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 minerogenesis. In sedimentology, soils are also considered as autochthonous sediments. However, ore deposits related to soil formation processes were presented in the preceding section.
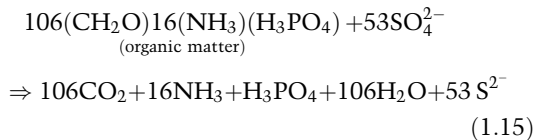
Many metalliferous sulphide, oxide, carbonate and sulphate deposits originate by autochthonous sedimentation following hydrothermal exhalation, precipitation of solutes and deposition of ore particles on the seafloor. *Sensu stricto*, all ores with this origin are "sedimentary". However, the different 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 anoxigenic 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:

$$\underset{\text{(organic matter)}}{106(CH_2O)16(NH_3)(H_3PO_4)} + 53SO_4^{2-}$$
$$\Rightarrow 106CO_2 + 16NH_3 + H_3PO_4 + 106H_2O + 53\,S^{2-}$$
$$(1.15)$$

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.
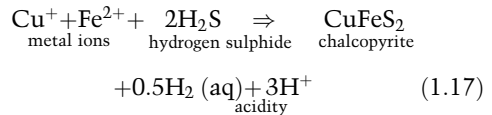
Anaerobic microbial sulphate reduction and concurrent methane oxidation:

$$SO_4^{2-} + CH_4 \Rightarrow HS^- + HCO_3^- + H_2O \qquad (1.16)$$

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:

$$\underset{\text{metal ions}}{Cu^+ + Fe^{2+}} + \underset{\text{hydrogen sulphide}}{2H_2S} \Rightarrow \underset{\text{chalcopyrite}}{CuFeS_2}$$
$$+ 0.5H_2\,(aq) + \underset{\text{acidity}}{3H^+} \qquad (1.17)$$

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 synsedimentary to early-diagenetic pyrite, favouring the production of significant amounts of H_2S 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 syngenesis) 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 fluviatile 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, fluviatile 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 transport, 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 reconcentrated 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).
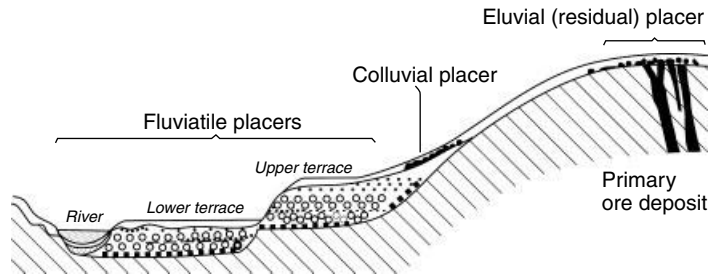
conglomerates (see below). Saxton *et al.* (2008) confirmed experimentally that high-grade longitudinal pebble to cobble bar systems trap gold during their formation from fast-moving suspension flows. Many alluvial placers in mountain stream valleys comprise the whole volume of the valley fill (Figure 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 practician 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
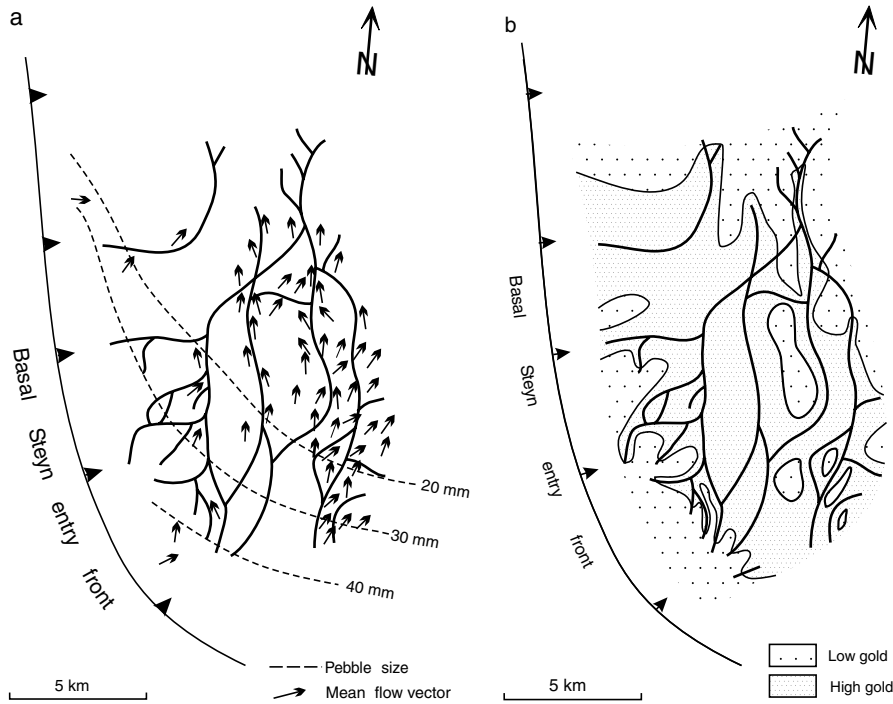
Figure 1.65a,b Facies control of gold deposition in the braided alluvial fan complex of the Basal and Steyn Reefs in the Steyn Mine, West Rand Goldfields, South Africa (after Minter *et al.* 1986). Courtesy Geological Society of South Africa.

