Former evaporite horizons in metasediments may be revealed by newly-formed scapolite and albite, or by remains of anhydrite and of saline fluid inclusions (Fisher & Kendrick 2008).

Example of dehydration reactions at the transition from greenschist to amphibolite:



Equation 1.25 illustrates the most important mineralogical changes, as chlorite and epidote are consumed and contribute to neoformation of the anorthite (Ca-rich) component of plagioclase and the tschermak (Ca) molecule of amphibole.

Water in metamorphic rocks occurs mainly in OH-groups of hydrous minerals and in fluid inclusions. Grain boundaries also host tiny inclusions. Some fluids fill open fissures and the pore space. Fluid inclusions in low-grade metamorphic rocks are made up of H_2O , Cl, CO_2 , CH_4 (e.g. in Alpine fissures) and H_2S and N_2 (Roedder 1984). Abundant cations include Na, Ca and Mg, but salt contents are mostly below 5%. Intermediate-grade metamorphic rocks have fluids with H_2O , HF, F,

CO_2 , CH_4 , CO, H_2 and HS^- . High-grade metamorphic fluids are melt-dominated. Deep drill holes in crystalline rocks sampled small amounts of highly saline fluids of a somewhat enigmatic origin. In the Black Forest, Germany, deep fluids in gneiss are probably derived from Mesozoic seawater (Stober & Bucher 1999). Derivation of deep continental brines at high latitudes by freezing of Pleistocene seawater may be an alternative (Frank *et al.* 2010). Reduction of sulphate in descending brines enriches CaCl_2 . In granulites, eclogites and sillimanite schists, water content is normally near zero; however, these rocks may contain pure CO_2 inclusions. Frequent daughter minerals in the microscopic inclusions are halite and sylvite that form by desiccation of episodic inflow of small batches of crustal fluids (Markl & Bucher 1998).

Mass balance calculations and isotopic investigations indicate that metamorphic fluids are not solely the product of prograde devolatilization but may mix with basinal and even meteoric fluids. Koons *et al.* (1998) illustrate the variable source of hydrothermal fluids in a cross-section of the New Zealand Alps. Obviously, hot metamorphic terrains build up large hydrothermal systems that are essentially comparable to the smaller convection systems established near magmatic intrusions. Metamorphic ore-forming hydrothermal systems at the deposit-scale can be long-lived (e.g. ~ 1 million years at Mt Isa: Matthäi *et al.* 2004).

Fluids liberated from rocks undergoing prograde metamorphism acquire economically interesting trace metals (e.g. gold) or other elements (arsenic), either together with the volatiles H_2O , F and Cl from the lattice of transforming minerals, or later along flow channels and in staging reservoirs by reaction of migrating fluids with the wall rocks. Controls of this transfer include the fluid to rock mass ratio, the fluid and rock chemistry, and T, P, pH, Eh and kinetic conditions of the system. Considering that metamorphic complexes will have a comparable average chemical constitution over large distances, expelled metamorphic fluids should also have an analogue composition over large areas (“compartmentalization”: Lefticariu *et al.* 2005). This hypothesis leads to the concept of “fluid provinces”. In the Eastern Alps, ore deposits formed in the Cretaceous during the

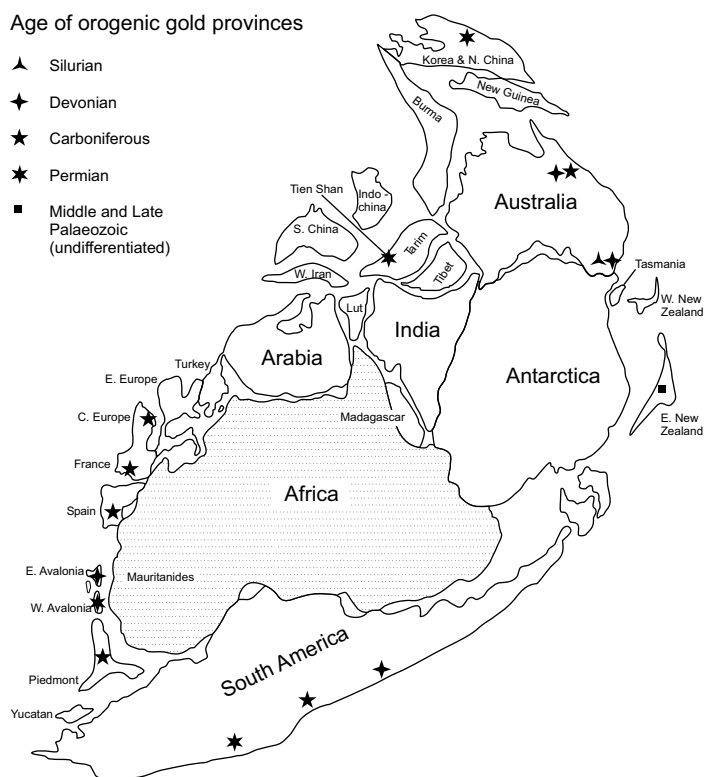
Eu-alpine Orogeny (e.g. siderite, copper, barite, talc) display similar inclusion fluids. This data was interpreted as evidence of a Synorogenic East-Alpine Fluid Province (Pohl & Belocky 1994, 1999). Note that preliminary data on fluid halogen mol ratios and Sm/Nd ages of ore and host rock suggest generation of siderites by deeply circulating evaporative brines in Late Triassic time (W. Prochaska, unpublished).

Many gold ore deposits are interpreted to have a metamorphogenic origin. Common examples are gold quartz veins with sulphides of arsenic, antimony and iron, which occur far from igneous intrusions in black schist, metaturbidites or in greenschist-facies metamorphic rocks. Commonly, they were formed in orogenic belts and at the time of waning orogeny, correlated with late-metamorphic uplift, lateral spreading, deep shear zones and intrusive activity. This is the rationale for the term “**orogenic gold deposits**” (Figure 1.84). Most of the fluids and the solutes are probably of

metamorphic origin, but a contribution from other sources including the mantle, magmatic and meteoric domains is possible. Although the gold concentration in metamorphic fluids is very low, focused mass flow through chemical and physical traps formed many large gold deposits.

Time and rate of fluid flow from rock bodies undergoing metamorphism is difficult to determine. Two end-member modes are possible: i) Either fluids formed in the rock mass are conserved and later expelled all at once (“batch volatilization”); or ii) fluids flow out as they are set free (“Rayleigh distillation”). In geological reality, it may be assumed that both processes act alternately and in various combinations, mainly due to physical boundary conditions (e.g. stress and strain, pore pressures, pressure gradient, permeability, temperature gradient, etc.) imposed by concomitant tectonics and the geological framework. The mineral specimen-rich Alpine fissures, for example, testify to retention of metamorphic fluids until after the

Figure 1.84 Large gold ore provinces formed in the Middle to Late Palaeozoic within Gondwana and adjacent plates (adapted from Haeblerlin *et al.* 2003 with permission from Elsevier). Active continental plate margins controlled the location of gold ore formation, illustrating the term “orogenic gold deposits”.



BOX 1.13 Two end member models of metamorphogenic ore formation

1. Prograde metamorphogenic ore formation. Normally, metamorphic fluids are expelled in the form of a wide and diffuse flow into regions of lower pressure (Hanson 1997, Jamveit & Yardley 1997). Large regional tectonic structures (shear zones, extensional faults and thrust faults) focus the diffuse flow, because they can be channels of higher permeability (Figure 1.85). The permeability of the lower ductile crust (~10–15 km beneath the surface, depending on the geothermal gradient) undergoing prograde metamorphism is very low with a flow of only 0.25 m/year (Beaudoin & Therrien 1999) and the pressure regime is lithostatic. Note, however, that even in the middle and lower crust, an interplay between brittle and ductile deformation may occur (Mancktelow 2006). In the brittle upper crust, permeability is much higher and flow in faults reaches 100–1000 m/year. When rising fluids enter this regime, pressure is released and approaches hydrostatic conditions. Descending (e.g. meteoric) water can penetrate as far as the brittle/ductile boundary (Ingebritsen & Manning 1999). Because of these particular conditions, the brittle/ductile transition at ca. 425–375°C is a very frequent location of metamorphogenic ore deposit formation.

