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.
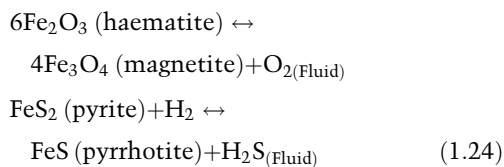
It is possible to distinguish another class of mineral deposits from metamorphosed ores and minerals, a class that owes its economic interest to largely isochemical metamorphic re-equilibration and recrystallization of pre-existing material which had no use in its original state. Examples provide alumina-rich 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 ~750°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:

$$6Fe_2O_3 \text{ (haematite)} \leftrightarrow$$
$$4Fe_3O_4 \text{ (magnetite)} + O_{2(Fluid)}$$
$$FeS_2 \text{ (pyrite)} + H_2 \leftrightarrow$$
$$FeS \text{ (pyrrhotite)} + H_2S_{(Fluid)} \qquad (1.24)$$

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 suprasubduction 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
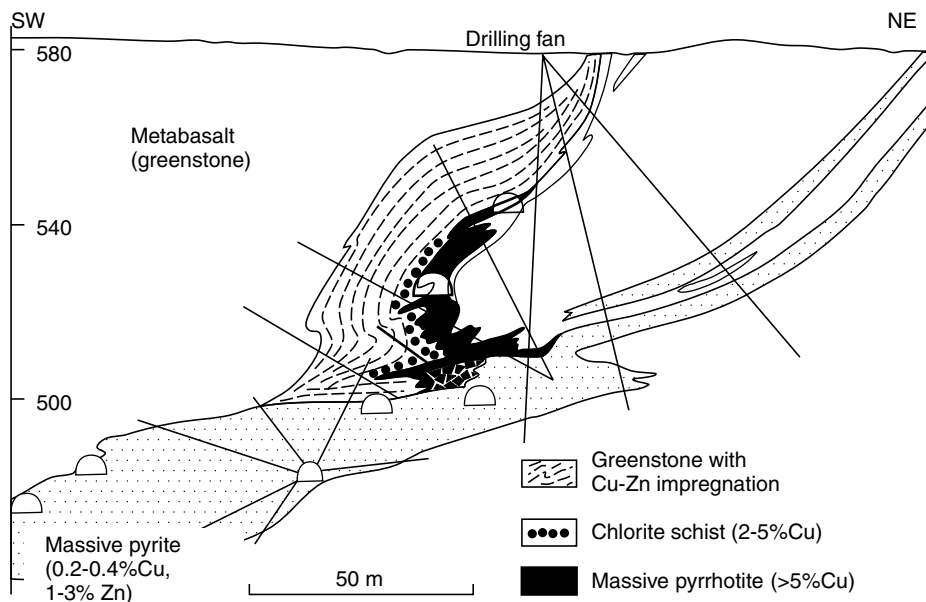

Figure 1.80 Section of Joma Cu-Zn mine in metabasalt northeast of Trondheim, Norway (Bowie *et al.* 1978). Reproduced with permission of The Institution of Mining and Metallurgy, the Mineralogical Society of Great Britain & Ireland and Maney Publishing www.maney.co.uk. This is an instructive example of orogenic, synmetamorphic deformation of massive sulphide orebodies. Note the drill pattern collared from the surface and from underground mine adits.
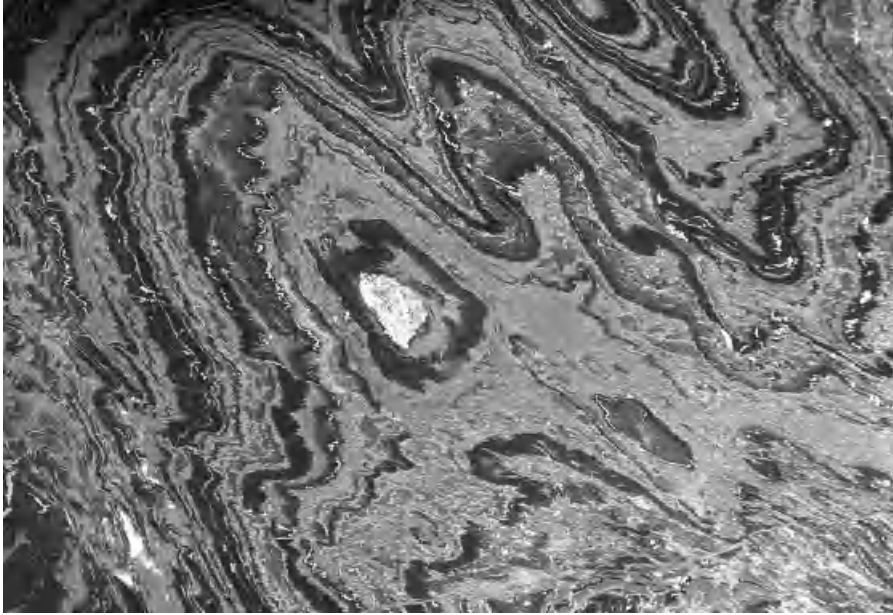
Figure 1.81 (Plate 1.81) Ductilely folded sedimentary bedding in very-low-grade metamorphic shale-banded Fe-Cu-Zn sulphide ore with wispy white dolomite laminae. Note the diffuse axial plane cleavage. Sample from the closure of the orebody synform, Rammelsberg, Germany. Width of image ~20 cm. Courtesy 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 premetamorphic 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 CO_2 and converts into magnetite or, in the presence of silica, to fayalite (Fe_2SiO_4).

