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Lower Carboniferous stratiform iron-manganese mineralizations (Rheinisches Schiefergebirge, Germany): products of submarine hydrothermal activity and diagenetic manganese redistribution

Hermann Huckriede
Institut und Museum für Geologie und Paläontologie, Goldschmidtstr. 3, D-37077 Göttingen, Germany

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Abstract

Lower Carboniferous iron-manganese ores of volcanic-sedimentary origin occur in the eastern part of the Rheinisches Schiefergebirge (Germany). Major constituents are rhodochrosite, bementite, hematite, and quartz. The ores are only weakly metamorphic and exhibit excellently preserved primary textures and fossils. Metamorphic equivalents of these ores are the manganese deposits of the Iberian Pyrite Belt.

Most strikingly, the iron-manganese ores show a clearly developed zonation. Positions of former hydrothermal vents are indicated by chert mounds which are intersected by vertical pipes of coarse-grained hematite. The chert mounds are covered and surrounded by beds of fine-grained hematite. Manganese ore forms the distal part of each deposit.

The formation of the ores was controlled by complex interactions of hydrothermal activity, intrusive and extrusive volcanism, formation of intramagmatic sulphide ores as well as diagenetic redistribution of certain elements: SiO_2, copper, nickel, and iron were mobilized due to hydrothermal alteration of basic subvolcanic intrusive rocks. Copper and nickel were mostly re-deposited as sulphides within the intrusives, whereas manganese, iron, and SiO_2 were transported by hot convecting waters to the sea floor. Here, SiO_2 and the dissolved metals were precipitated by mixing with oxygenated sea water. Subsequently, manganese was separated from iron by diagenetic reactions. Enrichments of cosmic spherules and conodonts indicate that this process required a long time.

Introduction

Lower Carboniferous manganese ores are widespread in central and western Europe. They are known from the Iberian Pyrite Belt (Hoyer 1911, Schütz 1985), the Betic Cordillera (Leyva et al. 1986), the French Pyrenees (Lougnon 1956, Pélissonier 1965, Boyer et al. 1974), and from the Rhenohercynian Zone in Germany (Riemann 1878, Schneider 1888, Hummel 1923, Haage 1964, Burchardt 1970, Schaeffer 1980).

At the end of the nineteenth and at the beginning of the twentieth century, several deposits were mined, but only those of the Iberian Pyrite Belt were of appreciable economic importance. Previously, most investigators believed in a volcanic-sedimentary origin of these deposits (Burchardt 1970, Leyva et al. 1986, Schaeffer 1980, Schütz 1985). However, results of a recent re-examination of many occurrences of Lower Carboniferous manganese ores in central and western Europe support a different view. Most deposits are restricted to the same narrow stratigraphic horizon, are low in iron, and reveal no sign of volcanic influence. Their origin can be explained by simple geochemical processes occurring within black-shale basins (Huckriede 1994). Only some deposits in the eastern part of the Rheinisches Schiefergebirge (Germany) and the manganese ores of the Iberian Pyrite Belt (Spain) are different: they are intimately associated with basic submarine volcanism, rich in iron, and often excellently zoned.

The ores of the Rheinisches Schiefergebirge are only weakly recrystallized because of the very low-

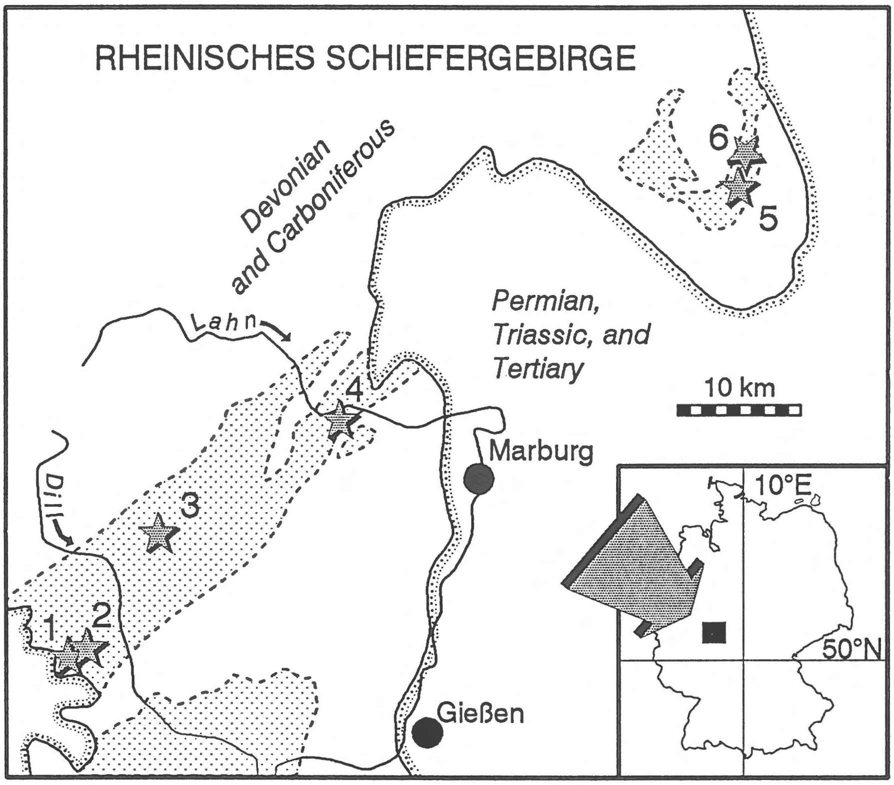

Figure 1. Occurrences of Lower Carboniferous volcanic-sedimentary iron-manganese ores in the eastern part of the Rheinisches Schiefergebirge, Germany. Dotted areas: Lower Carboniferous basic volcanic rocks. 1 = Hörbach (abandoned mine 'Freiherr Hugo') N 50° 40.22′ E 08° 15.45′ 2 = Hörbach (abandoned mine 'Damelfeld') N 50° 39.65′ E 08° 15.05′ 3 = Nanzenbach (Herrnberg): N 50° 46.12′ E 08° 21.98′ 4 = Carlshütte (Hohenfels): N 50° 51.64′ E 08° 35.18′ 5 = Bergfreiheit (Kleine Leuchte): N 51° 02.79′ E 09° 05.36′ 6 = Braunau (Lennkopf): N 51° 03.88′ E 09° 06.42′.

grade metamorphism in this region. Therefore, relicts of primary textures and well-preserved fossils occur within the ores. The discovery of feeding channels through which hydrothermal waters reached the sea floor, and the presence of very fossiliferous manganese ores which are also rich in cosmic spherules, raise questions concerning the origin and depositional environment of these mineralizations.