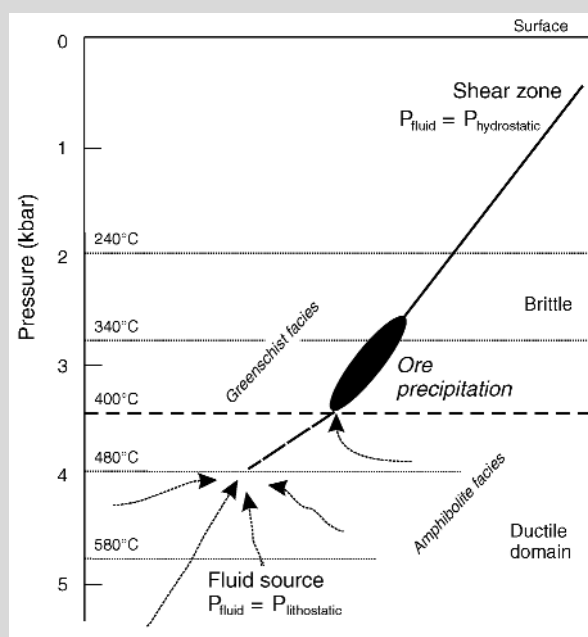
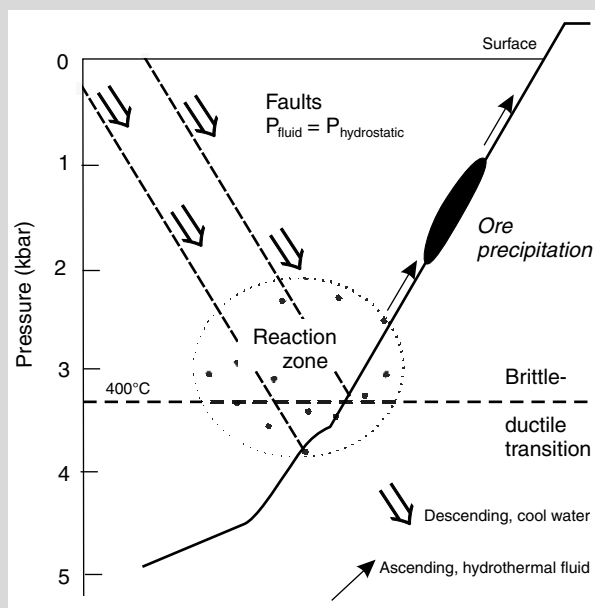


Figure 1.85 Ore deposit formation by prograde metamorphism. A shear zone focuses upflow of metamorphic fluids because of higher permeability. Its crustal-scale vertical extent facilitates transfer of fluids from lithostatic to hydrostatic pressure domains. Ore formation is a consequence of chemical or physical traps. The system is open, the mass flow is unidirectional.

2. Retrograde metamorphogenic ore formation. Many geological observations (e.g. concerning the structural control of orebodies) indicate that ore formation took place long after peak metamorphic conditions (or even totally unconnected to orogenic metamorphism). Petrographic investigations show that cooling and uplift of metamorphic complexes is accompanied by retrograde exothermic reactions of rocks with infiltrating fluids (mainly hydration; Haack & Zimmermann 1996, Yardley *et al.* 2000). Usually, these fluids will be derived from a near-surface reservoir (e.g. meteoric, marine or basinal water). The water descends along structural conduits and in contact with suitable rocks forms hydrous minerals. Oxygen is consumed in oxidation reactions. Tectonic preparation of a large rock surface (e.g. breccias) is favourable. In the reaction zone, rocks and surplus water are heated and country rocks sustain retrograde metamorphism. Heated fluids are charged with dissolved matter. Hydrothermal convection cells are established with hot fluids of low density rising back to the surface. Along the upflow channels, precipitation of dissolved matter from the fluids can form retrograde-metamorphogenic ore deposits (Pohl 1992, Figure 1.86). Convection cells may reach the brittle/ductile boundary, where descending waters mix with deeper prograde-metamorphic fluids, as shown by Templeton *et al.* (1997) in the Alps of

New Zealand. In the European Eastern Alps, many ore deposits are correlated with the second Eocene metamorphic phase. Gold quartz veins in the metamorphic core region of the Penninic unit (Tauern Mountains) were formed by ponded prograde fluids, whereas iron ore in higher tectonic units is the product of mixing of prograde fluids with descending meteoric water (Pohl & Belocky 1999).

Figure 1.86 Ore deposit formation by retrograde metamorphism. Tectonic extension opens flow paths for descending cool waters that react at depth with hot rocks ("reaction zone"), take up solutes and rise back to the surface as hydrothermal fluids. The pressure regime is usually hydrostatic and the convection system is essentially open.



An instructive concept of ore formation during late-metamorphic cooling processes was described from the Scottish Dalradian belt (Craw & Chamberlain 1996). Infiltrating meteoric water induced an oxidation front that migrated through the orogenic body and facilitated leaching of trace gold. The gold was precipitated in reducing environments of the hydrothermal upflow limb (e.g. in the Tyndrum deposit).

temperature and pressure maximum of metamorphism. Ore deposit formation is more probable when large masses of stored fluid flow off in a geologically short time. This may often be the period of uplift, shearing and distension of metamorphic complexes. Synchronous metamorphogenic ore deposit formation in large areas supports the concept of tectonically activated "fluid pulses".

Many ore deposits, which were formed in stable cratons during geologically short events of major plate reorganizations (Whittaker *et al.* 2007), may be regarded as members of the retrograde-metamorphogenic class. Prominent examples are the unconformity uranium ore deposits in Canada and Australia (cf. Chapter 2.5 "Uranium"). Ore depos-

its formed during phases of extensional plate deformation, such as Alpine and Irish type Pb-Zn-Ag, often display a retrograde-metamorphogenic component when convection systems reach down into older basement. This is easily revealed by Pb-isotope investigations.

Both models of metamorphogenic-hydrothermal ore deposit formation systems, prograde and retrograde, appear scientifically well founded, but the genetic attribution of specific deposits remains difficult. One reason is that orogenic metamorphism is widespread and operates in settings as different as active continental margins (Andes), in island arcs (New Zealand) and in zones of continental collision (Alps). Regions where mantle

magmas heat the crust from below (underplating, deep intrusions, continental extension, rifting) experience mobilization of volatiles and the establishment of deep convection systems. In all these settings, synchronous crustal melting and igneous activity are common, too. This causes difficulties in distinguishing metamorphogenic from magmatic ore deposits (Bucci *et al.* 2004). A severe problem is also that in nature, mixed variants of the theoretical end member models described seem to be prevalent.

1.7 METALLOGENY – ORE DEPOSIT FORMATION IN SPACE AND TIME

“Deciphering the predisposition of orogen segments for exceptional mineral endowment is one of the most critical as well as intractable metallogenetic research topics”

R.H. Sillitoe 2008

Metallogeny is the science of origin and distribution of ore deposits in geological space and time (de Launay 1913). The term includes both metallic and non-metallic mineral deposits, as does “minerogeny”. Note that the adjective form of the word “metallogeny” is metallogenetic, although the abbreviated “metallogenic” is also used. As we have seen in the preceding sections, metallogenesis (ore deposit formation) is a function of the Earth’s process systems. Mineral deposits are a by-product of dynamic processes in mantle and crust of the Earth, and of their interaction with hydrosphere and atmosphere. In geological time, these processes occur in geodynamic cycles that produce defined geological entities, such as the Alpine, Variscan and Caledonian orogenic belts, each with characteristic types of mineral deposits.

Important targets of metallogenetic studies are: i) the quest for the source of a valued element, ii) understanding mobilization and transport systems; and iii) the nature of the trap that caused the enrichment resulting in a mineral deposit. Some regions have similar ore deposits dating from more than one geodynamic cycle, for example Palaeozoic to Tertiary carbonate-hosted lead-zinc in the Mediterranean realm and gold in the North American Cordillera (Sillitoe 2008). This is

described but not explained by the term “metallogenetic heredity”. The word implies that the crust contains a geochemically distinct trace metal reservoir that is the source of repeated mobilization and mineralization. An opposing hypothesis dismisses this notion and claims that ordinary crust or mantle can be the source for most ore deposits. The formation of fertile tin granites, for example, can be traced to average crustal concentrations of tin; the critical factor is highly efficient magmatic differentiation (Lehmann 1990, Figure 1.18). There is no doubt, however, that both crust and mantle are geochemically highly heterogeneous. Anomalous metal contents are possible, and the heredity need not be based on an anomaly of a specific ore metal such as tin, but on other parameters such as redox state or elevated F, Cl, B and Li contents of source rocks that are conducive to mobilization and concentration of tin. This remains unproven, but with a more positive note, Plant *et al.* (1997) demonstrate that regional geochemical maps do allow important deductions about metallogenesis and metal endowment of an area.

The unidirectional evolution of the Earth in time is of superordinate rank compared to geodynamic cycles (Holland 2005, Sleep 2001, Windley 1995). In the 4500 million years (Ma) of geological history, Earth systems experienced severe changes reaching from the atmosphere, the biosphere and the oceans down into the mantle. Of course, metallogenetic evolution reflects these changes (Goldfarb *et al.* 2010). Several deposit-types occur only in certain periods of geological history. Examples include the komatiite-hosted nickel sulphides in Archaean greenstone belts (common from 3.8–2.5, rare until ~2 Ga), banded iron formations of the Superior type (2.6–1.8 Ga), granite-related tin deposits in the Late Palaeozoic and Mesozoic, and uranium in sandstones of Cretaceous and Tertiary age. Another important factor controlling the distribution of ore deposits in geological time is the preservation potential. Just as some rocks are more prone to erosion than others in long-term geological processes (Hawkesworth *et al.* 2009), so are ore concentrations. Preferential exhumation of near-surface deposits and their destruction by erosion must have occurred

throughout geological time. This is probably the reason why epithermal and porphyry copper deposits are much more frequent in Phanerozoic compared to Precambrian time (Wilkinson & Kesler 2009, Kesler & Wilkinson 2006).

Impacts of extraterrestrial bodies may have influenced metallogenesis more profoundly than we realize today. The impact origin of the giant structure of Sudbury, Canada and its ore deposits (Dietz 1964) is, of course, generally acknowledged. The bombardment of Earth from space was most intensive during early geological time (ca. 4500–3800 Ma). The imported matter must have been mixed into the mantle. Impact structures on the surface were erased by Archaean crust building and by plate tectonics. Today, about 400 younger impact structures are exposed but apart from Sudbury, there are hardly ever convincing relations with economic ore deposits. Yet, we may ask, for example, if the super-giant ore concentrations in southern Africa (e.g. Bushveld, Great Dyke) could be inherited from extraterrestrial material mixed into the mantle. In contrast, little doubt exists that part of the giant oil and gas resources in the Gulf of Mexico are intimately related to the Cretaceous-Palaeogene boundary Chicxulub impact (Grajales-Nishimura *et al.* 2000).