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 transgressional 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 subrosion. 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
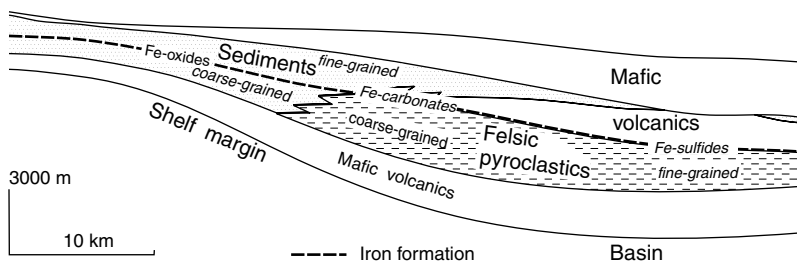

Figure 1.66 Stratigraphical context and facies zones of an Algoma Type volcanogenic iron formation in the Archaean Michipicoten Basin, Canada. Modified from Goodwin, A. M. 1973, Society of Economic Geologists, Inc., *Economic Geology* Vol. 68, Figure 2 p. 919.

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 $Fe(OH)_3$ and nontronite (near landmasses, oxic conditions), or precursors of magnetite, siderite and greenalite $[(Fe)_{2\text{-}3}Si_2O_5(OH)_4]$ (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 [(Fe,Mg)$_3$Si$_4$O$_{10}$(OH)$_2$], stilpnomelane, asbestiform amphiboles and many other Fe-rich silicates. Primary ores have an Fe$_2$O$_3$/SiO$_2$ ratio of 0.98–1.26, typically 25–45 wt.% Fe, <3% each of Al$_2$O$_3$, 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 Si(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:

$$2Fe^{2+} + 0.5O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 4H^+ \tag{1.18}$$
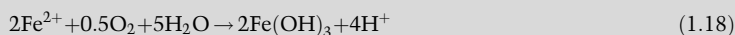
Many scientists support the following hypothesis: "The atmosphere may have been nearly free of oxygen, while the oxygen in the oceans started to increase. Seasonal blooms of the earliest photosynthetic micro-organisms (cyanobacteria) increased oxygen concentration in seawater that oxidized and precipitated 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 O_2-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 $\sim$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 PO_2 continued to rise, Mn^{2+} was oxidized to Mn^{3+} 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 ($\sim$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 (Otjosondu). 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. oxic, 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 crosscutting 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. Sturesson *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 (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 (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 associated 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 palaeosoil 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 Eylant, 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,
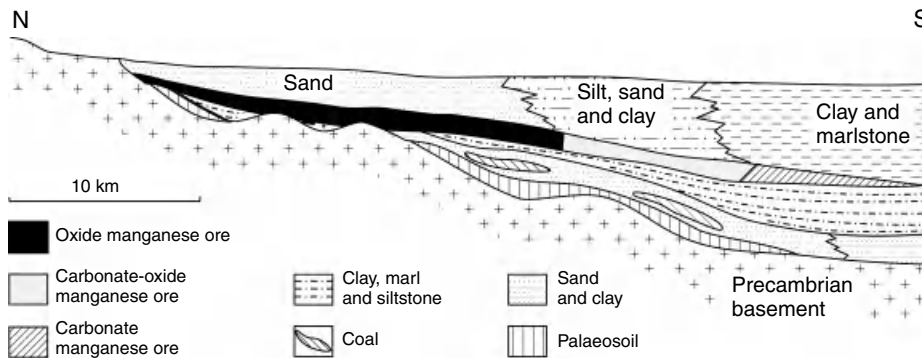