One general problem concerning the origin of volcanic-sedimentary manganese ores is the mechanism of separating manganese from iron. Since iron oxides precipitate first in an increasing Eh-gradient, manganese tends to be dispersed farther than iron from the submarine exits of hydrothermal passageways. Therefore, separation of manganese from iron should be rapid and contemporaneous with hydrothermal activity. However, enrichment of cosmic spherules within Lower Carboniferous manganese ores indicates a very low rate of sedimentation which is not expected in volcanic-sedimentary deposits. A solution to this problem will be presented in this paper.

As part of an extensive re-examination of Lower Carboniferous manganese ores in central and western Europe, numerous manganese deposits in the Rheno-Hercynian area were systematically sampled. Selected localities were mapped at a scale of 1 : 10 000. Volcanic-sedimentary deposits in the eastern part of the Rheinisches Schiefergebirge (Figure 1) were studied most intensely since primary textures are best preserved in this region. Today, few exposures of ore beds are accessible; therefore most samples had to be collected from waste piles of abandoned mines. Occurrences in the Iberian Pyrite Belt (between Riotinto and Calañas, province of Huelva) and in the French Pyrenees were studied for comparison.

The ores and their host rocks were examined by X-ray powder diffraction, polarization microscopy and ore microscopy. Ages are based on conodont stratig-

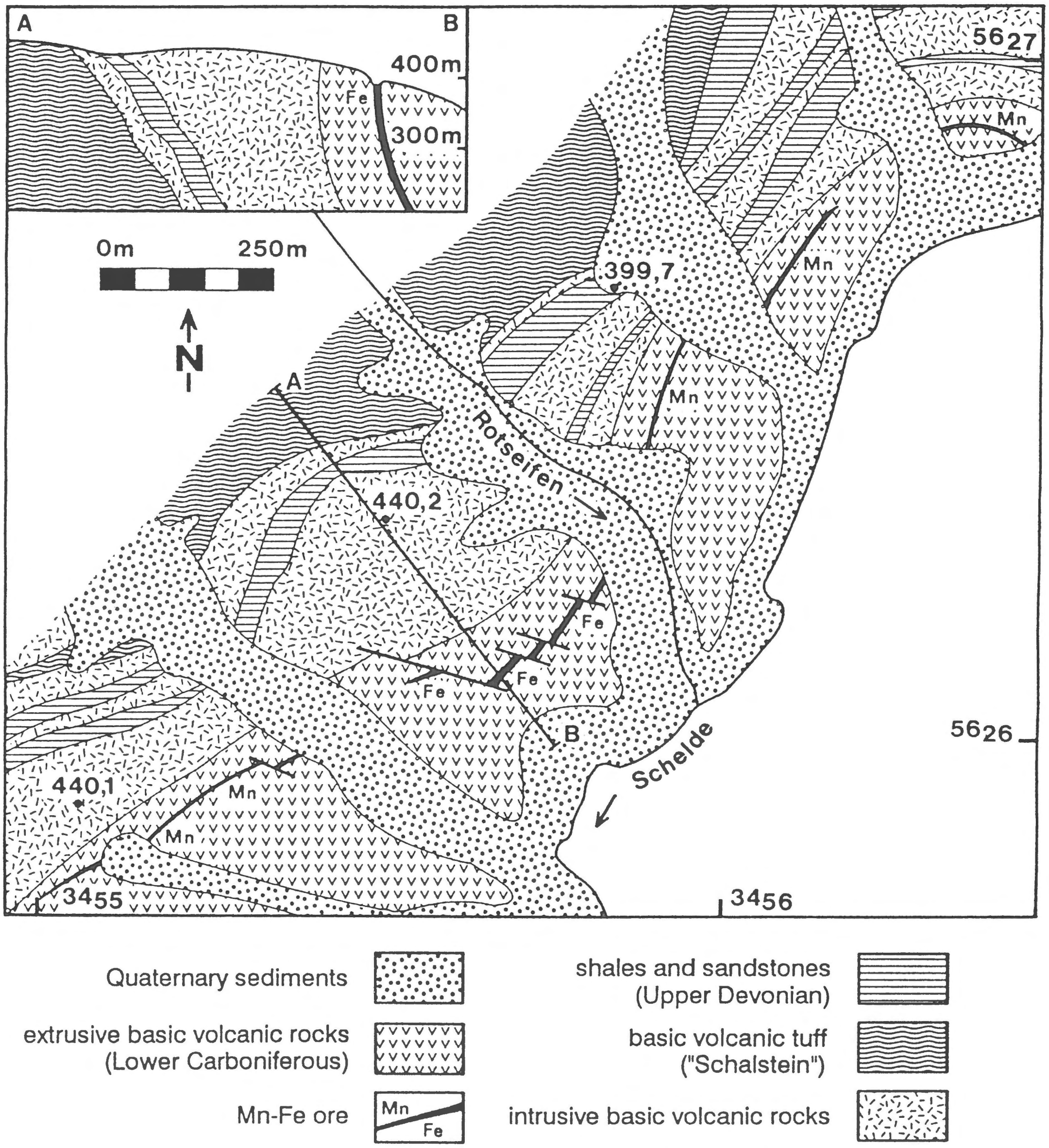

Figure 2. Geological setting of the iron-manganese ore bed at Nanzenbach.

raphy. Stable carbon and oxygen isotopes were determined by Michael Joachimski (Erlangen) using standard methods.