1.7.1 Metallogenetic epochs and provinces

Useful metallogenetic concepts and terms include (Petruscheck 1965):

- **Metallogenetic Domains** implicate crustal sectors with a comparable geological evolution that include a number of metallogenetic provinces of different ages; examples are the European Alps, the South American Cordillera, or the Archaean Pilbara Nucleus of the West-Australian Shield.
- **Metallogenetic, or Ore Province** combines all deposits that were formed in a major geotectonic unit during one geodynamic cycle, and that are closely related by chemical affinity, form and metal endowment; for example, the tin province in the Late Palaeozoic Erzgebirge of Germany and Czechia; metallogenetic provinces extend over large areas, in contrast to districts.
- **Metallogenetic District, or Zone** describes parts of an ore province; Sillitoe (2008) uses the term

“metallogenetic belt” with the same meaning; deposits within such a district are very closely related, single deposit types predominate, and metallogenetic activity was typically restricted to a short geological time. Marcoux & Jebrak (1999) distinguish migrating and stationary districts; the latter are thought to be more productive because an energy source (e.g. a mantle plume) remained stationary for a geologically longer time (>10 Ma).

- **Metal Province** describes the distribution of all deposits of one metal (or a group of metals such as Pb, Ag, Zn) irrespective of their age; this illuminates regions of possible metallogenetic heredity.
- **Metalloctects** are geological features that have caused formation or localization of mineral deposits; they include major crustal structures (Hough *et al.* 2007), metamorphic, volcanic and plutonic centres, regional geochemical barriers (the European Copper Shale) and discordances (uranium).

Utilization of metallogenetic terms tends to be vague, which is caused by problems of practical application. The main difficulty is often the age attribution of deposits, enforcing a loose definition of metallogenetic provinces and zones in respect of time (Routhier 1980). A statistical method to identify metallogenetic provinces and epochs was presented by Wilkinson & Kesler (2009), built from a large database on porphyry copper deposits. The authors propose to determine regions with a special endowment (metallogenetic provinces) and periods of enhanced deposit formation (metallogenetic epochs), after correcting the age-frequency and deposit-density distributions for loss by uplift and erosion as well as subsidence and burial. Although Wilkinson & Kesler (2009) reveal the Late Eocene and the Middle Miocene as epochs of enhanced porphyry copper mineralization in South America, they state that spatial distribution remains unpredictable. The key to “deciphering the predisposition of orogen segments for exceptional mineral endowment” (Sillitoe 2008) remains improvement of geological understanding.

Metallogenetic maps are produced in order to allow a synopsis of metallogenetic, geological (metalloctects) and basic economic data (e.g. the size of deposits). A generalized geological background is used to display information on size and nature of

ore deposits. Symbols aim at depicting generalized genetic and morphological information, and the nature of the main metal or mineral (Figure 1.87). Metals are indicated by colour, for example yellow for gold and silver, blue for lead and zinc, red for tin and tungsten, etc. The relative size of deposits is expressed by varying the size of symbols. Usually, boundaries of metallogenetic provinces and districts are shown. Many countries have published national metallogenetic maps. Europe is covered by several sheets of the *Metallogenetic Map of Europe and Neighbouring Countries* (scale 1:1 250 000; Emberger 1984) and by one sheet of the *Mineral Atlas of the World* (scale 1:10 000 000; published by the Commission de la Carte Géologique du Monde, CGMW, Paris, and the Geological Survey of Norway, NGU, Trondheim 1997 (Juve & Storseth 1977)). Metallogenetic maps and the supporting mineral deposit data banks serve scientific interests, but their main use is practical; they are indispensable for estimates of undiscovered mineral resources and for planning strategic exploration.

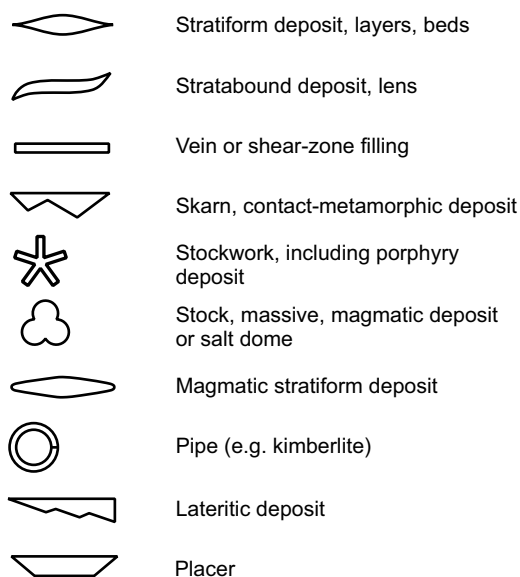


Figure 1.87 Common morphological and genetic symbols for different deposit types on metallogenetic maps.

1.7.2 Metallogeny and plate tectonics

About 60 years ago, the understanding of global tectonics experienced a revolutionary advance (Kearey *et al.* 2009). Until then, the Earth's crust was considered to move either up or down, but rarely in a horizontal direction. The new concept of plate tectonics recognized that the lithosphere is divided into a number of rigid plates, which display considerable lateral movement. The engine of plate tectonics is convective cooling of the mantle. The resulting lithosphere is in part recycled back into the mantle. Extensional and compressional interactions at plate boundaries are the cause of profusely fertile metallogenetic systems.

The Theory of Plate Tectonics was worked out only recently, but its foundations are much older. The similarity of the coastal geometry of South America, Africa and India, and their sharing Permian sediments with the striking *Glossopteris* flora made already Eduard Suess (1831–1914) speculate that continents were not fixed in time and that in the geological past, the three formed a large supercontinent that he called Gondwana (Suess 1885). Building on this, Alfred Wegener developed the hypothesis of continental drift (Wegener 1924) that is in large parts still valid. Modern understanding of plate tectonics led to great progress in many fields of the earth sciences, including metallogeny (Robb 2005, Sawkins 1990b). Several lines of evidence indicate that plate tectonics may have started to operate as early as 4.4 Ga when a stiff lithosphere had been established (Moyen *et al.* 2006, Furnes *et al.* 2007). Already in the Archaean, ore deposits are known that suggest a suprasubduction zone setting.

Main elements of plate tectonic process systems that are “**metallogenetic factories**” include:

The formation of intracontinental rifts, aulacogens and large sedimentary basins (incipient divergent plate boundaries)

Rifts originate by extensional deformation of lithospheric plates and may or may not evolve into a new plate boundary. Very often, rifting causes thinning of the crust, upflow of hot mantle and

updoming of rift shoulders (Tackley 2000). Volcanic activity within the rifts is a frequent consequence, often organized into large volcanic centres ("hot spots": Foulger & Natland 2003). Hot spots can be the origin of three diverging rifts (triple junction). Two of the three rift arms may widen to form a new ocean, whereas the third remains inactive and is called a failed rift arm. Several failed rift arms display thick sediments with bimodal volcanic rock suites, which were later folded by horizontal shortening. Considerable intrusive activity may occur. Settings like this have been called aulacogens (Eriksson & Chuck 1985).

Sediments of continental rifts include early, mainly terrestrial, alluvial clastic infill that can contain uranium, placers and coal deposits. In many cases, a freshwater, saline or marine-influenced lake stage succeeds with beds of salt, gypsum, magnesite, phosphate, valuable clays or oil shale. Full marine ingression into the widening rift and inception of oceanic spreading can induce submarine metalliferous exhalation of the black smoker or brine pool type (Red Sea) and the deposition of thick marine sedimentary sequences. Later, as diagenesis is enforced by rising temperature and pressure, oil and natural gas deposits are generated.

Hot spot-related ore-forming systems include the Bushveld in South Africa, tin-fertile A-granites in Nigeria and worldwide, many alkali-carbonate igneous complexes. When rifting reaches the stage of a deep graben with vertical displacement at marginal faults approaching kilometres (Scholz & Contreras 1998), hydrothermal convection systems may form, based on the permeable tensional structures, the heat contrast and the hydraulic head imposed by rift shoulder mountains. The ascending branch of these hydrothermal systems typically results in deposits of lead, zinc, silver, manganese, fluorine and barite, which take the form of veins and metasomatic replacement bodies in rift margin rocks, or of ore beds in the graben sediments. Good examples are many Pb-Zn and Mn occurrences in Tertiary sediments on both sides of the Red Sea, and part of the Ag-Pb-Zn-F-Ba veins along the Rhine graben in France and Germany (Figure 1.28). Carbonatites and alkali

intrusions with apatite, fluorine, niobium and rare earth element ores characterize the Cretaceous-Tertiary rifts in Eastern and Central Africa. Submarine, epicontinental rifts and half-grabens are related to base metal deposits of the sedex type.

Sullivan in British Columbia, Canada (base metals in the Neoproterozoic Alberta Rift), Mt Isa in Queensland, Australia (Pb-Zn-Cu in the early Mesoproterozoic) and the large deposits of native copper in basalts and of chalcocite in fine sands of the Nonesuch Shale in the Keweenaw Rift (USA, Late Mesoproterozoic) were proposed as remarkable examples of mineralization in aulacogens. The Panafrikan Damara Orogen in southern Africa has also been interpreted as an aulacogen, although with exceptionally strong tectonic shortening. Its main mineralizations are late to post-tectonic, including the giant hydrothermal karst pipe Tsumeb with polymetallic ores of Pb, Zn, Cu, Cd and Ge (Chetti & Frimmel 2000), and the uranium-deposit Rössing in alaskitic granite.