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 ($>250°C$) and chalcopyrite ($>300°C$), 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 (± *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 anatectic 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 Ophtalmia 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 metamorphogenic 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 mobilizates 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 mobilizates, 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.
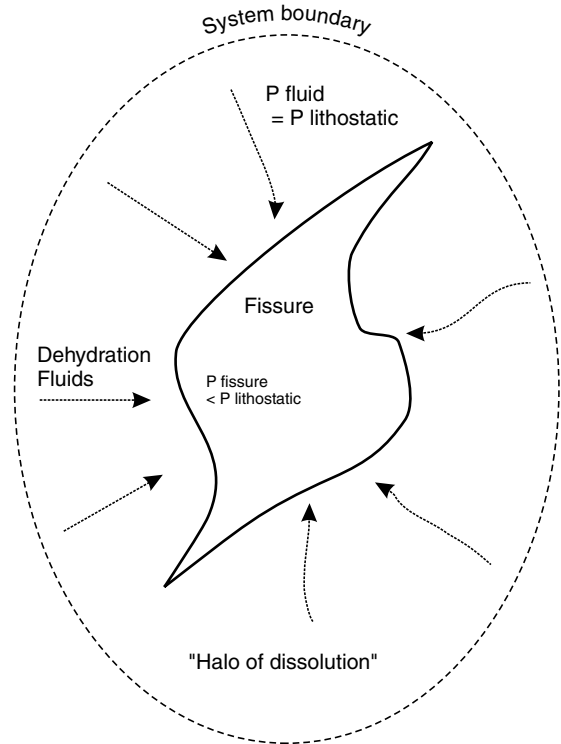
Figure 1.83 Principles of lateral secretion. Changes in the orogenic stress field lead to opening of a fissure. The resulting pressure gradient ($P_{fissure} < P_{lithostatic}$) enforces flow of metamorphic fluids into the fissure where minerals precipitate. The system is closed within narrow limits ("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
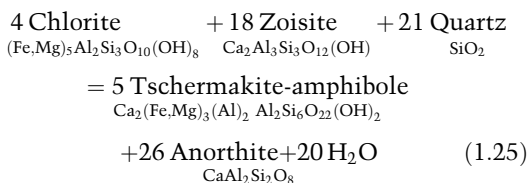
hydrothermal alteration of the wall rocks. Also, veins are surrounded by trace-metal halos with contents increasing as the vein is approached. Changes of this kind can only be explained by the influence of migrating fluids that have passed through the system. They originated in deeper parts of the orogenic 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 $\sim$90 kJ per 1 mol H_2O (Bucher & Frey 2002). Shales contain $\sim$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 calcsilicate 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:

$$4 \underset{\text{(Fe,Mg)}_5\text{Al}_2\text{Si}_3\text{O}_{10}\text{(OH)}_8}{\text{Chlorite}} + 18 \underset{\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}\text{(OH)}}{\text{Zoisite}} + 21 \underset{\text{SiO}_2}{\text{Quartz}}$$

$$= 5 \underset{\text{Ca}_2\text{(Fe,Mg)}_3\text{(Al)}_2 \; \text{Al}_2\text{Si}_6\text{O}_{22}\text{(OH)}_2}{\text{Tschermakite-amphibole}}$$

$$+ 26 \underset{\text{CaAl}_2\text{Si}_2\text{O}_8}{\text{Anorthite}} + 20 \, H_2O \qquad (1.25)$$

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. $\sim$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, expulsed 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