Manganese ores of the Rheinisches Schiefergebirge

Geological setting

The depositional environment of Lower Carboniferous volcanic-sedimentary ore deposits in the Rheinisches Schiefergebirge is characterized by an association of basic volcanic rocks (mostly spilites) with pelagic sediments (cherts and black shales). Ophiolites indicating oceanic crust are not present. This Lower Carboniferous volcanic-sedimentary complex is underlain by several hundred metres of Devonian slates and sandstones. During the Variscan orogeny, ores and host rocks were folded and weakly metamorphosed. The maximum degree of metamorphism is marked by mineral associations of the pumpellyite-prehnite facies (Herrmann & Wedepohl 1970).

The largest ore deposits are located within the Dill syncline near Nanzenbach and near Carlshütte. The other occurrences are very small, or are strongly weathered. However, they share many features with the deposits of Nanzenbach and Carlshütte and there is no doubt about similarity in origin.

The outcrop of the Nanzenbach ore bed can be mapped over a distance of 1800 m (Figure 2). Thicknesses of the ore bed vary from a few centimetres in the periphery to 8 m in the central part. The average strike is SW-NE, the dip 60 to 80° NW. The deposit is interbedded with spilitic basaltic effusives ('Deckdiabas'). Locally the base of the ore bed is marked by a thin layer of Lower Carboniferous black shales and cherts ('Alaunschiefer'). The Lower Carboniferous rocks are underlain by Upper Devonian sandstones and shales which are intruded by up to 250 m thick spilitic basalt sills and dikes ('Intrusivdiabas').

The central part of the ore bed has a length of approximately 250 m and consists of siliceous hematite ore. Massive hematitic cherts ('Eisenkiesel') with a thickness of some decimetres or metres are intercalated locally. Previously this part of the ore bed has been ascribed a late Middle Devonian to early Upper Devonian age (Krebs 1960). However, conodonts of the genus *Siphonodella* prove a Lower Carboniferous age. The south-western and north-eastern parts of the ore bed consist of manganese ore with only minor hematite intercalations. The manganese ore is about 1.5 m thick at maximum; the thickness decreases more or less continually towards the periphery.

The Carlshütte ore bed can be traced over a lateral distance of 1200 m at the western slope of the Hohenfels mountain (Figure 3). The ore bed dips 20° SE and consists predominantly of fine-grained red hematite ore up to 1.5 m thick. The ore is hosted by a sequence of submarine spilitic extrusive basalts and tuffs of Lower Carboniferous age. Like in the Nanzenbach ore bed, a thin layer of black shale marks the base of the ore bed, and the Lower Carboniferous rocks are underlain by Upper Devonian sandstones and shales which are frequently intruded by basaltic sills and dikes.

The hematite ore can be studied best within the galleries of the former iron mine 'Hachthal'. Here, mounds of massive hematitic chert are scattered within the ore bed (Figure 4). These chert mounds reach a diameter of up to 20 m and a maximum height of 4 m. Locally they are intersected by vertical dikes of black, coarse-grained hematite which are some centimetres up to 1 m thick. The surface of chert mounds is covered with bulges up to 10 cm high. These structures and numerous shrinkage cracks within the chert possibly indicate a former jelly-like consistency. Maximum thicknesses of fine-grained hematite ore occur at the margins of the chert mounds; towards the top and with increasing distance from the mounds the ore thickness decreases. The uppermost one or two centimetres of the hematite ore bed are rich in manganese. Pure manganese ore is restricted to the northern part of the deposit. Here, manganese-rich ores reach a thickness of up to 0.5 m whereas hematite ores and chert mounds occur only exceptionally.

Hydrothermal alteration is mostly restricted to the underlying spilites. Within the Carlshütte deposit, zones of argillaceous alteration concentrate below chert mounds. Most probably, they are connected with the veins of coarse-grained hematite intersecting the chert mounds, and are parts of the hydrothermal passageways through which the metalliferous fluids once were transported to the sea floor.

Most of the manganese and iron ores from Nanzenbach and Carlshütte are more or less distinctly bedded or laminated; only in some of the samples the sedimentary structures are disturbed or folded by sliding. Locally, massive manganese-rich debris flows intercalate with bedded manganese ore. These debris flows reach a maximum thickness of 15 cm, are rich in volcanic clasts and in randomly oriented conodonts.

A prominent feature of manganese ores from Nanzenbach and Carlshütte is the high frequency of tuffitic layers. They are up to several centimetres thick and consist of high-vesicular and of non-vesicular volcanic ash and lapilli. The non-vesicular ejecta are often intensely altered and rich in iron-, nickel-, and copper-sulphides (Figure 5). Some clasts contain 60 to 80 vol.% sulphides; primary magmatic silicates are mostly carbonatized or serpentinized.

Mineralogy

Major constituents of primary ores are hematite, bementite, calcite, rhodochrosite, Ca-Mn-carbonates, and quartz. Some samples contain additional braunite, manganite, pyrite, bravoite, chlorite, and inesite. Only as accessories occur magnetite, sphalerite, galenite, alabandite, millerite, covelline, marcasite, chalcopyrite, bornite, ilmenite, and native copper. The ores from Bergfreiheit consist predominantly of rhodochrosite, bementite, hausmannite, and tephroite. Veinlets crossing the ore beds of Carlshütte and Nanzenbach are filled with bementite, pyroxmangite, graphite, chalcopyrite, galenite, manganese-rich calcite, and native copper.