Intracontinental basins with prominent ore provinces include the European Copper Shale (Mesozoic), Witwatersrand gold (Late Archaean) and Mississippi Valley type lead-zinc-barite-fluorite deposits (Palaeozoic) in North America.

Major plate reorganizations affect both continental and oceanic systems intensely (Whittaker *et al.* 2007). Within short periods of a few million years, new subduction zones are installed, vectors of plate drift change (wander paths form "loops") and the plates are subjected to new stress fields. Oceanic and continental crust is stretched or sheared, new mantle regions experience partial melting, resulting in magma underplating, the formation of hotspots and the rise of mantle volatiles. Flood basalt volcanism may be a consequence, producing giant Cu-Ni-PGE deposits such as Noril'sk, as well as climate change and global extinction of life due to huge emissions of sulphur and chlorine such as those of the Dekkan traps at the end of the Cretaceous (Self *et al.* 2008). Enhanced heat flow and elevated permeability of the crust are favourable factors for the formation of deep convective hydrothermal systems and of mineral deposits. Mantle volatiles (mainly water and CO₂, with solutes like fluorine, arsenic, etc.) may rise, leach metals, mix with crustal fluids and

form ore deposits. Examples of mineralization caused by plate reorganization include the hydrothermal "Saxonian Mineralization" of Europe north of the Alps (Walther 1983), several kimberlite provinces and unconformity uranium ore deposits in Canada and Australia.

The evolution of passive continental margins and the disruption of older ore provinces (divergent plate boundaries)

The opening of new oceans passes from a high heat-flow rift stage into a marine transgression and thermal contraction phase. Relatively shallow, epicontinental seas may form. As the young ocean widens, passive continental margins develop. Sediments include salt, phosphate and hydrocarbon source rocks. Manganese ore beds of the Tertiary Black Sea province, Quaternary metalliferous marine placers and Palaeoproterozoic banded iron ores of the Superior type represent typical marine epicontinental shelf ore deposits.

The separation of continents by rifting and seafloor spreading may cut across older orogenic belts, cratons and other crustal-scale structures. With them, older ore provinces are ruptured and the fragments can be found on remote coasts across an ocean (e.g. the Atlantic borderlands of Africa and South America). In these cases, metallogenetic knowledge acquired on one coast is a valuable tool for work in its twin across the seas.

Seafloor spreading and the production of new lithosphere at mid-ocean ridges (oceanic-divergent, or "constructive" plate boundaries)

This is the domain of ore formation at mid-ocean ridges that was presented earlier in more detail (Section 1.1 "Ore Deposits at Mid-Ocean Ridges and in Ophiolites"). After obduction, the products of these processes are ophiolite-hosted deposits. Many ophiolites, however, were not formed at mid-ocean rifts but in tensional supra-subduction settings including back-arc spreading systems, or rifts of primitive island arcs (e.g. the Cyprus ophiolite). Yet, there is no doubt that all mid-ocean rifts display segments of hydrothermal activity, including black smokers. Related ores are sulphide mounds or mud-pools in a proximate position, iron-manganese oxides (ochres and numbers) and distal manganese crusts and nodules with important contents of Cu, Ni and Co. Oceanic transform faults that offset ridges are apparently not metallotects for mid-ocean metallogenesis.

Subduction of lithospheric plates at convergent ("destructive") plate boundaries

Subduction recycles oceanic lithosphere back into the mantle (Figure 1.88). The trace of subduction on the seafloor is marked by deep oceanic trenches. Volcanic arcs develop on the overriding plate. Between trench and arc, four structural zones are typically developed: Nearest to the

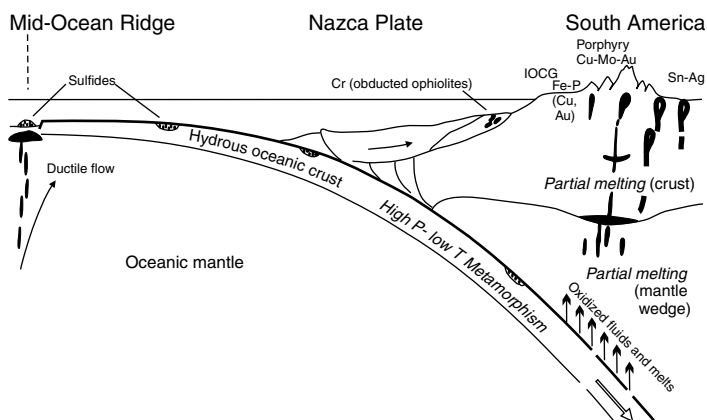


Figure 1.88 Metallogeny of active continental margins with the typical zonation, here illustrated by a schematic profile from the subducting Pacific Nazca Plate through the Central Andes (South America). Adapted from Sillitoe (1972, 2008).

trench (1) an accretionary complex of low-grade metamorphic sediments is followed by (2) a wedge of mainly continental crust with minor oceanic and hydrated mantle material of medium to high-pressure metamorphic grade. This is overlain by (3) a mega-scale melange composed of high-pressure and ultrahigh-pressure oceanic and continental crust fragments that are extruded from the subduction channel. Finally follows (4) the frontal part of the upper plate that carries the volcanic arc. Volcanic arcs in dominantly oceanic settings form island arcs, whereas active continental margins display continental or Cordilleran arcs. Recent primitive island arcs are geologically young (Tonga, Scotia), because maturation sets in quickly and produces arcs with a partially continental character (Japan, Kurile Islands). Other island arcs pass into continental collision belts (Sumatra-Malaysia-Himalaya). Andean volcanic arcs build upon older, strong upper crust that is largely of Precambrian age in both Americas. Behind the magmatic arcs appear back-arc spreading systems that include the back arc basins of island arcs, the continental “molasse” basins and broad distended regions such as the Basin and Range Province of North America.

There is a great diversity of subduction zone configurations, due to many variables including slab density, thickness and length (Schellart *et al.* 2007). Subduction zones show variously high or low trenchward plate velocities, trench retreat (or more rarely trench advance) velocities, slab dip angles and so forth. Trench retreat (“subduction rollback”) is caused by the negative buoyancy of the cold, dense descending slab. This places the overriding lithosphere into a state of tension as the subduction zone moves oceanwards and facilitates movement of magmas and fluids (Hamilton 1995). Slab rollback, slab breakoff and delamination of mantle lithosphere allow asthenospheric upwelling that can provide the heat pulses required for ore forming processes, including magmatism and regional hydrothermal fluid systems. Extensive intracontinental compressional deformation migrating cratonwards is explained by flat-slab subduction. This is probably caused by the subduction of oceanic plateaus and plume tracks (Livaccari *et al.*

1981), which typically ends in delamination (foundering) of the slab from the continental lithosphere. This is the environment of Basin-and-Range type tectonic and magmatic provinces (e.g. in Mesozoic South China: Li & Li 2007). Fertile anorogenic magmatism including alkaline basalts, bimodal volcanic rocks and I- and A-type granitoids are characteristic for this setting.

It is important to stress that most of the Earth’s richest ore provinces are found above subduction zones. This is conspicuously so along the margins of the Pacific Ocean, which are largely formed by long-lived destructive plate boundaries. Associated are numerous active volcanoes, accounting for the term “ring of fire”. Reconstruction of similar settings for stages in the geological past is crucial for strategic exploration planning (Haeberlin *et al.* 2003, Figure 1.84).

Island arc ore deposits may be either allochthonous, which implies tectonic transport, for example of slivers of oceanic lithosphere, or autochthonous, formed within the arc. Allochthonous are first of all the ophiolite-related ores, including chromite (Cuba, Luzon) and platinum placers; Cyprus type sulphide deposits are infrequent. Lateritic nickel ore deposits (New Caledonia) are autochthonous formations. Major autochthonous deposits are associated with the large mass of calc-alkaline to potassic intrusive and volcanic rocks. Of outstanding economic prominence are porphyry and skarn copper-gold deposits, epithermal gold deposits and volcanogenic massive sulphides. Similar to continental margin arcs, sources of the metals may be subducted oceanic crust or the mantle wedge above the subduction zone. The latter was confirmed for Lihir, Papua New Guinea (McInnes *et al.* 1999), which is a giant epithermal gold deposit of very recent geological age (ca. 690 ka). It is significant that some metals such as tin and mercury appear only in older, more complex island arcs with a partially continental character.

Active continental margin ore deposits are often more clearly zoned compared with island arcs, as a function of increasing distance from the subduction zone. In the apparently simple geotectonic setting of Central South America, the results are long and narrow ore provinces (Sillitoe 1972).

Prominent along the western coast within Precambrian basement and Cretaceous plutons are iron-apatite and iron oxide-copper-gold (IOCG) deposits associated with hydrous intermediate magmatism (Sillitoe 2003, Oyarzun *et al.* 2003). A belt of giant porphyry Cu-Mo-Au deposits follows towards the east, roughly along the Neogene-Recent volcanic arc. These mines currently dominate world copper production. Near the eastern margin of the Cordillera, a Sn-Ag belt is developed (Figure 1.88). However, neither this zonation nor all deposits in single belts are synchronous, but are the product of several regional metallogenetic episodes that range from Late Triassic (earliest tin deposits) to Cretaceous (iron and part of copper) and Tertiary ages (most of the copper and tin-silver). Subduction configurations during this time changed considerably (James & Sacks 1999).