Figure 1.69 Generalized section of facies zones in the Eocene-Oligocene marine-sedimentary manganese horizon in southern Ukraine (adapted from Varentsov & Muzylev 2001).

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:

$$CH_4 + 4MnO_2 + 7H^+ \rightarrow HCO_3^- + 4Mn^{2+} + 5H_2O$$
(1.19)
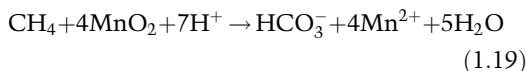
This process leads to enrichment of anoxic deep water with dissolved manganese (Mn^{2+}) while iron and other easily reduced metals are precipitated by hydrogen sulphide. Interaction of the Mn-enriched deep water with oxygen-rich marginal zones induces precipitation of Mn oxides, especially during transgressive phases (Roy 1992). This situation is demonstrated by the recent Black Sea with its high Mn^{2+}/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-SiO$_2$ 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% SiO$_2$ (Lenoble 1996). Minor contents of other
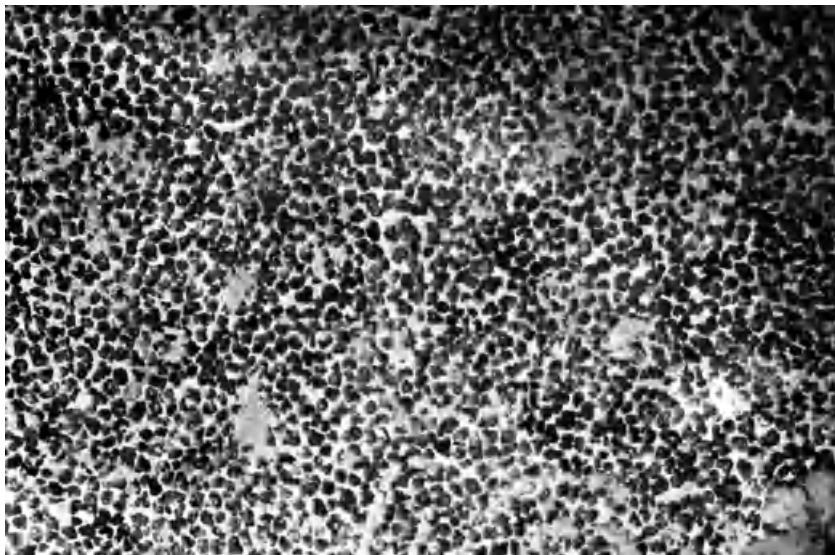

Figure 1.70 Seafloor aspect of polymetallic manganese nodules in the Clarion-Clipperton-Zone (CCZ) of the Central Pacific. The density is here about 20 kg/m². Individual nodules have diameters of 3 to 5 cm, the matrix is radiolarian ooze. Courtesy P. Halbach (FU Berlin).