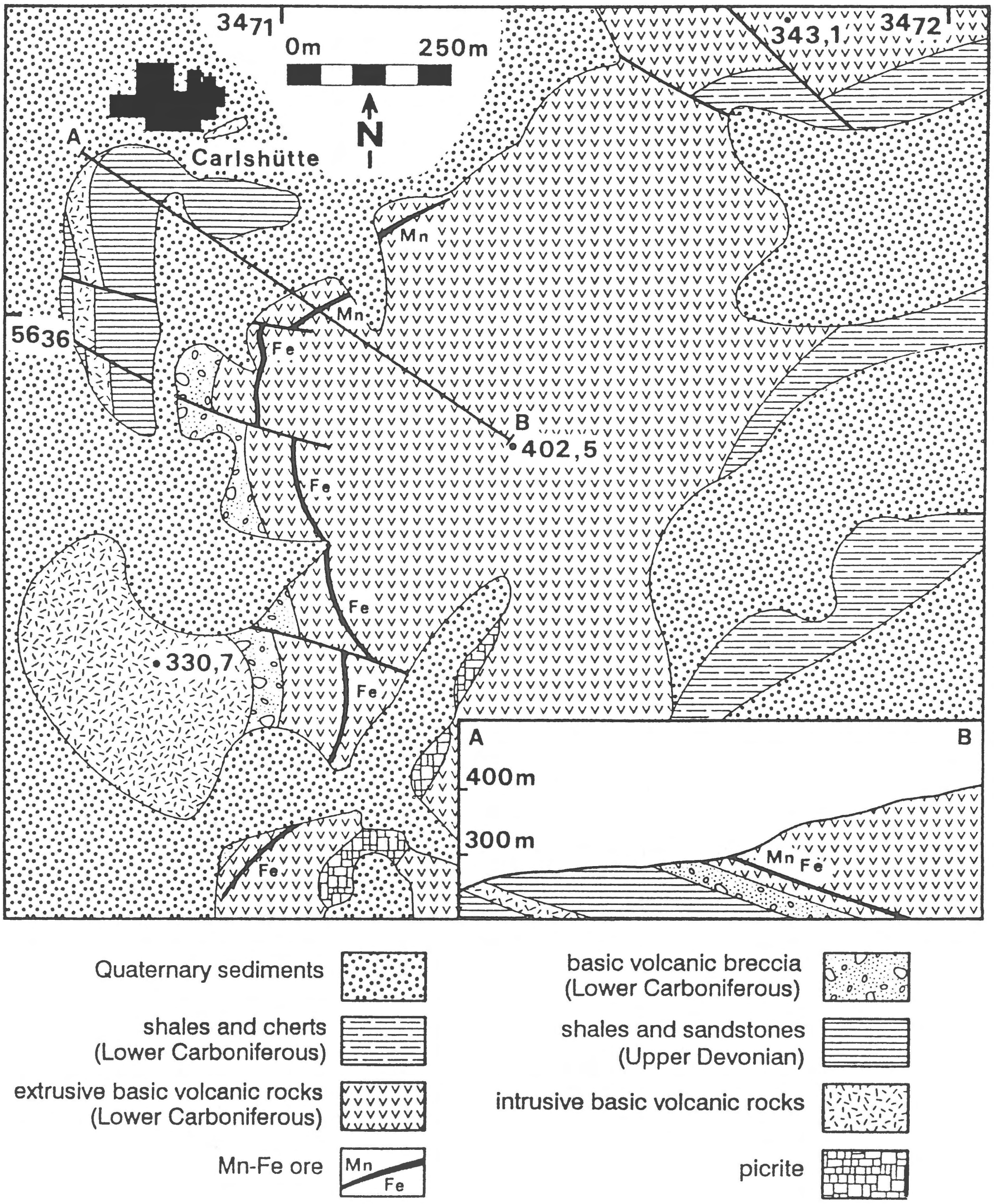

Figure 3. Geological setting of the iron-manganese ore bed at Carlshütte.

The major constituents form three different mineral associations:

1. Quartz, hematite, ± calcite,
2. Bementite, quartz, rhodochrosite, calcite, ± hematite,
3. Bementite, rhodochrosite, Ca-Mn-carbonates, ± hematite. No quartz.

Sulphide minerals as well as the oxides magnetite and ilmenite are restricted to tuffitic manganese ores. Volcanic components in these ores are often predominantly replaced by manganese minerals; therefore magmatic sulphides are directly enclosed within manganese minerals. Millerite, chalcopyrite, and pyrite additionally occur as autochthonous constituents with-

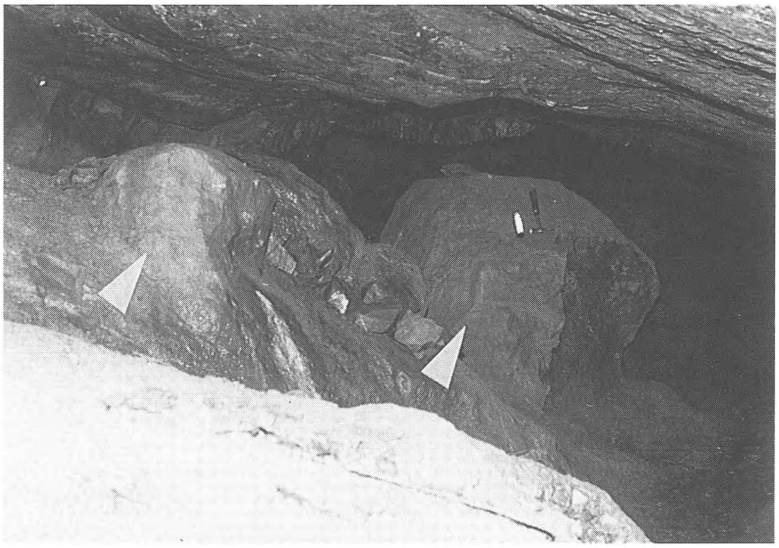

Figure 4. Chert mounds within the abandoned iron mine 'Hachthal' at Carlshütte. Hematitic iron ore is completely worked out, only hematitic chert mounds and the under- and overlying splilites are still present. Chert mounds (white arrows) indicate the positions of ancient hydrothermal vents. Scale (white rectangle on the chert mound at right) = 13 cm.