The structure of the North American Cordillera is even more complex. One example is the subducting East Pacific Ridge, which is a factor that enhances metallogenetic processes. Partial melting of young, hot subducting oceanic plates favours the formation of oxidized adakitic magmas and of important gold and copper-gold deposits (Cooke *et al.* 2005, Mungall 2002). South Alaskan gold deposits are thought to be related to ridge subduction (Haeussler *et al.* 1995). Another difference is the collage-like nature of the North American Cordillera that consists of many "suspect" or "exotic" terranes, which preserved distinct but interrelated geological records (Colpron & Nelson 2006). This complicates metallogenetic interpretation.

Ore deposit formation above subduction zones is causally tied to the fate of the subducting lithospheric slab of oceanic crust and mantle. At mid-ocean ridges, the crust is largely hydrated and oxidized. When the oceanic slab bends before entering the subduction zone, additional hydration appears to take place (Faccenda *et al.* 2009). Altered basalts, gabbros and depleted mantle peridotites enter the subduction zone as a "cold" slab at geothermal gradients of 15°C/km or less. Along the subduction plane, continental material can be scraped off ("subduction erosion") and taken down to the zone of dehydration and melting. The high-pressure/low-temperature metamorphism of sub-

duction zones converts the rocks to the typical blueschist and eclogite lithologies. Mantle rocks, oceanic crust and its sedimentary cover incur devolatilization and possibly, partial anatexis. Dehydration processes control the structure of slabs from ca. 40 to 150 km depth (Rondenay *et al.* 2008). As a function of T and P, hydrous fluids, anatectic melts or supercritical liquids may be set free (Kessel *et al.* 2005). The latter are characterized by high trace element solubilities and consist of H₂O, Cl, S, CO₂, etc., including large ion lithophile elements (LILE: Ba, K, Rb, Cs, Ca, Sr) and other incompatible elements (U and Pb). This transfer "metasomatizes" the mantle wedge above the subduction zone and triggers widespread melting. Because of relatively high *f*O₂ (roughly from fayalite-magnetite-quartz [FMQ] to FMQ + 2) sulphide (S₂₋) and sulphate (S₆₊) coexist and combine to high total sulphur contents in melts, which favours sulphur saturation and mineralization in the upper crust (Jugo 2009). Extensive formation of sulphide melt during metasomatism and partial melting of the hot mantle wedge would be detrimental, because sulphide melts scavenge chalcophile and siderophile elements such as copper and gold from silicate melt and being heavy, tend to remain trapped in the deep crust (Mungall 2002).

Magma batches rising through the crust continue to change by complex assimilation and contamination processes, until they reach the surface as calc-alkaline melts of andesitic-dioritic nature. These magmas have only ~50% material from the mantle, the other half is derived from the crust. Intrusive and extrusive activity of continental arcs is concentrated in short pulses of 10–15 My ("flare-ups") that occur during and after tectonic shortening (Ducea & Barton 2007). Porphyry copper-molybdenum-gold deposits are direct products of these processes within and above the subduction zone (Richards 2003, 2009). Among many other arguments, this can be substantiated by the observation that localization and metal contents of porphyries are largely independent of their specific setting (e.g. primitive or evolved island arcs, diverse types of active margins). The precise source of the chalcophile metals and gold – oceanic crust or mantle wedge – remains obscure (Dreher *et al.* 2005). A continental source, however, is

implied for the metals tin, tungsten and tantalum, because deposits appear only in regions with thick and old crust.

Continental collision

Oceans that were consumed by subduction leave a suture in the newly welded continent, which is marked by ophiolites. One of the most remarkable and metal-endowed sutures worldwide is the Palaeozoic accretionary orogenic collage of the Altai in Central Asia, with a length of 3000 km (Xiao *et al.* 2009). Usually, continental collision results in the subduction of continental crust (Ampferer or A-subduction), although this is limited by the buoyancy of crustal rocks. The process results in thickened crust below collisional belts and the formation of anatectic S-type granitoid melts. Less frequent are post-subduction Cu-Au porphyries and related epithermal gold deposits, which are formed where former magmatic arcs are involved in the collision (Richards 2009). Continental crust of the lower plate can be subducted to depths of more than 100 km and exhumed after ultrahigh-pressure metamorphism. Also, collision causes giant systems of hydrothermal fluid flow involving metamorphic, basinal and meteoric fluids (Mark *et al.* 2007, Craw *et al.* 2002, Oliver 1986). Similar features are reported from intracontinental mountain belts involving very narrow oceans (Alps, European Variscan Belt) and from purely intracontinental orogens (Kibariides in Central Africa: Pohl 1994). Typically, collisional orogens exhibit: i) granitoid-related deposits of tin, tungsten, gold and rare metals; and ii) deposits formed by migrating metamorphic fluids. Gold is especially common in this setting (orogenic gold deposits: Groves *et al.* 2003). Mineralization in orogenic belts is favoured by phases of extension, because melts and fluids can more easily rise to shallow depths. Extension may be related to orogenic collapse and other post-collisional processes.

Assemblage and break-up of supercontinents

The plate-tectonic evolution of the Earth's crust follows not only the relatively short Wilson cycles (opening and closure of oceans) but also a

trend of large-scale cycles of amalgamation of all continental plates into supercontinents and the following break-up. The Phanerozoic supercontinent Pangaea is well-known, existing from the Permian into the Jurassic (~300–175 Ma). Mesoproterozoic Rodinia (~1100–800 Ma) is generally accepted but its assemblage is more contentious because data are insufficient for a unique solution (Torsvik 2003). Older supercontinents are even less well-defined. Supercontinents can be related to specific characteristics of the metallogenetic evolution, including the incidence of anorogenic ore formation (e.g. titaniferous anorthosite-ferrodiorite complexes) and the prevalence of continental, sediment-hosted deposits (Kupferschiefer: Robb 2005). When Gondwana and Laurasia finally fused into the supercontinent Pangaea, the Variscan belt in Europe experienced a short-lived metallogenetic peak of unique fertility. Deep processes inducing initial crustal distension and break-up of Pangaea, at about the Triassic/Jurassic boundary, again produced an ore-forming heat and fluid pulse across much of Europe (Box 1.14).

Apart from the relatively simple plate tectonic model situations described above, many quite complex interaction fields are known today. One recent example is the Gulf of California, where a subducted oceanic ridge passes along strike into a continental rift and ultimately into an intracontinental transform structure (San Andreas Fault). Only rarely, connections such as these can be reconstructed for the geological past so that the precise plate-tectonic setting of some ore deposits may never be fully understood. Yet, the quest for solving a given plate-tectonic puzzle is always scientifically fascinating and results benefit applications of economic geology.

1.8 GENETIC CLASSIFICATION OF ORE AND MINERAL DEPOSITS

We can get so wrapped up in debating terms that we forget entirely about the subjects of our original interest: minerals, rocks, geology, and such...

Stephen A. Langford in *GSA Today*,
February 2002

BOX 1.14 The metallogenetic evolution of Europe

The following sketch of Europe's metallogenetic evolution is intended to serve as an example that may have implications for other continents. Although the second smallest of all continents (after Australia), Europe is made up of crustal rocks of all ages, starting with an Archaean nucleus in the Arctic North. In the Mediterranean South, subduction and mountain-building are still active. A detailed description of single deposits and districts with their geological frame and with references is available in *Mineral Deposits of Europe* (Volumes 1–5, Bowie *et al.* 1979; Dunning *et al.* 1982, 1989; Dunning & Evans 1986; Ridge 1990). Emberger (1984) provides a succinct report on metallogenetic mapping in Europe. The regional geology of Europe is accessibly presented in the encyclopaedia by Moores & Fairbridge (1997). A geodynamic analysis of metallogeny provide Blundell *et al.* (2005).

Northern Europe (Scandinavia and adjoining Russia) and Northwestern Europe (The British Isles) are largely built of Precambrian and Early Palaeozoic rocks. Mountain belts formed in this time are deeply eroded, so that many preserved ore deposits are metamorphosed or metamorphogenic. The region comprises the Precambrian Baltic Shield and the Lower Palaeozoic Caledonides. In Northern Finland and Sweden, the Baltic Shield contains an Archaean nucleus with attached Proterozoic orogenic belts younging to the southwest, namely the Svecokareliides (ca. 2.0–1.54 Ga) and the Sveconorwegian Province (1200–850 Ma). The Archaean nucleus hosts greenstone belts with little notable mineralization. More prospective seems to be a belt of Ni-Cu-PGE mineralized layered mafic intrusions (Andersen *et al.* 2006), which appear to record a Palaeoproterozoic (2.44 Ga) rifting event. In contrast, the Svecokarelian (also called Svecofennian) belt is well endowed with important mines. Northern Sweden is renowned for “Kiruna-type” magmatic iron oxide-apatite deposits within bimodal metavolcanic rocks and also contains a number of recently discovered iron-oxide-copper-gold deposits (Weihed & Williams 2005). Further south, the Svecokareliides host a broad belt of volcanogenic sulphide ore deposits (Cu, Zn, Pb, Au, Ag, Ni, Co) that extend from Boliden in the Skellefte volcanic arc (Sweden) to Outokumpu-Pyhäsalmi (Finland) and further east to Lake Ladoga (Russia). The geological environment of ore formation included island arcs and oceanic rifting (Nironen 1997; Sundblatt & Parr 1994; Gaal 1990). Recently, exploration for diamonds (in the Archaean), for orogenic gold deposits (both in Archaean and Proterozoic units: Sundblatt 2003) and for platinum in mafic intrusions, resulted in a number of new mines and many promising prospects. Meso- to Neoproterozoic units are moderately mineralized. Only the orthomagmatic titanium ore of the Egersund District in southwest Norway (920 Ma) is of more than local significance. This region was part of the collision zone between Fennoscandia and Laurentia when the Supercontinent Rodinia was assembled.