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 oxihydroxides. 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, H_2S 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 (SiO_2, 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
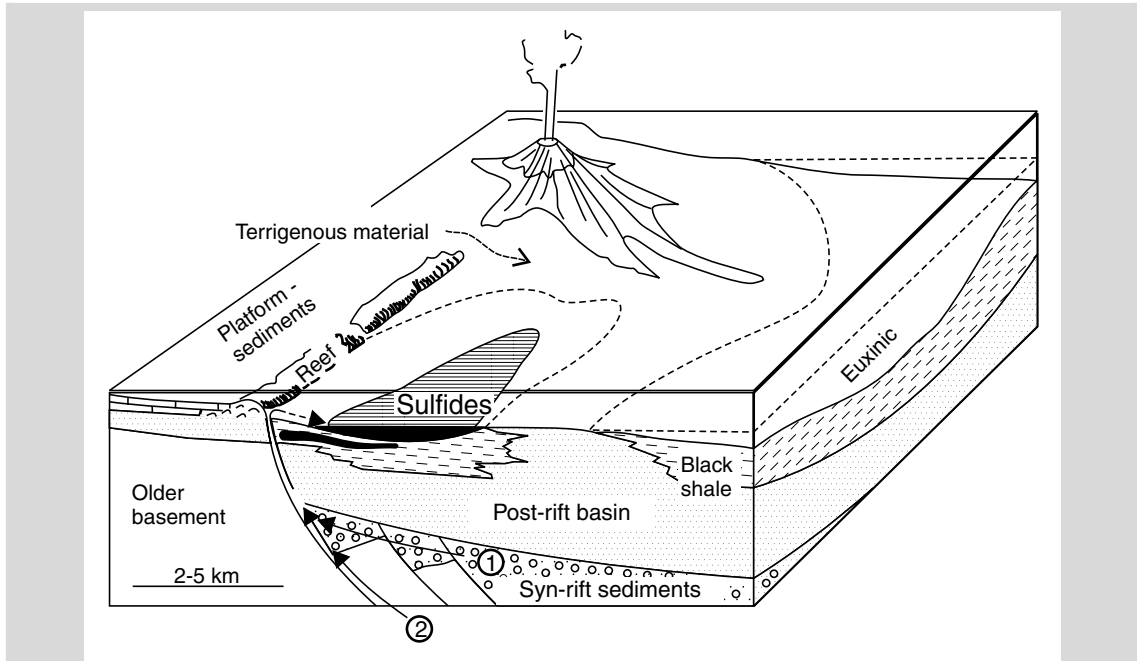
Figure 1.71 Schematic sketch of the geological setting of an exhalative-sedimentary (sedex) sulphide (-barite) ore deposit in a black shale basin. Note distal rift-related basaltic and felsic volcanic centres.
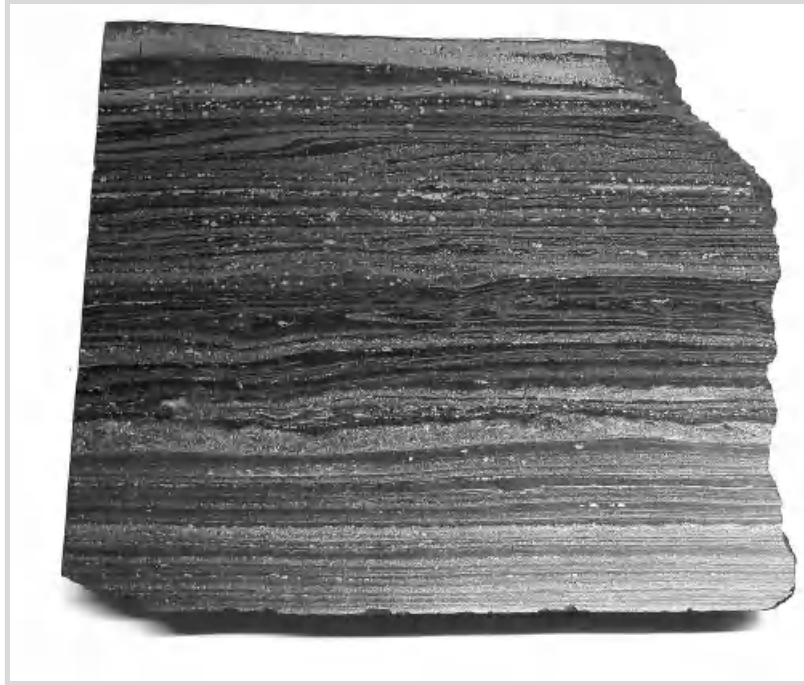

Figure 1.72 (Plate 1.72) Undeformed shale-banded copper-zinc dominated sulphide ore from Rammelsberg sedex deposit (Germany) displays ductile soft-sediment deformation and cross-lamination. Width of image ~20 cm. Courtesy B. Lehmann, Clausthal.