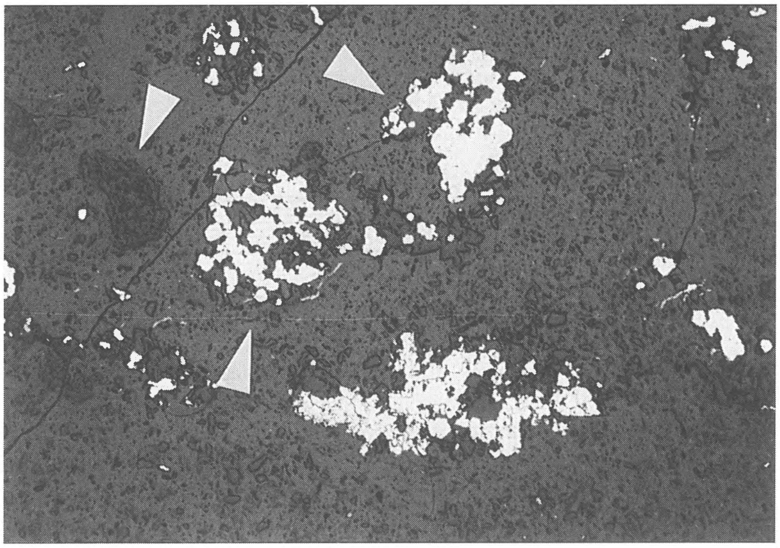

Figure 5. Tuffitic manganese ore rich in pyrite, chalcopyrite, and millerite. Tuffitic components (white arrows) are slightly darker and show a higher relief than the manganese-rich matrix; sulphides are white. Nanzenbach ore bed, polished section, reflected plane polarized light. Photo length = 2.5 mm.

in some of the manganese-rich ores. A characteristic feature of tuff-derived sulphides is the dendritic intergrowth between chalcopyrite, millerite, pyrite, and bravoite. Millerite mostly forms granular aggregates; only authigenic crystals are acicular. The unusual granular millerite crystals are possibly pseudomorphs after pentlandite. Lamellar twinning of chalcopyrite indicates inversion of cubic high-temperature chalcopyrite, which is stable at temperatures above approximately 500° C, to tetragonal low-temperature chalcopyrite.

Figure 6. Tuffitic manganese ore rich in conodonts (white arrows) and tuff-derived sulphides. The enrichment of conodonts and cosmic spherules (Figure 8) indicates very low sedimentation rates. Nanzenbach ore bed, polished section, reflected plane polarized light. Photo length = 2.4 mm.

Fossils

Manganese ores are often rich in conodonts, inarticulate brachiopods, and stromatolitic structures. Exceptionally fossil-rich manganese ores containing up to 20 vol.% conodonts occur at Nanzenbach and Carlshütte (Figure 6). Occasionally conodont apparatuses are incompletely disarticulated. Recognized species are typical of the *isosticha* – Upper *crenulata* Zone (Sandberg et al. 1978):

- *Siphonodella crenulata* (Cooper 1939)
- *Siphonodella obsoleta* Hass 1959
- *Siphonodella quadruplicata* (Branson & Mehl) 1934
- *Gnathodus punctatus* (Cooper 1939)
- *Gnathodus delicatus* Branson & Mehl 1938
- *Polygnathus inornatus* Branson 1934
- *Elictognathus laceratus* (Branson & Mehl 1934)
- *Polygnathus communis communis* Branson & Mehl 1934
- *Neoprioniodus barbatus* (Branson & Mehl 1934)

Inarticulate brachiopods (*Lingula* sp., *Orbiculoida* sp.) occur in most samples but in smaller numbers than conodonts. Radiolaria seem rare except within some of the siliceous manganese ores from Nanzenbach that consist predominantly of siliceous spheres with diameters up to 300 μm. Because no internal skeleton is recognizable, a determination as radiolaria is doubtful.

A characteristic feature of manganese-rich samples are structures resembling small stromatolites (Figure 7). They are built of 1 to 10 μm thick laminae, show columnar growth structures, and reach a size up to 1500 μm. Mineralogically they consist either of quartz and hematite or of rhodochrosite, bementite, and quartz. It cannot be excluded that these stromatolites are inorganic pseudomorphs after growth structures of manganese oxides, but the oriented growth, the similarity to stromatolites and the regularity of microlayers are best explained by an organic origin.

Cosmic spherules

Ten magnetite spherules have been found in polished sections of manganese ores from Nanzenbach. Their apparent diameters range from 30 to 230 μm. Most spherules occur in ore layers which are exceptionally rich in conodonts; the mean concentration in polished sections is about 1 spherule per 7 cm^2. Some of the larger spherules show an acentric circular cavity up to 140 μm wide (Figure 8). These spherules are similar to the 'Group I' magnetic particles isolated from deep-sea manganese nodules by Finkelman (1970). The acentric cavity is the former metallic nucleus, which has been completely leached during diagenesis. According to Finkelman (1970), these particles are ablation products of iron meteorites.