The Caledonides are the largest metallogenetic domain of the region, with a length of 2700 km and a maximum width of 250 km. The belt resulted from convergence of Baltica and Laurentia, and final closure and suturing of Iapetus Ocean in the Silurian. The Caledonian orogen comprises metasediments and magmatic rocks of Eocambrian to Silurian age, and a large number of significant ore deposits (Grenne *et al.* 1999). During the early rift phase of its evolution (at ~550 Ma), the famous alkali-carbonatite complex at Fen in southern Norway was emplaced. This is the location where terms such as *fenite* and *søvite* were coined. Periodically, niobium, iron, thorium and cerium were produced from the Fen carbonatite. Volcanic-hosted massive sulphide deposits resembling the Cyprus type formed in back-arc rifts or in primitive island arcs. In Norway, they were important sources of copper and zinc (Figure 1.80). More recently, exploitable metamorphogenic gold deposits were found in Ireland, Wales and Scotland. Along the thrust front of the Caledonides in Sweden, a number of stratiform lead ore deposits occur in Early Cambrian platform quartzites. These galena impregnation deposits of the “Laisvall type” are thought to be derived from metamorphic fluids, which were mobilized from autochthonous and parautochthonous sediments under the eastward advancing Caledonian nappe sheets. In the Middle and Late Cambrian in Sweden, the platform sediments include oil shales (“alum shales”) that represent giant potential resources of synthetic oil, uranium, vanadium, phosphorous, molybdenum and nickel. A “Late Caledonian” phase (~350 Ma) of alkaline intrusions is expressed by the Sokli carbonatite in Finland, exploited for apatite (with by-products niobium and rare earth elements).

The Oslo Graben is an important magmatic, tectonic and metallogenetic rift province in southwest Norway. It is considered here because of its location, although its active phase dates from the Carboniferous and the Permian. The Oslo Graben Province displays remarkable silver and base metals veins (Kongsberg, Figure 1.22), molybdenum impregnations in granite and felsic volcanics, and iron skarn ore. Of about the same age is the alkali ring intrusion of Khibiny on Kola Peninsula (Russia) with its important apatite and nepheline resources.

Central Europe and large parts of Southwestern Europe are underlain by rocks of the Late Palaeozoic Variscan orogen, although large areas are covered by younger platform sediments. Regions near the Mediterranean Sea are shaped by the later (Mesozoic-Cenozoic) Alpine orogeny.

The European Variscides are a complex mosaic of Precambrian microcontinents and of Palaeozoic orogenic belts that were finally welded together and deformed by the Variscan orogeny in the Late Carboniferous (Tait *et al.* 1997).

The Variscan chain in Europe is part of the 10,000 km collisional zone suturing Gondwana and Laurasia when the Rheic Ocean closed to form Supercontinent Pangaea. The development of the Variscan orogen involved major crustal shortening and subduction of substantial amounts of supracrustal rocks, continental and oceanic crust, and mantle lithosphere. Yet, ophiolites derived from Palaeozoic oceanic lithosphere are rare and contain little economic mineralization. Marginal to the region considered in this chapter, however, large ophiolites are present in the Ural Mountains, hosting deposits of chromite, platinum and base metal sulphides (Herrington *et al.* 2003). Silurian submarine hot-spot volcanism is probably the crucial metallotect of the unique and giant mercury deposit Almadén in Spain (Figure 1.89). Large synsedimentary ore deposits were formed during extensional tectonics in Devonian marine strata of the Rhenohercynian shallow sea (volcanogenic iron ore and sedex type zinc-copper-lead sulphides with barite, e.g. Rammelsberg, Germany). Still in a tensional setting during the Early Carboniferous of southern Spain and Portugal, volcanic massive sulphide (VMS) and brine pool sedex deposits in shale constitute the giant massive sulphide ore province of the Iberian Pyrite Belt with pyrite, copper, tin, lead, zinc and gold (Figure 1.89). At about the same time, the syngenetic-diagenetic Irish zinc-lead-silver deposits formed in a shallow sea. Peak synkinematic and synmetamorphic processes during the Variscan orogeny were not fertile. However, giant coal deposits formed from forest mires at tropical latitudes during the Westphalian (Late Carboniferous), located in foreland and intramontane basins of the Variscan orogen. The coal belt in Europe has an east-west extension of ~3000 km and a north-south width of 800 km (Ziegler 1982).

Following the orogenic peak, regional exhumation and post-collisional collapse of the Variscides was strongly affected by transtensional and transpressional wrench-deformation, detachment of subducted lithospheric slabs, asthenospheric upwelling and thermal thinning of the mantle-lithosphere. At ~300 Ma (Stephanian-Early Permian), when Gondwana and Laurasia finally sutured to form Pangaea, the deep-reaching disturbance of the Variscan domain reached its climax with widespread melting of the uppermost asthenosphere and the lithospheric boundary layer. Mantle-derived basic melts underplated the crust, inducing anatexis and the intrusion of granites in the upper crust throughout the Variscides. The most evolved, and youngest phase of these granites was highly fertile: Tin and copper deposits were formed in Cornwall, tin, tungsten, bismuth and uranium ore in the Erzgebirge (Baumann *et al.* 2000, Breiter *et al.* 1999, Stemprok & Seltnann 1994), tungsten, tin, uranium, arsenic, lithium and fluorine in the French Massif Central, tungsten in the Pyrenees, and tungsten (Panasqueira) and tin in Portugal (Figure 1.89). At the same time, C-O-H-N fluids were released from the deep crust that deposited orogenic gold-arsenic-antimony ores in the French Massif Central. It is thought that the reason for this short-lived late-orogenic “metallo-genetic peak” was devolatilization of the lower crust by granulite metamorphism (Marignac & Cuney 1999).

In the late Early Permian, magmatism ceased and increasingly larger areas subsided below the erosional base level forming a new system of intracratonic basins. Terrestrial and coastal sediments of the Rotliegend desert sediments contain several deposits and numerous occurrences of uranium. In the Late Permian (Zechstein), the giant salt deposits of Germany, Poland and England formed in a restricted sea, which invaded the desert basins of Pangaea from the north. Potassium salt resources of this basin are second only to those of Canada. The Copper Shale stratum at the base of the transgressive marine Zechstein evaporites is evidence of an early euxinic stage; along the southern basin margins, it trapped epigenetic copper concentrations emplaced in the Triassic. The end of the Permian brought the biggest mass extinction of life in geological history, with the loss of ~95% of all species. Its cause is generally believed to be the eruption of the Siberian and South Chinese Emeishan trap basalts (Kamo *et al.* 2003).

Announcing the break-up of Pangaea, a new Wilson cycle started with crustal distension in the Triassic, which culminated near the Triassic/Jurassic boundary with the formation of a giant magmatic province resembling trap basalts in the later Central Atlantic Ocean (Olsen 1999). This initiated opening of the Tethys and the Atlantic Ocean, and induced a heat and fluid pulse across much of Europe. Copper Shale ore deposits were emplaced as well as numerous karst and vein deposits of Pb-Zn-F-Ba (e.g. Poland: Sass-Gustkiewicz 1996; Germany: Walther 1983). The deposits are located both in Variscan basement (e.g. Schwarzwald, Massif Central) and in the Mesozoic cover from Poland to Spain. Mesozoic, mainly marine sediments of the platform rocks contain oil and natural gas deposits, oil shale and sedimentary oolitic iron ore (Lorraine district in France).

In the Mesozoic and Cenozoic, Alpine and Mediterranean Europe was part of the giant Tethyan-Eurasian metallogenetic domain, which is the product of convergence, subduction and collision of Eurasia with fragments of Gondwana. European Alpine chains include the Pyrenees, the Alps, the Apennines, the Carpathians, the Balkan Mountains, Dinarides, Helennides and Caucasus. Along the convoluted trace of the orogen, the geodynamic character changes from segments with major calc-alkaline magmatism to segments with extensive regional metamorphism. This is attributed to the complex geometry of the collision interface, with numerous microplates and transient oceans (Heinrich & Neubauer 2002). Orogenic compression including formation of the great nappes (thrust sheets of thick rock bodies that moved many kilometres over each other) culminated in the Late Cretaceous and the Early Tertiary. Palaeozoic, and even Precambrian rocks are either part of the nappes or form the basement of microplates. They contain some mineral deposits

that are clearly older than the Alpine cycle. Other deposits in pre-Alpine rock units originated during the Alpine metallogenetic cycle (e.g. the large metasomatic siderite deposit Erzberg in Austria and orogenic gold-quartz veins in gneisses of the Eastern and Western Alps).

Pre-Alpine basement rocks that are exposed within the Alpine belts allow the reconstruction of a protracted plate tectonic evolution throughout the Palaeozoic, including ocean subduction and the obduction of ophiolites. Some important pre-Alpine mineral deposits in the basement are: i) granite-related tungsten stockwork orebodies at Mittersill (Tauern, Eastern Alps); and ii) sparry metasomatic magnesite lenses in the Eastern Alps and in the Carpathians. The second is clearly different from the Variscan north of the Alps, but the first recalls the rare metal metallogeny of the German Erzgebirge.