Eoalpine 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 expulsed 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
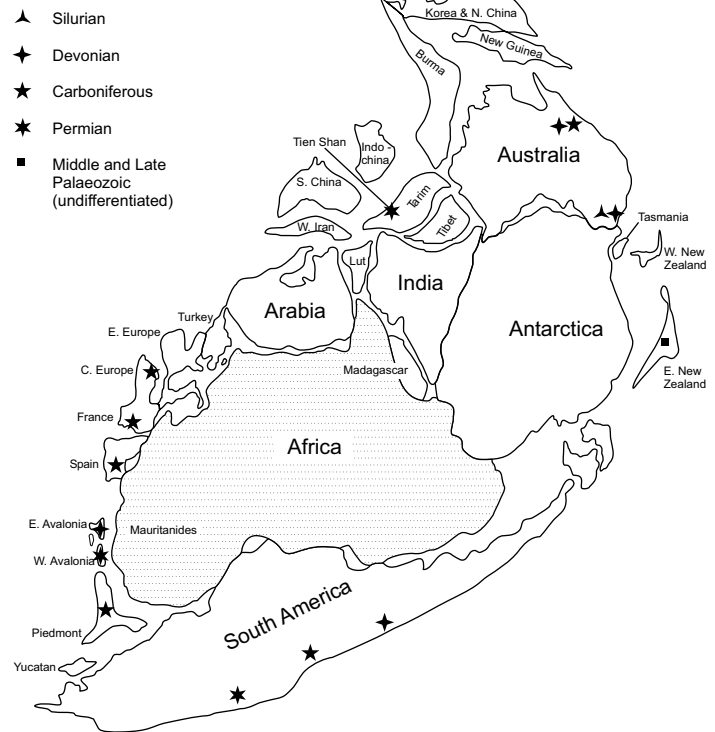

Figure 1.84 Large gold ore provinces formed in the Middle to Late Palaeozoic within Gondwana and adjacent plates (adapted from Haeberlin *et al.* 2003 with permission from Elsevier). Active continental plate margins controlled the location of gold ore formation, illustrating the term "orogenic gold deposits".

BOX 1.13   Two end member models of metamorphogenic ore formation

1. Prograde metamorphogenic ore formation. Normally, metamorphic fluids are expulsed 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 ($\sim$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.
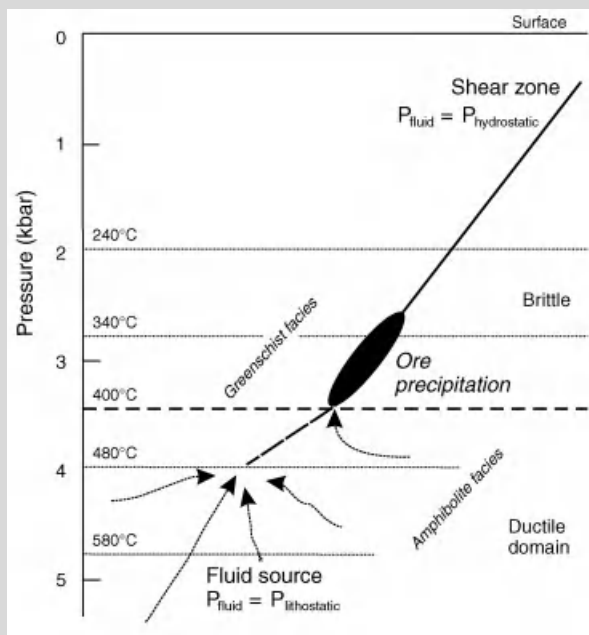

Figure 1.85 Ore deposit formation by prograde metamorphism. A shear zone focuses upflow of metamorphic fluids because of higher permeability. Its crustal-scale vertical extent facilitates transfer of fluids from lithostatic to hydrostatic pressure domains. Ore formation is a consequence of chemical or 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.
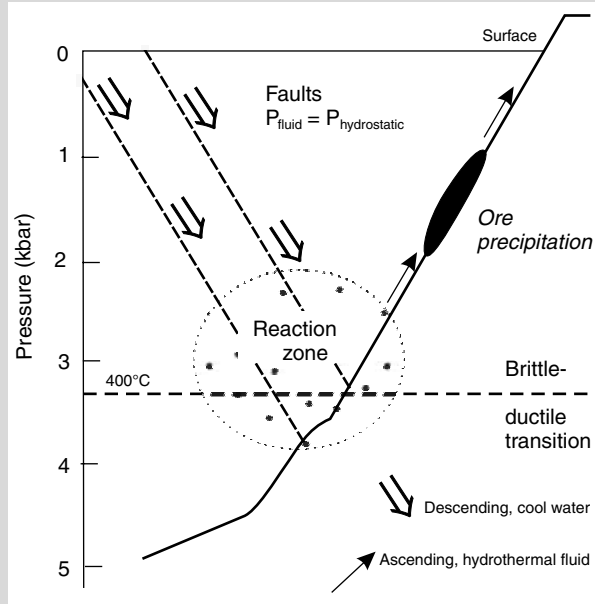
An instructive concept of ore formation during late-metamorphic cooling processes was described from the Scottish Dalradian belt (Craw & Chamberlain 1996). Infiltrating meteoric water induced an oxidation front that migrated through the orogenic body and facilitated leaching of trace gold. The gold was 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