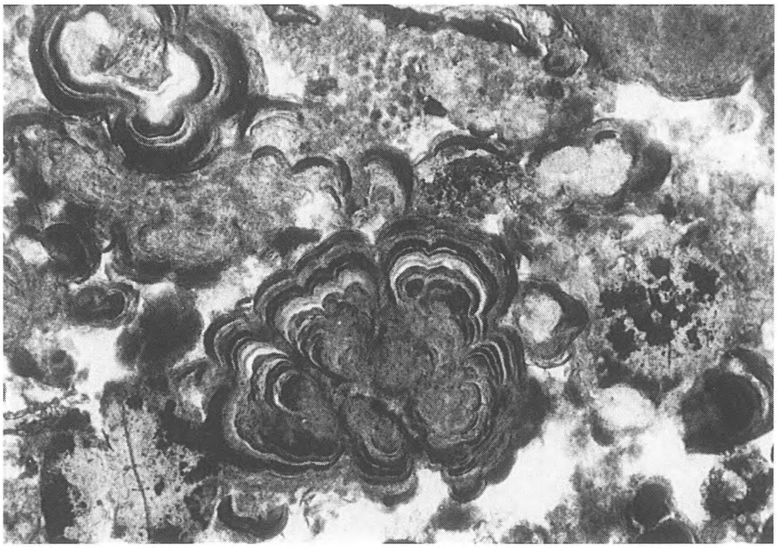

Figure 7. Stromatolitic structures within manganese-rich ore from the Nanzenbach ore bed. An organic origin of these structures is still doubtful. Thin section, plane polarized light. Photo length = 1.3 mm.

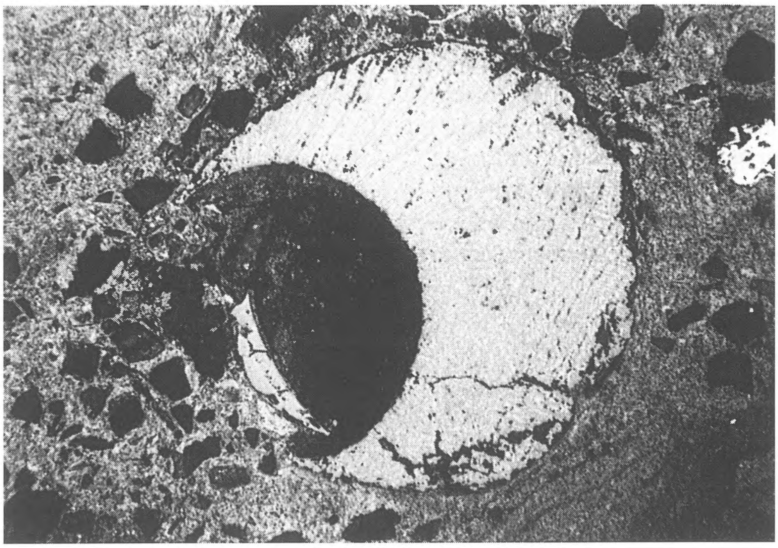

Figure 8. Cosmic magnetite spherule. The partly collapsed circular cavity was formed by a metallic nucleus, which has been completely leached during diagenesis. Nanzenbach ore bed, polished section, reflected plane polarized light. Photo length = 0.5 mm.

Intramagmatic sulphide ores

In 1841, massive sulphide ores containing on average 3% copper and 2% nickel were discovered some 120 m below the western part of the Nanzenbach ore bed. Until 1869, 14 000 metric tons of ore were mined (Laspeyres 1893). Several similar sulphide mineralizations were found by intensive prospecting near the Nanzenbach iron-manganese mineralization and within the Dill syncline, but most of them were economically insignificant (Mosebach 1932, Ahlfeld 1933).

The sulphide mineralizations occur in hydrothermally serpentinized and carbonatized subvolcanic basic intrusions within Devonian slates and sandstones, and are characterized by the ore minerals pyrite, bravoite, millerite, and chalcopyrite. Additionally, pyrrhotine and pentlandite were mentioned by Mosebach (1932) and Ahlfeld (1933). The mineral assemblages and the textures of the ores are similar to the sulphides in tuffitic manganese ores at Nanzenbach and Carlshütte. Unusual granular millerite aggregates, lamellar twinning of chalcopyrite, and dendritic intergrowth of sulphides are characteristics of the massive intramagmatic sulphides and tuffitic manganese ores.

Manganese ores of the Iberian Pyrite Belt

The south-western part of the Iberian Peninsula is crossed by a 230 km long east-west trending zone of Lower Carboniferous keratophyric and spilitic volcanic rocks. The occurrence of large volcanic sedimentary sulphide deposits is the reason for the name 'Iberian Pyrite Belt'. Apart from these economically important deposits, many manganese deposits were mined until 1973.

According to Schütz (1985), volcanic activity was separated in two main phases. The first phase was dominated by keratophyric pyroclastics and minor lavas, the second by keratophyric and spilitic effusives and trondjhemitic intrusives. Sulphide ores were produced at the end of the first phase, manganese ores were the hydrothermal termination of the second phase. Sedimentary wall rocks of sulphide deposits are black shales and cherts, whereas manganese ores are associated with red and violet shales and basic tuffs. The entire sequence was subjected to regional metamorphism of low-grade stage.

Some deposits within the Province Huelva (southern Spain) were examined for comparison with the ores from Nanzenbach and Carlshütte. Most ores consist of quartz, rhodochrosite, braunite, spessartine, albite, hematite, and rhodonite. Additionally, some samples contain pyroxmangite, magnetite, and chlorite. Joints are often filled with coarse-grained albite and rhodonite. Due to the low-grade metamorphism, primary textures and fossils occur only in relicts. These are represented by heavily corroded white-coloured conodonts, recrystallized radiolaria in hematitic cherts, and stromatolitic structures in siliceous manganese ores resembling the stromatolitic structures from Nanzenbach and Carlshütte.

All studied deposits are zoned. Manganese ores, hematitic manganese ores, and hematitic cherts prevail in different parts of the deposit. Hematitic cherts occur in massive, up to 20 m thick layers and form remarkable rocky ridges extending up to several kilometres. Manganese ores are found within the cherts in irregularly formed lenses or in continuous layers up to several metres thick in the periphery of large occurrences of hematitic cherts.