In Alpine and Mediterranean Europe, widespread extensional tectonic strain and heating in Mid-Triassic to Early Jurassic time are related to the break-up of Pangaea and caused a major metallogenetic pulse (Jankovic 1997). In the Balkans, associated volcanism is implied in formation of the exhalative iron ore strata at Vareš (Bosnia), the rift-bound mercury deposit of Idria (Slovenia) and a number of lead-zinc deposits. The large lead-zinc deposits in the Southern Alps (e.g. Bleiberg, Mežica) formed in a shallow marine rift zone distal to volcanic activity. Larger oceanic basins existed mainly in the Jurassic and were closed in the Cretaceous. Obducted ophiolites in the Balkans host important chromite mineralization. Cyprus type sulphides are rare and have little economic relevance. Alpine ophiolites are largely barren, from the Eastern Alps to the Pyrenees.

With the inception of the Cretaceous, the tectonic regime in the Alpine realm changed to subduction and convergence. From Romania through Serbia to Bulgaria, arc magmatism is represented by a Late Cretaceous (90–60 Ma) ore-bearing igneous belt, which is referred to as the Banatitic Metallogenetic Belt (or, geographically, the Apuseni-Banat-Timok-Srednogorie belt; Heinrich & Neubauer 2002). Banatites are calc-alkaline intermediate intrusive and extrusive igneous rocks of I-type and magnetite series character. The belt extends for ~750 km with a width of 30–70 km. Copper-gold porphyry and high-sulphidation epithermal gold-copper deposits occur from the Timok district in Serbia (e.g. Bor and Majdanpek) in the west to Bulgaria (Panagyurishte district) in the east. Iron-lead-zinc skarn ore deposits (including Ocna de Fier in Romania; Nicolescu *et al.* 1999) and smaller deposits of iron, molybdenite and bismuth are also considered as legacies of this magmatic metallogenetic belt.

In the western Carpathians (Slovakia) and in the Eastern Alps (Austria), Cretaceous magmatic activity is practically absent. Instead, the onset of continental collision and subduction induced a pervasive flow of metamorphic fluids that produced metamorphogenic deposits of siderite (Erzberg), talc (Rabenwald), and smaller deposits of copper and barite (Pohl & Belocky 1999, Figure 1.90). Coal seams in Late Carboniferous sediments were metamorphosed to exploitable graphite.

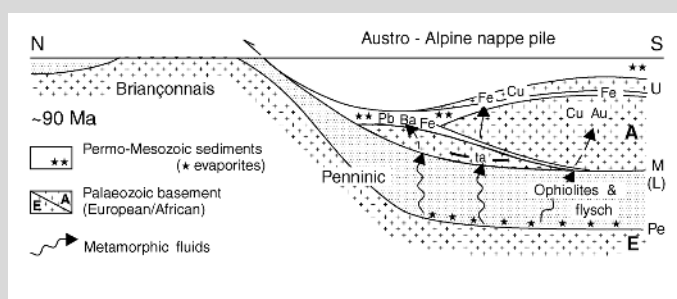


Figure 1.90 Metamorphogenic ore formation in the European Eastern Alps. During peak conditions of metamorphism in the Turonian (Late Cretaceous), dehydration affected deeper parts of the nappe pile including Penninic autochthonous cover, oceanic crust and marine sediments with evaporite horizons. ta – Talc at Rabenwald, Pe – Penninic nappes, L-M-U – Lower, Middle and Upper East Alpine thrust sheets.

Intermittent emersion of wide regions of the European and African plates allowed the formation of supergene alteration deposits, most famously bauxite in southern France (Les Baux is the name-giving district), Hungary, Italy and Greece, and nickel laterites in Albania and Greece. Cretaceous convergence between African and European plates caused a wave of compressional deformation in the northern foreland of the Alps ("inversion tectonics"), which can be demonstrated even in North Sea oilfields over 1000 km distant.

In the Early to Mid-Tertiary, major continental blocks collided in the Eastern and Western Alps (Neubauer *et al.* 2000). This led to extensive Barrovian-type regional metamorphism, commonly preceded by an eclogite-facies stage. During the following orogenic collapse and rise of high-grade metamorphic domes, numerous small orogenic gold vein deposits were formed (Monte Rosa, Tauern). Giant lignite basins developed in Germany and Poland, mainly in the Eocene-Oligocene.

Also in the Early to Mid-Tertiary, oceanic sub-basins in the Inner Carpathians and the Apuseni Mountains closed, continental microplates indented into the evolving orogen, and slab break-off and mantle delamination caused asthenospheric incursions (Heinrich & Neubauer 2002). De Boorder *et al.* (1998) suggested that orogenic collapse and slab rupture caused the heat and fluid flow responsible for the subsequent (mainly Miocene) mineralization. In the Apuseni Mountains, gold and base metal ores are related to localized centres and short belts of Tertiary andesitic and rhyolitic volcanism (Neubauer *et al.* 2005). For thousands of years until today, this region was the source of much of the gold produced in Europe. In the Inner Dinarides and the Rhodope Mountains, lead, zinc and antimony deposits occur in similar settings. This magmatic and ore formation style extends into Greece and the Greek islands, where it lasts longer (into the Pliocene and locally, into the Holocene) and where manganese, barite and gold gain a more central role. In Western Europe, Tertiary mineralization includes skarn deposits of magnetite and haematite on the island of Elba, above a granite cupola that intruded Mesozoic sediments some 6 Ma ago. Across the sea in Italy, volcanogenic deposits in the Toscana include epithermal mercury at Monte Amiata. In southern Spain near Almeria, andesitic and rhyolitic volcanoes host epithermal deposits of gold, silver, lead and zinc (Rodalquilar, Figure 1.89). Messinian evaporites along the Mediterranean shores are exploited for gypsum, sulphur, rock salt and potassium salts. The giant strontium deposit at Montevives in the Sub-Betic zone of southern Spain is especially remarkable.

In the Late Tertiary and the Holocene north and west of the Alps, a broad mantle plume caused basaltic volcanism (Goes *et al.* 1999) of little metallogenetic significance. The plume is related to the large crustal break that traverses Europe from the mouth of the River Rhone to the Oslo Graben in Norway. The Upper Rhine Rift is a section of this structure and is endowed with historically important hydrothermal lead-zinc-silver ore veins in the rift shoulders (Figure 1.28), and with oil and gas deposits as well as potassium salt beds in the Tertiary graben fill.

In spite of this reminder that terms and classes are not the first target of science, efforts towards classification are both necessary and useful. Classifications are needed because they clarify terms and provide a common reference frame, and this makes them useful for scientific communication and practical application. Various geological aspects are employed to classify ore deposits, including the presence of certain metals or minerals (e.g. silver, haematite), the form of the orebody (vein, bed, etc.), the local geological environment (submarine or terrestrial volcanism), the plate tectonic setting (island arc, continental margin) and other genetic characteristics such as formation temperatures and fluid chemistry. The thoughts of Lindgren (1933), Niggli (1948) and Schneiderhöhn (1932, 1962) represent important stages of metallogenetic classification. Because ores and useful minerals are basically just rocks, although usually rare ones, a petrogenetic approach is obviously practicable. Main petrogenetic process systems are magmatism, sedimentation, diagenesis, meta-

morphism and surficial weathering (Figure 1.1). Parallel to other classification systems in science, these five main classes are the root for a branching order of subclasses. Apart from petrogenesis, criteria for ordering often include the local, regional and plate tectonic situation.

However, a stringent genetic classification of mineral deposits is very difficult. One reason for this is that many ore deposits represent a position in a complex multi-dimensional space of well-defined end members. The formation of Kuroko ore deposits, for example, is an interplay of volcanic, intrusive, sedimentary and diagenetic processes. The origin of high-grade BIF-haematite ore seems to comprise sedimentation induced by proliferating marine life, later passage of saline basinal brines and supergene components. May I remind the reader that already Charles Darwin (1859) described lucidly how impossible it is for the naturalist to define species, families and genera of plants and animals only by structural differences. Darwin states "All true classification is

genealogical". Ore deposit classification is certainly not easier than establishing biological systems and should also aim for a genetic logic.

Scientific progress continuously modifies and improves genetic models. An ever more detailed understanding of ore-forming processes is the result (Robb 2005). Some practitioners of exploration and mining think little of genetic models and

prefer a pragmatic and empirical classification. Many scientists employ non-genetic terms of classification, such as "granite-related" or "sediment-hosted stratiform" deposits. Economic geologists use terms such as "deposit styles" (Hough *et al.* 2007) or "deposit types" (Cox & Singer 1986; e.g. copper porphyry type, orogenic gold, lateritic nickel). Attribution to certain styles and types is

Table 1.6 A simple genetic classification of ore deposits

I. Magmatogenic Ore Deposits

1. Orthomagmatic Deposits:

Sulphide Fe-Ni-(Cu-PGE) ore hosted by Archaean komatiites and subvolcanic ultramafic intrusions; Alpine type Cr-PGM in ophiolites, and seams in layered mafic intrusions; Cu-Ni-PGM "reefs" in layered mafic intrusions; complex mafic-ultramafic intrusions with, for example, conduit-hosted Cu-Ni-PGM; impact magma bodies with Ni-Cu-PGM; Ural-Alaska type ultramafic ring intrusions with Cr-PGM; Ti-Fe in Mesoproterozoic anorthosite-ferrodiorite complexes; orthomagmatic iron ore deposits of iron oxides and apatite in intermediate to felsic igneous rocks (Kiruna type); apatite-Fe-Nb-Zr, or REE-U-F in carbonatite plugs and nephelinite intrusions