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 μm), 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 ~125 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 63g/t Ag.

Structures and textures of sedex ores confirm the synsedimentary 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 syngenesis 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).
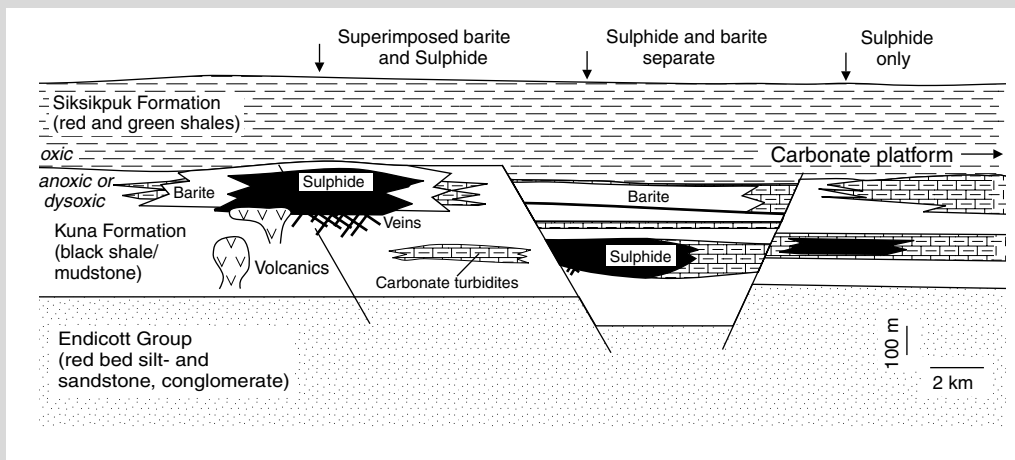

Figure 1.73 Horst-and-graben architecture of the Late Mississippian Brooks Range Basin, Alaska, hosting the giant Red Dog Zn-Pb-Ge-Ag massive sulphide (and barite) sedex deposits. Modified from Kelley, K.D. & Jennings, S. 2004, Society of Economic Geologists, Inc., *Economic Geology* Vol. 99, Figure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

ppm (parts TDS per million TDS+H_2O)

mg/L (milligrams per litre)

$$= \text{ppm/density (mg/cm}^3) \qquad (1.20)$$

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
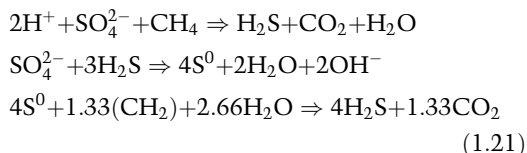
by flowing upwards and to the margin of sedimentary basins. Drilling for hydrocarbons revealed that water in sediments frequently attains temperatures of more than 100°C and reaches a maximum of about 300°C. By reacting with rocks, the "formation water" acquires a high content of dissolved matter. Where 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 HCO_3, 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 H_2S. 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 CH_4 (and CO_2) 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 CO_2 (Childers *et al.* 2002). In the absence of microbes,

for example at higher temperature (>80°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):

$$2H^+ + SO_4^{2-} + CH_4 \Rightarrow H_2S + CO_2 + H_2O$$
$$SO_4^{2-} + 3H_2S \Rightarrow 4S^0 + 2H_2O + 2OH^-$$
$$4S^0 + 1.33(CH_2) + 2.66H_2O \Rightarrow 4H_2S + 1.33CO_2$$
$$(1.21)$$

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).
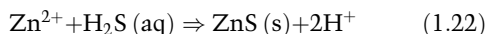
Not all basinal fluids are reduced, and oxidized formation waters are commonly enriched in SO_4. This is possible when the source rocks include predominantly haematitic sandstone and mudrock, limestone, anhydrite and halite, for example in the Rotliegend (Permian) desert and salt lake sediments of Northern 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.
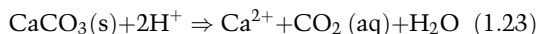
Metal uptake in the source region (reaction zone) or along flow paths is a function of kinetic and thermodynamic factors, including rock and water chemistry, T, P, Eh and pH. In contact with formation waters, several common minerals are unstable, including amphibole, pyroxene, olivine and epidote. Their 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:

$$Zn^{2+}+H_2S\,(aq) \Rightarrow ZnS\,(s)+2H^+ \qquad (1.22)$$

Dissolution of calcite:

$$CaCO_3(s)+2H^+ \Rightarrow Ca^{2+}+CO_2\,(aq)+H_2O \quad (1.23)$$

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 rhythmites" (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
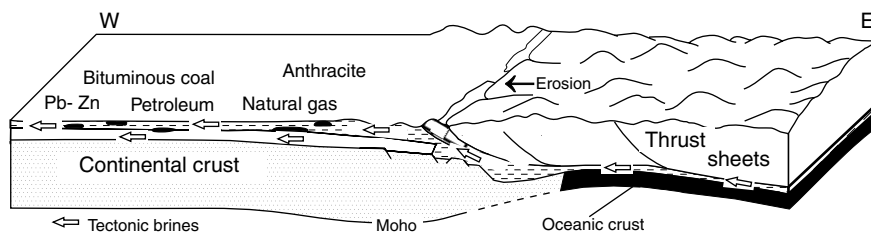

Figure 1.74 Expulsion of fluids ("tectonic brines") towards the foreland from underneath the west-moving nappe pile of the Appalachian Mountain Belt (modified from Oliver 1986).

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 $600,000 \, km^2$. 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 H_2S. Continent-derived clastic sediment import was very

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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 (Fe^{2+} 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, Al_2O_3 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).
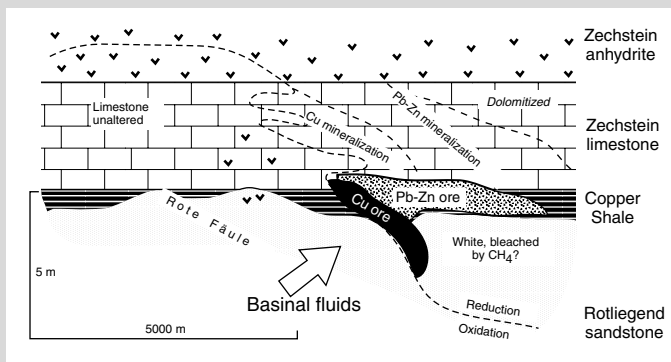

Figure 1.75 Schematic section of a Copper Shale deposit in Northern Germany and Poland (modified from Jowett 1992 with permission from Elsevier).

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 synsedimentary 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 $\delta^{34}S$ 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 $\delta^{18}O$ between 3 and 6‰, and δD from −10 to +3‰, 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 Bonneterre Formation and dolomites with shale beds.

Most orebodies occur in the Bonneterre Formation within an offshore stromatolitic reef that separates a micritic-clayey basinal 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.
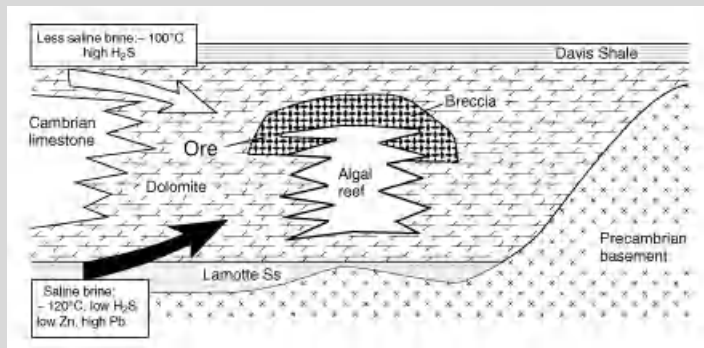
Figure 1.77 Simplified genetic model of the Pb-dominated deposits of Mississippi Valley Type (MVT) in the Viburnum Trend, Missouri. After Plumlee, G.S., Leach, D.L., Hofstra, A.H., Landis, G.P., Rowan, E.L. and Viets, J.G. 1994, Society of Economic Geologists, Inc., *Economic Geology* Vol. 89, Figure 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 km^2. 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 CaCl$_2$; 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/cm^3.
• 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.
• CH$_4$ 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 (H$_2$S-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 ^{87}Sr. 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).

Metallogenetic 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