Genetic model

Some of the observations seem to be contradictory: on the one hand high concentrations of cosmic spherules, conodonts and inarticulate brachiopods indicate extraordinary low sedimentation rates, whereas on the other hand zoned deposits, feeding channels with hydrothermal alteration, and contemporaneous volcanism clearly prove a volcanic-sedimentary ore formation, which is usually a rapid event. Evidently, ore formation took place in two steps (Figure 9). During the Lower Carboniferous, basic magmas of basaltic composition intruded into unconsolidated Devonian clays and sands. Large amounts of pore water and sea water were heated and reacted with the hot magmatic rocks. Many silicates, especially olivine, were leached, carbonatized or serpentinized. The basalts were altered into rocks consisting of albite, serpentine, chlorite, epidote, calcite, and little quartz. Large quantities of SiO_2, iron, manganese, copper, and nickel were mobilized and transported by hot convective fluids. Simultaneously, hydrogen sulphide was formed by reduction of sulphate within the hydrothermal system (Bonatti et al. 1976) and fixed copper, nickel, and iron as massive and disseminated intramagmatic sulphide ores. Manganese, SiO_2 and a part of the leached iron were transported to the sea floor. Due to rapidly decreasing temperature, SiO_2 was precipitated directly around the hydrothermal vents forming chert mounds. Redissolution of SiO_2 along the hydrothermal passageways caused vertical dikes which were filled with coarse-grained hematite. Within the oxygen-rich sea water, iron was rapidly oxidized and formed flakes which accumulated near the chert mounds. Due to coprecipitation, manganese was fixed within these flakes.

Subsequently, pore waters of the hydrothermal sediment became anoxic and manganese was reduced to Mn^{2+} and removed from the sediment by diffusion and upward movement of pore waters. At the sediment–water interface, Mn^{2+} was oxidized to fine-grained oxide flakes, which were then transported by currents and small debris flows into deeper areas in the periphery of the central iron-rich ore bed. Stromatolitic crusts

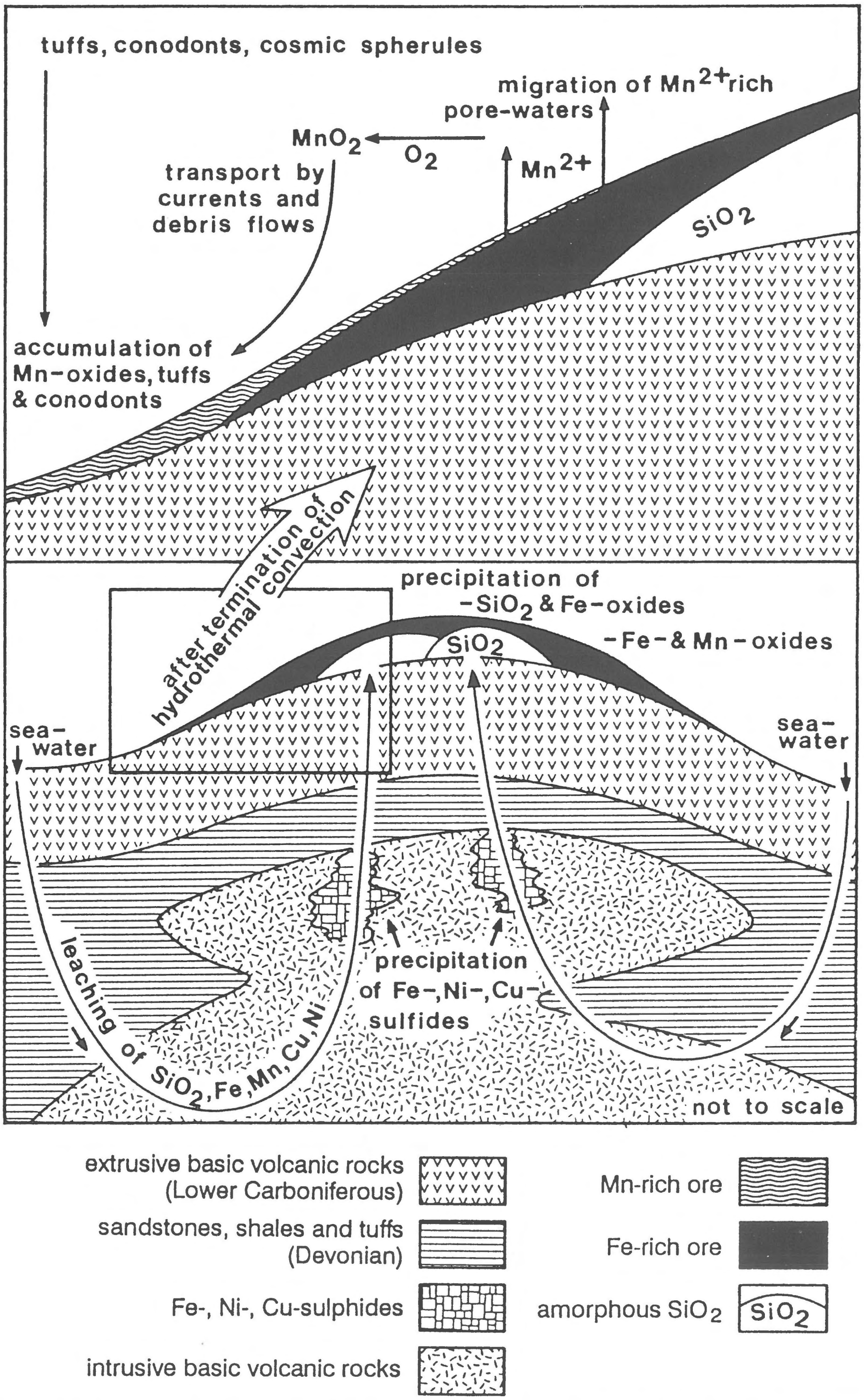

Figure 9. Origin of Lower Carboniferous volcanic sedimentary iron-manganese ores. The lower part of the figure shows the active hydrothermal system, the upper part a detail of the ore bed after termination of hydrothermal convection. Manganese is reduced to Mn^{2+} within anoxic pore waters of the hydrothermal sediment and transported to the sediment–water interface. Here, manganese is again oxidized to particulate oxides and transported by currents and small debris flows to deeper areas in the periphery of the central iron-rich ore bed. Cosmic spherules, conodonts, and inarticulate brachiopods are enriched within the manganese ore due to very low sedimentation rates.

and aggregates consisting of manganese oxide were probably built by Mn^{2+} oxidizing bacteria.