2. Pegmatites with ore of Be, Li, Rb, Cs, Ta (Nb), U, Th, REE, Mo, Bi, Sn and W, industrial minerals, gemstones

3. Magmatic-Hydrothermal Deposits:

Skarn ore, with magnetite-Cu-Co-Au, W, Zn-Pb-Ag, Mo-Bi-Au and Sn-As-Pb-Zn-W-Mo; contact-metasomatic ore (Pb, Ag, Zn); Fe-oxide-Cu-Au (U-REE) deposits (IOCG); porphyry deposits (Cu-Mo-Au, Sn-W); submarine volcanogenic (Kuroko) and volcanic-hosted massive sulphide deposits (VMS); vein deposits (Sn, W, Cu); terrestrial epithermal Ag-base metal deposits; epithermal Au-Ag deposits

II. Supergene Ore Deposits

1. Residual (Eluvial) Deposits:

Residual placers (e.g. W, Sn); bauxite; lateritic Au, Fe and Mn ore deposits

2. Supergene Enrichment Deposits:

Enriched sulphide ore (Cu, Ag); lateritic Ni

3. Infiltration Deposits

U in sandstone; Pb-Zn-F-Ba and Mn in karst cave systems

III. Sedimentary Ore Deposits

1. Allochthonous:

Colluvial, alluvial (gold, columbite, cassiterite, wolframite, platinum) and coastal (rutile, ilmenite, zircon, monazite) placers

2. Autochthonous:

Sulphide deposits, mainly in black shales; polymetallic deposits of Cu-Sb-Zn-Pb-Ag (-Au), mostly of sedex type; Palaeoproterozoic banded Fe ore (BIF) of Algoma and Superior type, and banded Mn ore; oolitic Fe and Mn ore; deep sea manganese nodules and crusts (Mn-Cu-Ni-Co-PGM)

IV. Diagenetic-Hydrothermal Ore Deposits

1. Stratabound and/or stratiform sediment-hosted Cu deposits:

European Copper Shale (Cu); Central African Copper Belt (Cu, Co, Pb, Zn, U)

2. Mississippi Valley type (MVT) Pb-Zn-F-Ba deposits (hosted in marine carbonates)

3. Saline brine-related deposits

Pb-Zn-F-Ba, metasomatic siderite, preconcentration of high-grade hematite

V. Metamorphosed and Metamorphic Ore Deposits

Metamorphism of pre-existing ore generally improves processing characteristics of ore, but is rarely a factor of metal accumulation and ore formation; metamorphic examples include *in situ* redistribution, concentration and recrystallization of gold

VI. Metamorphogenic-Hydrothermal Ore Deposits

Prograde and retrograde metamorphogenic-hydrothermal ore deposits (e.g. orogenic Au deposits in accretion-subduction-collision complexes; part of the Central African Cu-Co ore deposits; Cu in Mt Isa, Australia).

determined by descriptive attributes and relations to certain rock associations (e.g. “turbidite-hosted gold deposits”, “alkaline igneous association”—Laznicka 1985, 1993). In this book also, descriptive terms are frequently used. The advantage is that short denominations facilitate communication and that changes of genetic understanding do not enforce new terms. Also, this solves the problem of classifying deposits of intermediate position between genetic end members. Yet, genetic concepts are a strong element in finding new ore deposits (Kreuzer *et al.* 2008), guide rational exploitation and mine closure. Therefore, genesis must be reflected in ore deposit classification.

Guilbert & Park (1986) admirably describe the problems of ore deposit classification but nevertheless argue for the exercise, in spite of shortcomings. In this spirit, I endeavour to provide a simple genetic classification that should help the reader to understand the logic of this chapter's arrangement. As a general rule, the geological setting and the last concentrating process (e.g. sedimentation) determine placement in a certain class, for example formation of metalliferous sediments by hydrothermal fluids venting from the seafloor resulting in sedimentary exhalative (sedex) deposits. In Table 1.6, ore deposit groups and types presented in Section 1.1 are listed with the intention to summarize the genetic panorama. In Chapter 3, a similar overview is provided for selected non-metallic minerals and rocks.

1.9 SUMMARY AND FURTHER READING

Ore formation is an integral component of the Earth's dynamics and of petrogenetic process systems. Ore deposits, however, typically result from the interaction of several processes and modifying factors. Reducing the complexity to simple end member concepts leads to the following shortlist of genetic variety.

Orthomagmatic ore deposits of metal oxides (magnetite, ilmenite, chromite), sulphides (Ni, Cu) and of precious metals (Pt, Pd, Au) are formed by the segregation of solid ore minerals or of ore

melt from a large liquid silicate magma body. Gravitational settling of segregates is the basic concentrating factor (Boxes 1.1 and 1.2).

Metalliferous pegmatites originate by fractionation of volatiles (water, boron, fluorine) and rare metals (Be, Li, Rb, Cs, Ta, Sn) into the very last silicate melt batches of crystallizing parental granites.

Magmatic-hydrothermal deposits are formed from metal-enriched magmatic volatile phases which are released by solidifying magma bodies. Copper porphyry systems (Box 1.3) provide economically outstanding examples. Note the great variety within this class, including skarn (e.g. Cu, Zn-Pb-Ag, Mo, Bi, Au) and contact-metasomatic deposits, Fe-oxide-Cu-Au (U-REE) deposits (IOCG), and tin, copper and tungsten veins in the roof of parent intrusions (Box 1.4). Whereas the former are related to intrusive and subvolcanic magma bodies, volcanic-hosted massive sulphides (VMS, Box 1.5) and epithermal gold and silver deposits (Box 1.6) originate near the surface in volcanic centres, either beneath the sea or on land.

Supergene ore deposits result from weathering, which describes the interaction of Earth materials with air, water, life and the energy flow from the sun. During decomposition of rocks, metals are concentrated either *in situ* as an insoluble residuum (e.g. bauxite) or by precipitation after some movement in soil and ground water (e.g. lateritic nickel deposits: Box 1.7). Lateral transport distances of 1 to 100 km characterize infiltration deposits of some metals such as copper and uranium (Box 1.8).

Sedimentary ore deposit formation is foremost the product of exogenous process systems with physical and chemical transport in water. Part of the metals moved is concentrated in rivers (alluvial placers, e.g. Au) and along coasts (coastal placers, e.g. Ti). Most enter the marine realm in aqueous solution from the land or from hydrothermal sources underneath the seafloor. The world's largest metal concentrations formed in the Early Proterozoic when photosynthetic cyanobacteria expanded rapidly, oxidizing the seawater and precipitating iron dissolved in the oceans (banded iron formations; Box 1.9). Many giant base metal deposits (sedimentary-exhalative, “sedex” Cu, Pb, Zn)

are the product of hot metalliferous fluids venting on the seafloor. In contrast to mid-ocean black smoker activity, sedex deposits are formed by rifting in shallow epicontinental seas (Box 1.10).

Diagenetic ore deposits are a consequence of physical and chemical changes affecting basinal sediments. With rising temperature and pressure, pore fluids are charged with dissolved matter and eventually are expelled towards lower pressure regions, commonly basin margins where metals are precipitated. Traps are often low-permeability barriers, which is evident for the most valued products of diagenesis, oil and natural gas. Low permeability and reducing power of the European Copper Shale acted together in concentrating metals transported by oxidized brines (Box 1.11). Worldwide, reduced brines, which resemble reservoir water in oil pools, generated numerous diagenetic carbonate-hosted Pb and Zn deposits (Box 1.12).

Metamorphism affects previously established metal concentrations in two different ways. One group of minerals such as sulphides of Cu, Pb and Zn hardly changes and we call this class metamorphosed ore deposits. Other materials that are only valuable because of transformation into an exploitable ore (e.g. originally dilute traces of gold concentrated by *in-situ* redistribution) may be called metamorphic ore deposits.

Prograde metamorphic recrystallization of large rock volumes liberates a giant mass of dehydration fluids, which transport trace metals into shallow crust where chemical and physical traps precipitate ore (e.g. orogenic gold deposits); this is the prograde metamorphogenic class (Box 1.13). Cooling metamorphic massifs are flooded by surface water, which induces hydration and re-equilibration of high-grade metamorphic rocks. Where

tectonic fragmentation provides sufficient permeability, hydrothermal convection systems are established that produce retrograde metamorphogenic deposits (Box 1.13).

Metallogeny is the synthesis of scientific endeavours to understand ore formation. Plate tectonics provide the unifying frame. The world's most prolific metallogenetic domains include supra-subduction island arcs and continental margins (e.g. the Pacific "ring of fire"). The Bushveld in southern Africa, however, with its giant resources of Cr, Pt and V, and many other large ore districts of the world are not related to subduction.

Europe, briefly described as an example of metallogenetic evolution (Box 1.14), is one of the smallest continents and yet provides a fascinating diversity of metallogenetic activity throughout geological history. It can be seen as an assemblage of orogenic belts younging southwards from an Archaean nucleus in the North. Along its Mediterranean margins, subduction, volcanism and ore-forming processes are still active.

For readers who wish to pursue the theme of ore-forming processes to greater detail, Robb (2005) is highly recommended. The present state of the science of economic geology is illustrated and described in the impressive *Economic Geology 100th Anniversary Volume* (Hedenquist *et al.* 2005); be aware, however, that the treatment is selective and at a highly demanding scientific level. An admirable insight into the complexity of ore-forming systems gives Sillitoe (2010) in his paper on "Porphyry copper systems". For details on single deposits and districts, search the extensive and systematic descriptions of thousands of ore deposits worldwide by Laznicka (1985, 1993). Global tectonics is comprehensively presented by Kearey, Klepeis & Vine (2009).