Background sedimentation was near zero because ore beds were situated on submarine volcanic sills. Therefore, no dilution with terrigenous detritus occurred, and planktonic organisms and cosmic material became strikingly enriched within the manganese ore. Tuff layers rich in intramagmatic sulphides and highly vesicular lapilli were additionally enriched within the extraordinary slowly accumulating manganese ore. These tuff layers indicate that formation of intramagmatic sulphide ores was often accompanied by phreatomagmatic explosions which occurred in adjacent areas nearly simultaneously with the deposition of the manganese ore.

The two different manganese-rich mineral associations indicate a primary origin for the mixed Mn-Ca-carbonates. During metamorphism, (Mn, Ca)CO_3 and SiO_2 reacted to bementite and calcite. Ca-Mn-carbonates were only preserved within ores low in SiO_2. $\delta^{13}C$-values of Mn-Ca-carbonates are near –12‰ vs. PDB whereas $\delta^{13}C$-values of pure rhodochrosite are in the range of –20 to –34‰. It is very likely that pure rhodochrosite originated due to the reduction of manganese oxides by hydrocarbons. Relics of these hydrocarbons are present as amorphous, partly graphitic masses of carbon ('Impsonite, Kohlenblende') which impregnate pore spaces within the ore and the adjacent tuff-layers.

The manganese ores of the Iberian Pyrite Belt share many features with the deposits of Nanzenbach and Carlshütte. The only significant difference is the more intensive metamorphic overprint which destroyed most primary ore-structures. It is very likely that the genetic model described above is also applicable to the ores of the Iberian Pyrite Belt.

Summary

Stratiform iron-manganese deposits of Lower Carboniferous age occur in the eastern part of the Rheinisches Schiefergebirge (Germany). Due to the very weak metamorphic overprint, manganese ores exhibit a wide variety of primary textures and are rich in well-preserved fossils. The deposits offer insights into a complete fossil submarine hydrothermal system and into diagenetic processes within the volcanic-sedimentary ore. The largest deposits are located within the central Dill syncline; the outcrops can be traced over distances up to 1800 m. The average thickness of ore beds is roughly 1 m.

The ore-deposits are associated with Lower Carboniferous pelagic sediments (black shales and cherts) and spilitic volcanic rocks. This volcanic-sedimentary sequence is underlain by several hundred metres of Devonian shales, tuffs, and sandstones which are intruded by basic sills and dikes. Due to intensive hydrothermal alteration, intrusive volcanic rocks are often entirely carbonatized or serpentinized. Locally they contain massive and disseminated enrichments of Ni- and Cu-rich sulphides.

Most strikingly, iron-manganese ore beds are laterally and vertically zoned in the sequence SiO_2-Fe-Mn. The centre of each ore occurrence consists of several metres thick mounds of hematitic chert surrounded and covered by fine-grained red hematite ore. Vertical dikes of coarse-grained black hematite intersect the chert mounds and end abruptly at the tops of these mounds. Spilites beneath the ore beds are rich in argillaceous alteration zones, which are missing in the overlying spilites. Manganese-rich ores are restricted to the uppermost centimetres of the central ore bed, and, more important, to outer parts of the ore bed. They are conspicuously enriched in conodonts, inarticulate brachiopods, and cosmic spherules.

Major constituents of ores are hematite, quartz, rhodochrosite, calcium-rich rhodochrosite, bementite, calcite, manganite, and braunite. Additionally, tuffitic ores contain pyrite, bravoite, millerite, and chalcopyrite. These sulphides are derived from sulphide-rich tuffs and resemble the sulphides within basaltic sills underlying the Lower Carboniferous volcanic-sedimentary complex.

Ores were formed by the following processes. During the Lower Carboniferous, basaltic magmas intruded unconsolidated Devonian clays and sandstones. Large amounts of sea water and pore water were heated and circulated through the hot volcanic rocks, leaching large quantities of SiO_2, manganese, iron, copper, and nickel. Copper and nickel were fixed within the intrusions as sulphides; only SiO_2, manganese, and iron were transported to the sea floor. Due to rapid cooling, SiO_2 was instantly precipitated at the hydrothermal vents, forming mounds of chert. Veins filled with coarse-grained hematite intersecting the chert mounds are the remnants of feeding channels through which the hydrothermal solutions reached the sea floor.

Subsequently, manganese and iron were separated by diagenetic reactions. Manganese was reduced to Mn^{2+} by anoxic pore waters and transported by

diffusion to the sediment–water interface, where manganese was again oxidized. A thin layer of manganese oxides consisting mostly of loose flakes was formed at the surface of the ore bed. These flakes were easily redistributed by currents and therefore were transported to deeper areas surrounding the central, iron- and SiO_2-rich ore bed. Due to an elevated location of the ore deposits on submarine sills, no dilution by terrigenous detritus occurred. The separation of manganese required a long time. Therefore, remnants of planktonic organisms and cosmic spherules were significantly enriched within the manganese ore.

Manganese ores from the Iberian Pyrite Belt are more intensely metamorphosed but share many features with the ores from Nanzenbach and Carlshütte. Therefore the genetic model proposed for the latter deposits should also be applicable to the Iberian manganese ores. Generally, zoned volcanic-sedimentary iron-manganese deposits should be re-examined for diagenetic separation of manganese.

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